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**European IPPC Bureau**

## Integrated Pollution Prevention and Control

## Draft Reference Document on
## Best Available Techniques for the

# Non-Ferrous Metals Industries

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This document is one from the series of documents listed below

| **Reference Document on Best Available Techniques . . .** | **Code** |
|---|---|
| Large Combustion Plants | LCP |
| Mineral Oil and Gas Refineries | REF |
| Production of Iron and Steel | I&S |
| Ferrous Metals Processing Industry | FMP |
| ***Non-Ferrous Metals Industries*** | ***NFM*** |
| Smitheries and Foundries Industry | SF |
| Surface Treatment of Metals and Plastics | STM |
| Cement and Lime Manufacturing Industries | CL |
| Glass Manufacturing Industry | GLS |
| Ceramic Manufacturing Industry | CER |
| Large Volume Organic Chemical Industry | LVOC |
| Manufacture of Organic Fine Chemicals | OFC |
| Production of Polymers | POL |
| Chlor-Alkali Manufacturing Industry | CAK |
| Large Volume Inorganic Chemicals - Ammonia, Acids and Fertilisers Industries | LVIC-AAF |
| Large Volume Inorganic Chemicals - Solids and Others industry | LVIC-S |
| Production of Speciality Inorganic Chemicals | SIC |
| Common Waste water and Waste Gas Treatment/Management Systems in the Chemical Sector | CWW |
| Waste Treatments Industries | WT |
| Waste Incineration | WI |
| Management of Tailings and Waste-Rock in Mining Activities | MTWR |
| Pulp and Paper Industry | PP |
| Textiles Industry | TXT |
| Tanning of Hides and Skins | TAN |
| Slaughterhouses and Animals By-products Industries | SA |
| Food, Drink and Milk Industries | FDM |
| Intensive Rearing of Poultry and Pigs | IRPP |
| Surface Treatment Using Organic Solvents | STS |
| Industrial Cooling Systems | ICS |
| Emissions from Storage | EFS |
| Energy Efficiency | ENE |
| **Reference Document . . .** | |
| General Principles of Monitoring | MON |
| Economics and Cross-Media Effects | ECM |

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# EXECUTIVE SUMMARY

**To Be Updated**

The BAT (best available techniques) Reference Document (BREF) entitled "Reference Document on Best Available techniques in the Non-ferrous metals Industries" reflects an information exchange carried out under Article 17(2) of the codified IPPC Directive 2008/1/EC (IPPC Directive). This executive summary describes the main findings, a summary of the principal BAT conclusions and the associated consumption and emission levels. It should be read in conjunction with the Preface, which explains this document's objectives; how it is intended to be used and legal terms. It can be read and understood as a standalone document but, as a summary, it does not present all the complexities of this full document. It is therefore not intended as a substitute for this full document as a tool in BAT decision making.

## Scope of this document

To deal with the complex area of the production of non-ferrous metals, an approach was adopted to cover production of the metals from both primary and secondary raw materials together in one document and to deal with the metals in 10 groups. Those groups are:

- copper (including Sn and Be) and its Alloys
- aluminium
- zinc, Lead and cadmium, (plus Sb, Bi, In, Ge, Ga, As, Se, Te)
- precious metals
- mercury
- refractory Metals
- ferro-alloys
- alkali and alkaline earth metals
- nickel and cobalt
- carbon and graphite.

Carbon and graphite production was also included as a separate group as many such processes are associated with primary aluminium smelters. Processes for roasting and sintering of ores and concentrates and for the production of alumina were also included within these groups where applicable. Mining and ore treatment at the mine site are not covered in the document.

In the document, information is presented in twelve chapters covering: general information in Chapter 1, common processes in Chapter 2 and then metallurgical production processes for ten groups of metals in Chapters 3 to 12. Chapter 1 presents the conclusions and recommendations. Annexes covering costs and international regulations are also included. The common processes in Chapter 2 are divided as follows:

- use of the chapter - complex installations
- use and reporting of emission data
- management, design and training
- process control and optimisation of feedstock
- receipt, storage and handling of raw materials
- preprocessing and pretreatment of raw materials and transfer to production processes
- metal production processes - furnace types and process control techniques
- gas collection and air abatement techniques
- PCDD/F
- sulphur dioxide
- effluent treatment and water re-use
- minimisation, recycling and treatment of process residues (including by-products and waste)

- energy and waste heat recovery
- cross-media issues
- noise and vibration
- odour
- safety aspects
- de-commissioning.

Each of Chapters 2 to 12 includes sections on applied processes and techniques, present emission and consumption levels, techniques to consider in the determination of BAT and BAT conclusions. For Chapter 2 the BAT conclusions are only drawn for material handling and storage, process control, gas collection and abatement, PCDD/F removal, sulphur dioxide recovery, mercury abatement and effluent treatment/water re-use. The BAT conclusions contained in all of the chapters should be consulted for a complete understanding.

The sections of this document entitled "Techniques to consider in the determination of BAT" set out techniques considered generally to have potential for achieving a high level of environmental protection in the industries within the scope of the document. The techniques are described in each of Chapters 2 to 10 and includes management systems, process-integrated techniques and end-of-pipe measures, but a certain amount of overlap exists between these three when seeking the optimum results.

Prevention, control, minimisation and recycling procedures are considered as well as the re-use of materials and energy.

Techniques may be presented singly or as combinations to achieve the objectives of the IPPC Directive. Annex IV to this Directive lists a number of general considerations to be taken into account when determining BAT and techniques within this chapter will address one or more of these considerations. As far as possible, a standard structure is used to outline each technique, to enable comparison of techniques and an objective assessment against the definition of BAT given in the IPPC Directive.

The content is not an exhaustive list of techniques and others may exist or be developed which may be equally valid within the framework of IPPC and BAT.

The standard structure used to outline each technique is shown in Table 4.1.

| **Type of information considered** | **Type of information included** |
|---|---|
| Description | Technical description of the technique (including drawings, schematics if necessary) |
| Achieved environmental benefits | Main environmental benefits (including energy, water, raw material savings, as well as production yield increases, energy efficiency, etc.) addressed by the technique |
| Cross-media effects | Main environmental side effects and disadvantages to other media caused by using the technique. Details of the environmental effects of the technique in comparison with others |
| Operational data | Data on consumption and emission levels from operational plants using the technique (including any reference conditions and monitoring methods used). Any other relevant information on how to operate, maintain and control the technique |
| Applicability | Indication of the type of plants in which the technique may be applied, considering, e.g. plant age (new or existing), plant size (large or small), techniques already installed and type or quality of product |
| Economics | Information on costs (both investment and operational) and any possible savings (e.g. reduced raw material or energy consumption, waste charges) or revenues including details on how these costs/savings or revenues have been calculated/estimated |
| Driving force for implementation | Local conditions or requirements which lead to, or may stimulate, implementation. Information on reasons other than environmental ones for implementation (e.g. increase in productivity, safely) |
| Example plants | Reference to (a) plant(s) in which the technique is applied and from which information has been collected and used in writing the section |
| Reference literature | Literature or other reference material (e.g. books, reports, studies, websites) that was used in writing the section and that contain more details on the technique |

## 1. Non-Ferrous Metal Industry

At least 42 non-ferrous metals plus ferro-alloys and carbon and graphite are produced in EU and are used in a variety of applications in the metallurgical, chemical, construction, transport and electricity generation/transmission industries. For example high purity copper is essential for electricity generation and distribution and small amounts of nickel or refractory metals improve the corrosion resistance or other properties of steel. They are also used in many high technology developments, particularly in the defence, computing, electronic and telecommunications industries.

Non-ferrous metals are produced from a variety of primary and secondary raw materials. Primary raw materials are derived from ores that are mined and then further treated before they are metallurgically processed to produce crude metal. The treatment of ores is normally carried out close to the mines. Secondary raw materials are indigenous scrap and residues and may also undergo some pretreatment to remove coating materials.

In Europe, ore deposits that contain metals in viable concentrations have been progressively depleted and few indigenous sources remain. Most concentrates are therefore imported from a variety of sources worldwide.

Recycling constitutes an important component of the raw material supplies of a number of metals. Copper, aluminium, lead, zinc, precious metals and refractory metals, among others, can be recovered from their products or process residues and can be returned to the production process without loss of quality in recycling. Overall, secondary raw materials account for a high proportion of the production, thus reducing the consumption of raw materials and energy.

The product of the industry is either refined metal or what is known as semis or semi manufactures, i.e. metal and metal alloy cast ingots or wrought shapes, extruded shapes, foil, sheet, strip, rod, etc.

The structure of the industry varies metal by metal. No companies produce all non-ferrous metals although there are a few pan-European companies producing several metals, e.g. copper, lead, zinc, cadmium, etc.

The size of the companies producing metals and metal alloys in Europe varies from a few employing more than 5000 people and a large number having between 50 and 200 employees. Ownership varies between pan-European and national metals groups, industrial holdings groups, standalone public companies and private companies.

Some metals are essential as trace elements but at higher concentrations are characterised by the toxicity of the metal, ion or compounds and many are included under various lists of toxic materials. Lead, cadmium and mercury are of the greatest concern.

## 2. Environmental Issues for the Industry

The main environmental issues for the production of most non-ferrous metals from primary raw materials are the potential emission to air of dust and metals/metal compounds and of sulphur dioxide to if roasting and smelting sulphide concentrates or using fuels that contain sulphur or other materials. The capture of sulphur and its conversion or removal is therefore an important factor in the production of non-ferrous metals. The pyrometallurgical processes are potential sources of dust and metals from furnaces, reactors and the transfer of molten metal.

Energy consumption and the recovery of heat and energy are important factors in the production of non-ferrous metals. They depend on the efficient use of the energy content of sulphidic ores, the energy demand of the process stages, the type and supply method of energy used and the use of effective methods of heat recovery. Working examples are given in Chapter 2 of the document.

The main environmental issues associated with the production of non-ferrous metals from secondary raw materials are also related to the off-gases from the various furnaces and transfers that contain dust, metals and in some process steps, acid gases. There is also the potential for the formation of PCDD/F due to the presence of small amounts of chlorine in the secondary raw materials; the destruction and/or capture of PCDD/F and VOCs is an issue that is being pursued.

The main environmental issues for primary aluminium are the production of poly-fluorinated hydrocarbons and fluorides during electrolysis, the production of solid waste from the cells and the production of solid waste during the production of alumina.

The production of solid waste is also an issue for the production of zinc and other metals during the iron removal stages.

Other processes often use hazardous reagents such as HCl, $HNO_3$, $Cl_2$ and organic solvents for leaching and purification. Advanced processing techniques are able to contain these materials and recover and re-use them. Reactor sealing is an important issue in this respect.

In the majority of cases these process gases are cleaned in fabric filters and so the emissions of dust and metal compounds such as lead are reduced. Gas cleaning using wet scrubbers and wet electrostatic precipitators is particularly effective for process gases that undergo sulphur recovery in a sulphuric acid plant. In some cases, where dust is abrasive or difficult to filter, wet scrubbers are also effective. The use of furnace sealing and enclosed transfers and storage is important in preventing diffuse emissions.

In summary the main issues for the production processes for each of the groups of metals comprise the following components:

- for the production of copper: $SO_2$, dust, metal compounds, organic compounds, waste water (metal compounds), residues such as furnace linings, sludge, filter dust and slag. PCDD/F formation during treatment of secondary copper materials is also an issue
- for the production of aluminium: fluorides (including HF), dust, metal compounds, $SO_2$, COS, PAH, VOCs, greenhouse gases (PFCs and $CO_2$), PCDD/F (secondary), chlorides and HCl. Residues such as bauxite residue, spent pot lining, filter dust and salt slag and waste water (oil and ammonia)
- for the production of lead, zinc and cadmium: dust, metal compounds, VOCs (including PCDD/F), odours, $SO_2$, other acid gases, waste water (metal compounds), residues such as sludge, the iron rich residues, filter dust and slag
- for the production of precious metals: VOCs, dust, metal compounds, PCDD/F, odours, $NO_X$, other acid gases such as chlorine and $SO_2$. Residues such as sludge, filter dust and slag and waste water (metal compounds and organic compounds)
- for the production of mercury: mercury vapour, dust, metal compounds, odours, $SO_2$, other acid gases, waste water (metal compounds), residues such as sludge, filter dust and slag
- for the production of refractory metals, hard metal powder and metal carbides: dust, solid hard metal and metal compounds, waste water (metal compounds), residues such as filter dust, sludge and slag. Process chemicals such as hydrogen fluoride (HF) are used for processing tantalum and niobium and are highly toxic. This should be taken into account in the handling and storage of these materials
- for the production of ferro-alloys: dust, metal compounds, CO, $CO_2$, $SO_2$, energy recovery, waste water (metal compounds), residues such as filter dust, sludge and slag
- for the production of alkali and alkaline earth metals: chlorine, HCl, PCDD/F, SF6, dust, metal compounds, $CO_2$, $SO_2$, waste water (metal compounds), residues such as sludge, aluminate, filter dust and slag
- for the production of nickel and cobalt: VOCs, CO, dust, metal compounds, odours, $SO_2$, chlorine and other acid gases, waste water (metal compounds and organic compounds), residues such as sludge, filter dust and slag

- for the production of carbon and graphite: PAH, hydrocarbons, dust, odours, $SO_2$, waste water prevention, residues such as filter dust.

## 3. Applied processes

The range of raw materials available to the various installations is wide and this means that a variety of metallurgical production processes is used. In many instances the process choice is governed by the raw materials. Tables 2, 2 and 3 summarise the furnaces used for the production of non-ferrous metals:

| Furnace | Metals Used | Material Used | Comment |
|---|---|---|---|
| Steam coil dryer<br>Fluid bed dryer<br>Flash dryer | Cu and some others | Concentrates | |
| Rotary Kiln | Most metals for drying.<br>Fuming ZnO. Calcining alumina, Ni and ferro alloys.<br>Burning of photographic film for precious metal production.<br>De-oiling Cu and Al scrap | Ores, concentrates and various scrap and residues. | Drying, calcining and fuming applications.<br>Use as an incinerator. |
| Fluidised bed. | Copper and zinc<br>$Al_2O_3$ | Concentrates.<br>$Al(OH)_3$ | Calcining and roasting. |
| Up-draught sintering machine. | Zinc and lead. | Concentrates and secondary. | Sintering. |
| Down-draught sintering machine | Zinc and lead. | Concentrates and secondary. | Sintering. |
| Steel Belt sintering machine | Ferro-alloys, Mn, Nb. | Ore. | Other applications possible |
| Herreshoff | Mercury.<br>Molybdenum<br>(rhenium recovery) | Ores and concentrates. | Roasting, calcining. |

**Table 1: Drying, roasting, sintering and calcining furnaces**

| Furnace | Metals Used | Material Used | Comment |
|---|---|---|---|
| Enclosed refractory lined crucibles | Refractory metals, special ferro-alloys | Metal oxides | |
| Open Pit | Refractory metals, special ferro-alloys. | Metal oxides | |
| Baiyin | Copper | Concentrates | |
| Electric Arc Furnace | Ferro-alloys | Concentrates, ore | |
| Contop/Cyclone | Copper | Concentrates | |
| Submerged Electric Arc Furnace | Precious metals, copper, ferro-alloys. | Slag, secondary materials, concentrates. | For the production of ferro-alloys the open, semi-closed and closed types are used. |
| Rotary | Aluminium, lead, copper, precious metals | Scrap and other secondary, blister copper | Oxidation and reaction with substrate. |
| Tilting Rotary Furnace | Aluminium<br>Lead | Scrap and other secondary | Minimises salt flux use. |
| Reverberatory | Aluminium, copper, others | Scrap and other secondary, black copper | Smelting of Cu concentrates elsewhere in the World. |
| Vanyukov | Copper | Concentrates | |
| Ausmelt/ISA Smelt | Copper, lead, | Intermediates, concentrates and secondary materials. | |

| Furnace | Metals Used | Material Used | Comment |
|---|---|---|---|
| QSL | Lead | Concentrates and secondary | |
| Kivcet | Lead<br>Copper | Concentrates and secondary | |
| Noranda | Copper | Concentrates | |
| El Teniente | Copper | Concentrates | |
| TBRC<br>TROF | Copper (TBRC), Precious metals | Most secondary inc. slimes | |
| Mini Smelter | Copper/lead/tin | Scrap | |
| Blast Furnace and ISF | Lead, lead/zinc, copper, precious metals. | Concentrates, most secondary | |
| Inco Flash Furnace | Copper, nickel | Concentrates | |
| Outotec Flash Smelter | Copper, nickel | Concentrates | |
| Mitsubishi process | Copper | Concentrates and anode scrap | |
| Peirce Smith | Copper (converter), Ferro-alloys, Metal Oxide Production | Matte and anode scrap | |
| Hoboken | Copper (converter) | Matte and anode scrap | |
| Outotec Flash Converter | Copper (converter) | Matte | |
| Noranda Converter | Copper (converter) | Matte | |
| Mitsubishi Converter | Copper (converter) | Matte | |

**Table 2: Smelting and refining furnaces**

| Furnace | Metals Used | Material Used | Comment |
|---|---|---|---|
| Induction | Most | Clean metal and scrap. | Induced stirring assists alloying. Vacuum can be applied for some metals |
| Electron Beam | Refractory metals | Clean metal and scrap. | |
| Rotary | Aluminium, lead | Various scrap grades. | Fluxes and salts used for complex matrices. |
| Reverberatory | Aluminium (primary and secondary) | Various scrap grades. | Bath or hearth configuration can vary. Melting or holding |
| Contimelt | Copper | Copper anode, clean scrap and blister copper. | Integrated furnace system. |
| Shaft | Copper | Copper cathode and clean scrap. | Reducing conditions. |
| Drum (Thomas) | Copper | Copper scrap | Melting, fire-refining |
| Heated Crucibles (indirect kettles) | Lead, zinc | Clean scrap. | Melting, refining, alloying. |
| Direct heated crucibles | Precious metals | Clean metal | Melting, alloying. |

**Table 3: Melting Furnaces**

Hydrometallurgical processes are also used. Acids and alkalis (NaOH, sometimes also $Na_2CO_3$) are used to dissolve the metal content of a variety of calcines, ores and concentrates before refining and electrowinning. The material to be leached is usually in the form of the oxide, either as an oxidic ore or an oxide produced by roasting. Direct leaching of some concentrates or mattes is also performed at both elevated and atmospheric pressure. Some copper sulphide ores can be leached with sulphuric acid or other media, sometimes using natural bacteria to promote oxidation and dissolution, but very long residence times are used.

Air, oxygen, chlorine or solutions that contain ferric chloride can be added to leaching systems to provide the appropriate conditions for dissolution. The solutions that are produced are treated in a number of ways to refine and win the metals. Common practice is to return the depleted solutions to the leaching stage, where appropriate, to conserve acids and alkaline solutions.

## 4. Current Emissions and Consumption

The range of raw materials is also a significant factor and affects the use of energy, the amount of residues produced and the quantity of other materials used. An example is the removal of impurities such as iron into slags; the amount of impurity present governs the amount of slag produced and the energy used.

Emissions to the environment depend on the collection or abatement systems that are used. The current ranges reported for a number of abatement processes during the exchange of information are summarised in Table 4:

| **Abatement Technique** | **Reported emissions** | | | **Specific emission (amount per t of metal produced)** |
|---|---|---|---|---|
| | **Component** | **Minimum** | **Maximum** | |
| Fabric filter, hot ESP and cyclone. | Dust (Metals dependent on composition) | <1 mg/Nm$^3$ | 100 mg/Nm$^3$ | 100 - 6000 g/t |
| Carbon filter | Total C | <20 mg/Nm$^3$ | | |
| Afterburner (including temperature quench for PCDD/F) | Total C | <2 mg/Nm$^3$ | 100 mg/Nm$^3$ | 10 - 80 g/t |
| | PCDD/F (ITEQ) | <0.1 ng ITEQ/Nm$^3$ | 5 ng ITEQ/Nm$^3$ | 5 - 10 µg/t |
| | PAH (EPA) | <1 µg/Nm$^3$ | 2500 µg/Nm$^3$ | |
| | HCN | <0.1 mg/Nm$^3$ | 10 mg/Nm$^3$ | |
| Wet or semi-dry scrubber | $SO_2$ | <50 mg/Nm$^3$ | 250 mg/Nm$^3$ | 500 - 3000 g/t |
| | Hydrocarbon as C | <10 mg/Nm$^3$ | 200 mg/Nm$^3$ | |
| | Chlorine | <2 mg/Nm$^3$ | | |
| Alumina scrubber | Dust | <1 mg/Nm$^3$ | 20 mg/Nm$^3$ | |
| | Hydrocarbon as C | <1 mg/Nm$^3$ | 50 mg/Nm$^3$ | |
| | PAH (EPA) | <20 µg/Nm$^3$ | 2000 µg/Nm$^3$ | |
| Chlorine recovery | Chlorine | <5 mg/Nm$^3$ | | |
| Optimised combustion Low-$NO_X$ burner | $NO_X$ | 10 mg/Nm$^3$ | 500 mg/Nm$^3$ | |
| Oxidising scrubber | $NO_X$ | | <100 mg/Nm$^3$ | |
| Sulphuric acid plant reported as conversion of $SO_2$ | double contact | 99.3 % | 99.7 % | 1 - 16 kg/t |
| | single contact | 95 | 99.1 % | |
| Cooler, ESP, lime/carbon adsorption and fabric filter | PAH (EPA) | 0.1 mg/Nm$^3$ | 6 mg/Nm$^3$ | |
| | Hydrocarbons as C | 20 mg/Nm$^3$ | 200 mg/Nm$^3$ | |

**Table 4: Reported range of current emissions**

Process gases are captured and then cleaned in fabric filters to reduce the emissions of dust and metal compounds such as those of lead. Modern filter fabrics offer significant improvements in performance, reliability and life. Afterburners and carbon absorption are used to remove PCDD/F and VOCs.

Uncaptured gases or diffuse emissions, however, are not treated. Dust emissions also occur from storage, handling and the pretreatment of raw materials where diffuse dust emissions also play an important role. This is true for both primary and secondary production, as their significance can be much greater than captured and abated emissions. Careful plant design and process operations are needed to capture and treat process gases where diffuse emissions are significant.

Table 5 shows that diffuse or uncaptured emissions are important issues:

| | **Dust emission (kg/yr)** | |
|---|---|---|
| | **Before additional secondary gas collection (1992)** | **After additional secondary gas collection (1996)** |
| Anode production (t/yr) | 220000 | 325000 |
| Diffuse emissions | | |
| Total Smelter | 66490 | 32200 |
| Smelter roofline | 56160 | 17020 |
| Primary smelter stack emissions | | |
| Smelter/acid plant | 7990 | 7600 |
| Stack-secondary hoods | 2547 | 2116 |

**Table 5: Comparison of abated and diffuse dust loads at a primary copper smelter**

Many processes use sealed cooling and process water systems but there is still the potential to discharge metals to water. The methods to reduce water use and waste water generation and to treat process waters are reviewed in Chapter 2.

The production of residues is also a significant factor in this industry, but the residues often have recoverable metal quantities and it is common practice to use residues on-site or in other installations to recover metals. Many slags that are produced are inert, non-leachable and are used in many civil engineering works. Other slags, such as salt slag, can be treated to recover other components for use in other industries, but the industry should ensure that these recovery operations are operated to a high environmental standard.

## 5. General BAT Conclusions

The exchange of information during the preparation of the BREF for non-ferrous metal production has allowed conclusions on BAT to be reached. The sections in each of the chapters that describe BAT should therefore be referred to for a complete understanding of BAT and the associated processes and emissions. The general findings are summarised below.

- **Up-stream Activities**

Process management, supervision and the control of the process and abatement systems are very important factors. Good training practices and operator instruction and motivation are also important especially to prevent environmental pollution. Good techniques for raw material handling can prevent diffuse emissions. Other important techniques include:

- consideration of the environmental implications of a new process or raw material at the earliest stages of the project with reviews at regular intervals thereafter
- design of the process in accordance accept the anticipated range of raw material and any changes in raw materials. Severe problems can result for example if gas volumes are too high or if the energy use of the material is higher than anticipated. The design stage is the most cost-effective time to introduce improvements in overall environmental performance

- use of an audit trail of the design and decision-making process to show how various processes and abatement options were considered
- planning of commissioning procedures for new or modified plant
- planned maintenance of the plant and process equipment including the provision of spare parts for equipment that is critical to environmental performance.

Table 6 summarises the techniques for raw material storage and handling on the basis of type and characteristics of the material.

| **Raw material** | **Metal group** | **Method for handling** | **Method for storage** | **Comments** |
|---|---|---|---|---|
| Concentrates: | All - if dust-forming | Enclosed conveyors or pneumatic | Enclosed building | Prevention of water contamination. |
| | All - if non dust-forming | Covered conveyors | Covered store | |
| Fine grained material (e.g. metal powder) | Refractory metals | Enclosed conveyors or pneumatic<br>Covered conveyors | Closed drum, bins and hoppers | Prevention of water contamination and diffuse air emissions |
| Secondary raw materials: | All - Large items | Mechanical loader | Open | Prevention of water contamination or reactions with water. Oily drainage from swarf |
| | All - Small items | Charge skips | Covered bays | |
| | All - Fine material | Enclosed or agglomerated | Enclosed if dusty | |
| Fluxes: | All - if dust-forming | Enclosed conveyors or pneumatic | Enclosed building | Prevention of water contamination. |
| | All - if non dust-forming | Covered conveyors | Covered store | |
| Solid fuel & coke: | All | Covered conveyors If not dust-forming | Covered store If not dust-forming | |
| Liquid fuels and LPG | All | Overhead pipeline | Certified storage<br>Bunded areas. | Back venting of delivery lines |
| Process gases: | All | Overhead pipeline<br>Reduced pressure pipeline (Chlorine, CO) | Certified storage | Pressure loss monitoring, Alarms for toxic gases. |
| Solvents | Cu, Ni, Zn group, PM, Carbon | Overhead pipeline<br>Manual | Drums, tanks | Back venting of delivery lines. |
| Products - Cathodes, wire-rod, billets, ingots, cakes, etc. | All | Depends on conditions. | Open concrete area or covered storage. | Appropriate drainage system. |
| Process residues for recovery. | All | Depends on conditions. | Open, covered or enclosed depending on dust formation and reaction with water. | Appropriate drainage system. |
| Wastes for disposal. (e.g. furnace linings) | All | Depends on conditions. | Open covered or enclosed bays or sealed (drums) depending on the material. | Appropriate drainage system. |

**Table 6: Summary of raw material and handling techniques**

Furnace design, the use of suitable pretreatment methods and process control were identified as important features of BAT.

The use of raw material blending to optimise the process prevents inappropriate material being used and maximises process efficiency. Sampling and analysis of feed materials and the segregation of some materials are important factors in this technique.

Good design, maintenance and monitoring are important for all process and abatement stages. Sampling and monitoring of emissions to the environment should be carried out according to national or international standard methods. Important parameters that can be used for the control of process or abatement should be monitored. Continuous monitoring of key parameters should be carried out if practical.

- **Process control**

Process control techniques that are designed to measure and maintain optimum parameters such as temperature, pressure, gas components and other critical process parameters, etc. are considered to be BAT.

Sampling and analysis of raw materials to control plant conditions. Good mixing of different feed materials should be achieved to get optimum conversion efficiency and reduce emissions and rejects.

The use of feed weighing and metering systems, the use of microprocessors to control material feed-rate, critical process and combustion conditions and gas additions allow process operation to be optimised. Several parameters can be measured to allow this and alarms provided for critical parameters, which include:

- on-line monitoring of temperature, furnace pressure (or depression) and gas volume or flow
- monitoring of gaseous components ($O_2$, $SO_2$, CO, dust, $NO_X$, etc)
- on-line monitoring of vibration to detect blockages and possible equipment failure
- on-line monitoring of the current and voltage of electrolytic processes
- on-line monitoring of emissions to control critical process parameters
- monitoring and control of the temperature of melting furnaces to prevent the production of metal and metal oxide fume by overheating.

Operators, engineers and others should be continuously trained and assessed in the use of operating instructions, the use of the modern control techniques and the significance of alarms and the actions to be taken when alarms are given.

Optimisation of levels of supervision to take advantage of the above and to maintain operator responsibility.

- **Gas collection and abatement**

The fume collection systems used should exploit furnace or reactor sealing systems and be designed to maintain a reduced pressure that avoids leaks and diffuse emissions. Systems that maintain furnace sealing or hood deployment should be used. Examples are: through electrode additions of material; additions via tuyères or lances and the use of robust rotary valves on feed systems. Secondary fume collection is expensive and consumes a lot of energy, but is needed in the case of some furnaces. The system used should be an intelligent system capable of targeting the fume extraction to the source and duration of any fume.

Overall for dust and associated metal removal, fabric filters (after heat recovery or gas cooling) can provide the best performance provided that modern wear resistant fabrics are used, the particles are suitable and continuous monitoring is used to detect failure. Modern filter fabrics (e.g. membrane filter) offer significant improvements in performance, reliability and life and therefore offer cost savings in the medium term. They can be used in existing installations and can be fitted during maintenance. They feature bag burst detection systems and on-line cleaning methods. Dust should be monitored continuously where there is a potentially significant emission.

Planned maintenance of the abatement equipment including the provision of spare parts for equipment that is critical to environmental performance.

For sticky or abrasive dusts, wet electrostatic precipitators or scrubbers can be effective provided that they are properly designed for the application.

Gas treatment for the smelting or incineration stage should include a sulphur dioxide removal stage and/or afterburning if this is considered necessary to avoid local, regional or long-range air quality problems or if PCDD/F may be present.

There may be variations in the raw materials that influence the range of components or the physical state of some components such as the size and physical properties of the dust produced. These should be assessed locally.

- **Prevention and the destruction of PCDD/F**

The presence of PCDD/F or their formation during a process should be considered for many of the pyrometallurgical processes used to produce non-ferrous metals. Particular instances are reported in the metal-specific chapters and in these cases the following techniques are considered to be BAT for the prevention of the formation of PCDD/F and the destruction of any that are present. These techniques may be used in combination. Some non-ferrous metals are reported to catalyse de novo synthesis and it is sometimes necessary to have a clean gas prior to further abatement:

- quality control of scrap inputs depending on the process used. The use of the correct feed material for the particular furnace or process. Selection and sorting to prevent the addition of material that is contaminated with organic matter or precursors can reduce the potential for PCDD/F formation if the furnace does not meet all of the requirements to destroy PCDD/F
- the use of correctly designed and operated afterburners and rapid quenching of the hot gases to <250 °C
- the use of optimum combustion conditions. The use of oxygen injection in the upper part of a furnace to ensure complete combustion of furnace gases to achieve this.
- Absorption onto activated carbon in a fixed bed or moving bed reactor or by injection into the gas stream, and removal as filter dust
- the use of very high efficiency dust removal for example, ceramic filters, high efficiency fabric filters or the gas-cleaning train prior to a sulphuric acid plant
- the use of a catalytic oxidation stage or fabric filters that incorporate a catalytic coating.
- the treatment of collected dusts in high temperature furnaces to destroy PCDD/F and to recover metals.

The emission concentrations that are associated with the above techniques range from <0.1 to 0.5 ng ITEQ/Nm$^3$ depending on the feed, the smelting or melting process and the techniques or combination of techniques that are used for PCDD/F removal.

- **Metallurgical Processes**

The range of raw materials available to the various installations is wide and means that there is a need to include a variety of metallurgical production processes in the BAT sections of the majority of the metal groups. In many instances the process choice is governed by the raw materials, so the type of furnace has only a minor effect on BAT, provided that the furnace has been designed for the raw materials used and energy recovery is used where practicable.

There are exceptions. For example, the use of multiple point feeding of alumina to centre worked prebake cells was identified as BAT for primary aluminium, as was the use of sealed furnaces in the production of some ferro-alloys to allow collection of high calorific value gas. For primary copper the reverberatory furnace is not considered to be BAT. The other major influences are the blending of the raw materials, process control, management and the collection of fume. The hierarchy in the choice of a new or changed process was identified as:

- thermal or mechanical pretreatment of secondary material to minimise organic contamination of the feed
- the use of sealed furnaces or other process units to prevent diffuse emissions, allow heat recovery and allow the collection of process gases for other use (e.g. CO as a fuel and $SO_2$ as sulphuric acid) or for abatement
- the use of semi-sealed furnaces where sealed furnaces are not available
- the minimisation of material transfers between processes
- where such transfers are unavoidable, the use of launders in preference to ladles for molten materials
- in some cases, the restriction of techniques to those that avoid molten material transfers may prevent the recovery of some secondary materials that would then enter the waste stream. In these cases the use of secondary or tertiary fume collection is appropriate so that these materials can be recovered
- hooding and ductwork design to capture fume arising from hot metal, matte or slag transfers and tapping
- furnace or reactor enclosures may be required to prevent release of fume losses into the atmosphere
- where primary extraction and enclosure are likely to be ineffective, then the furnace can be fully closed and ventilation air drawn off by extraction fans to a suitable treatment and discharge system
- the maximum use of the energy content of sulphidic concentrates.

- **Emissions to Air**

Emissions to air arise from the storage, handling, pretreatment, pyrometallurgical and hydrometallurgical stages. Transfer of materials is particularly important. Data provided has confirmed that the significance of diffuse emissions in many processes is very high and that diffuse emissions can be much greater than those that are captured and abated. In these cases it is possible to reduce environmental impact by following the hierarchy of gas collection techniques from material storage and handling, reactors or furnaces and from material transfer points. Potential diffuse emissions must be considered at all stages of process design and development. The hierarchy of gas collection from all of the process stages is:

a. Process optimisation and minimisation of emissions;
b. Sealed reactors and furnaces;
c. Targeted fume collection;

Roofline collection of fume is very energy consuming and should be a last resort.

The potential sources of emissions to air are summarised in Table 7, which also gives a review of prevention and treatment methods. Emissions to air are reported on the basis of collected emissions. Associated emissions are given as daily averages based on continuous monitoring during the operating period. In cases where continuous monitoring is not practicable as the average over the sampling period. Standard conditions are used: 273 K, 101.3 kPa, measured oxygen content and dry gas with no dilution of the gases.

Sulphur capture is an important requirement when sulphidic ores or concentrates are roasted or smelted. The sulphur dioxide produced by the process is collected and can be recovered as sulphur, gypsum (if no cross-media effects) or sulphur dioxide or can be converted to sulphuric acid. The process choice depends on the existence of local markets for sulphur dioxide. The production of sulphuric acid in a double contact sulphuric acid plant with a minimum of four passes, or in a single contact plant with gypsum production from the tail gas and using a modern catalyst, are considered to be BAT. Plant configuration will depend on the concentration of sulphur dioxide produced in the roasting or smelting stage.

| **Process stage** | **Component in off-gas** | **Treatment method** |
|---|---|---|
| Material handling and storage. | Dust and metals. | Correct storage, handling and transfer. Dust collection and fabric filter. |
| Grinding, drying. | Dust and metals. | Process operation. Gas collection and fabric filter. |
| Sintering/roasting<br>Smelting<br>Converting<br>Fire refining | VOCs, PCDD/F. | Afterburner, adsorbent or activated carbon addition. |
| Slag treatment. | Dust and metal compounds. | Gas collection, gas-cleaning in fabric filter, heat recovery. |
|  | Carbon monoxide | Afterburner |
|  | Sulphur dioxide | sulphuric acid plant (for sulphidic ores) or scrubber |
|  | Dust and metals. | Gas collection, cooling and fabric filter. |
|  | Sulphur dioxide. | Scrubber. |
|  | Carbon monoxide. | Afterburner |
| Leaching and chemical refining. | Chlorine. | Gas collection and re-use, wet chemical scrubber. |
| Carbonyl refining. | Carbon monoxide.<br>Hydrogen. | Sealed process, recovery and re-use.<br>Afterburner and dust removal in fabric filter for tail gas. |
| Solvent extraction. | VOC. (depends on the solvent used and should be determined locally to assess the possible hazard). | Containment, gas collection, solvent recovery, carbon adsorption. |
| Thermal refining. | Dust and metals. | Gas collection and fabric filter. |
|  | Sulphur dioxide. | Scrubber. |
| Molten salt electrolysis | Fluoride, chlorine, PFCs | Process operation. Gas collection, scrubber (alumina) and fabric filter. |
| Electrode baking, graphitisation | Dust, metals, $SO_2$, Fluoride, PAH, tars | Gas collection, condenser and ESP, afterburner or alumina scrubber and fabric filter.<br>Scrubber for $SO_2$. |
| Metal powder production | Dust and metals | Gas collection and fabric filter. |
| Powder production | Dust, Ammonia | Gas collection and recovery.<br>Acid medium scrubber. |
| High temperature reduction | Hydrogen. | Sealed process, re-use. |
| Electrowinning. | Chlorine.<br>Acid mist. | Gas collection and re-use. Wet scrubber. Demister. |
| Melting and casting. | Dust and metals. | Gas collection and fabric filter. |
|  | VOCs, PCDD/F (organic feed) | Afterburner (Carbon injection) |
| NB: Dust arrestment using a fabric filter may require the removal of hot particles to prevent fires. Hot electrostatic precipitators would be used in a gas-cleaning system prior to a sulphuric acid plant or for wet gases. |  |  |

**Table 7: Summary of sources and treatment/abatement options**

A summary of the BAT-AELs for the non-ferrous metal processes are shown in Table 8. More details are given in the BAT conclusions in the metal-specific chapters.

| **Abatement Technique** | **Associated Range** | **Comment** |
|---|---|---|
| Fabric filter | Dust <1 - 5 mg/Nm$^3$<br>Metals - dependent on dust composition | Depends on characteristics of dust. Dust should be monitored continuously |
| Carbon or Bio filter | Total organic C <20 mg/Nm$^3$ | Phenol <0.1 mg/Nm$^3$ |
| Afterburner (including temperature quench for PCDD/F removal) | Total organic C <5 - 15 mg/Nm$^3$<br>PCDD/F <0.1 - 0.5 ng ITEQ/Nm$^3$ ITEQ<br>PAH (OSPAR 11) <200 µgCNm$^3$<br>HCN <2 mg/Nm$^3$ | Designed for gas volume.<br>Other techniques are available to reduce PCDD/F further by carbon/lime injection, catalytic reactors/filters. |
| Optimised combustion conditions | Total organic C <5 - 50 mg/Nm$^3$ | |
| Wet ESP<br>Ceramic filter | Dust <5 mg/Nm$^3$ | Depends on characteristics, e.g. dust, moisture or high temperature |
| Wet or semi-dry alkaline scrubber | $SO_2$ <50 - 200 mg/Nm$^3$<br>Tar <0 mg/Nm$^3$<br>Chlorine <2 mg/Nm$^3$ | |
| Alumina scrubber | Dust <1 - 5 mg/Nm$^3$<br>Hydrocarbon <2 mg/Nm$^3$<br>PAH (OSPAR 11) <200 µgC/Nm$^3$ | |
| Chlorine recovery | Chlorine <5 mg/Nm$^3$. | Chlorine is re-used. Possible accidental diffuse emissions. |
| Oxidising scrubber | $NO_X$ <100 mg/Nm$^3$ | From use of nitric acid - recovery followed by removal of traces. |
| Low-$NO_X$ burner. | <100 mg/Nm$^3$ | Higher values are associated with oxygen enrichment to reduce energy use. In these cases gas volume and mass emission are reduced. |
| Oxy-fuel burner. | <100 - 300 mg/Nm$^3$ | |
| Sulphuric acid plant | >99.7 % conversion (double contact) | Including mercury scrubber using Boliden/Norzink process or thiosulphate scrubber Hg <1 ppm in acid produced |
| | >99.1 % conversion (single contact) | |
| Cooler, ESP, lime/carbon adsorption and fabric filter | PAH (OSPAR 11) <200 µgC/Nm$^3$<br>Hydrocarbons (volatile) as C <20 mg/Nm$^3$<br>Hydrocarbons (condensed) as C <2 mg/Nm$^3$ | |

NB: Collected emissions only. Associated emissions are given as daily averages based on continuous monitoring during the operating period with standard conditions of 273 K, 101.3 kPa, measured oxygen content and dry gas without dilution of the gases with air. In cases where continuous monitoring is not practicable as the average over the sampling period. For the abatement system used, the characteristics of the gas and dust will be taken into account in the design of the system and the correct operating temperature used. For some components, the variation in raw gas concentration during batch processes may affect the performance of the abatement system.

**Table 8: Emissions to air associated with the use of BAT**

Several specific reagents are used in chemical treatment of solutions of metals or in various metallurgical processes. Some of the compounds, sources and treatment methods of gases produced from the use of these reagents are given below:

| Process/ Reagent Used | Component in off-gas | Treatment Method |
|---|---|---|
| Use of arsenic or antimony oxide. (refining of Zn/Pb) | Arsine/stibine | Permanganate scrubbing |
| Pitch, etc. | Tars and PAH | Afterburner, condenser and ESP or dry absorber. |
| Solvents, VOCs | VOC, Odour | Containment, condensation. Activated carbon, bio-filter |
| Sulphuric acid (+ sulphur in fuel or raw material) | Sulphur dioxide | Wet or semi-dry scrubber system. Sulphuric acid plant. |
| Aqua Regia | NOCl, $NO_X$ | Caustic scrubber system |
| Chlorine, HCl | $Cl_2$ | Caustic scrubber system |
| Nitric acid | $NO_X$ | Oxidise and absorb, recycle, scrubber system |
| Na or KCN | HCN | Oxidise with hydrogen peroxide or hypochlorite |
| Ammonia | $NH_3$ | Recovery, scrubber system |
| Ammonium chloride | Aerosol | Recovery by sublimation, scrubber system |
| Hydrazine | $N_2H_4$ (possible carcinogen) | Scrubber or activated carbon |
| Sodium borohydride | Hydrogen (explosion hazard) | Avoid if possible in PGM processing (especially Os, Ru) |
| Formic acid | Formaldehyde | Caustic scrubber system |
| Sodium chlorate/HCl | $Cl_2$ oxides (explosion hazard) | Control of process end point |

**Table 9: Overview of chemical treatment methods for some gaseous components**

- **Emissions to water**

Emissions to water arise from a number of sources and a variety of minimisation and treatment options are applicable depending on the source and the components present. In general the waste waters can contain soluble and non-soluble metal compounds, oil and organic material. Table 10 summarises the potential waste waters.

| Source of waste water | Associated process | Minimisation methods | Treatment methods |
|---|---|---|---|
| Process water | Alumina production,<br>Lead-acid battery breaking.<br>Pickling. | Return to process as far as possible. | Neutralisation and precipitation.<br>Electrolysis. |
| Indirect cooling water | Furnace cooling for most metals.<br>Electrolyte cooling for Zn | Use of sealed or air cooling system.<br>System monitoring to detect leaks. | Settlement. |
| Direct cooling water | Al, Cu, Zn castings.<br>Carbon electrodes. | Settlement<br>Closed cooling system. | Settlement.<br>Precipitation if needed. |
| Slag granulation | Cu, Ni, Pb, Zn, precious metals, ferro-alloys | | Settlement.<br>Precipitation if needed. |
| Electrolysis | Cu, Ni, Zn | Sealed system.<br>Electrowinning of electrolyte bleed. | Neutralisation and precipitation. |
| Hydrometallurgy (blowdown) | Zn, Cd | Sealed system. | Settlement.<br>Precipitation if needed. |
| Abatement system (blowdown) | Wet scrubbers.<br>Wet ESPs and scrubbers for acid plants. | Re-use of weak acid streams if possible. | Settlement.<br>Precipitation if needed. |
| Surface water | All | Good raw materials storage and prevention of diffuse emissions | Settlement.<br>Precipitation if needed.<br>Filtration. |

**Table 10: Overview of BAT for waste water streams**

Waste water treatment systems can maximise the removal of metals using sedimentation and possibly filtration. The reagents used for precipitation may be hydroxide, sulphide or a combination of both, depending on the mix of metals present. It is also practicable in many cases to re-use treated water.

| | **Main components (mg/l)** | | | | | |
|---|---|---|---|---|---|---|
| | **Cu** | **Pb** | **As** | **Ni** | **Cd** | **Zn** |
| Process water | <0.1 | <0.05 | <0.01 | <0.1 | <0.05 | <0.15 |

NB: The associated emissions to water are based on a qualified random sample or a 24-hour composite sample. The extent of waste water treatment depends on the source and the metals contained in the waste water.

**Table 11: Example of emissions to water associated with the use of BAT**

- **Process Residues**

Process residues are produced at various stages of the process and are highly dependent on the constituents of the raw materials. Ores and concentrates contain quantities of metals other than the prime target metal. Processes are designed to obtain a pure target metal and to recover other valuable metals as well.

These other metals tend to concentrate in the residues from the process and in turn these residues form the raw material for other metal recovery processes. Table 11 gives an overview of some process residues and the options available to deal with them.

| **Source of the residues** | **Associated Metals** | **Residue** | **Options for dealing with them** |
|---|---|---|---|
| Raw materials Handling, etc. | All metals | Dust, sweepings | Feed for the main process |
| Smelting furnace | All metals | Slag | Construction material after slag treatment. Abrasive industry<br>Parts of slag may be used as refractory material, e.g. slag from the production of chromium metal |
| | Ferro-alloys | Rich slag | Raw material for other ferro-alloy processes |
| Converting furnace | Cu | Slag | Recycle to smelter |
| Refining furnaces | Cu | Slag | Recycle to smelter |
| | Pb | Skimmings or dross | Recovery of other valuable metals |
| | Precious metals (PMs) | Skimmings or dross and slag | Internal recycle |
| Slag treatment | Cu and Ni | Cleaned slag | Construction material. Matte produced |
| Melting furnace | All metals | Skimmings or dross<br>Slag and salt slag. | Return to process after treatment.<br>Metal recovery, recovery of salt and other material |
| Electrorefining | Cu | Electrolyte bleed<br>Anode remnants<br>Anode slime | Recovery of Ni.<br>Return to converter<br>Recovery of precious metals |
| Electrowinning | Zn, Ni, Co, PMs | Spent electrolyte | Re-use in leaching process |
| Fused salt electrolysis | Al | Spent Pot Lining<br>Excess bath<br>Anode stubs | Carburant or disposal<br>Sale as electrolyte<br>Recovery |
| | Na and Li | Cell material | Scrap iron after cleaning |
| Distillation | Hg | Residues (Hollines) | Re-use as process feed |
| | Zn, Cd | Residues | Return to process |

| Source of the residues | Associated Metals | Residue | Options for dealing with them |
|---|---|---|---|
| Leaching | Zn | Ferrite residues | Safe disposal, re-use of liquor |
| | Cu | Residues | Safe disposal |
| | Ni/Co | Cu/Fe residues | Recovery, disposal |
| Sulphuric acid plant | | Catalyst | Regeneration |
| | | Acid sludges | Safe disposal |
| | | Weak acid | Leaching, disposal |
| Furnace linings | All metals | Refractory | Use as slagging agent, disposal |
| Milling, Grinding | Carbon | Carbon and graphite dusts | Use as raw material in other processes |
| Pickling | Cu, Ti | Spent acid | Recovery |
| Dry abatement systems | Most - using fabric filters or ESPs | Filter dust | Return to process<br>Recovery of other metals |
| Wet abatement systems | Most - using scrubbers or wet ESPs | Filter sludge | Return to process or recovery of other metals (e.g. Hg). Disposal |
| Waste water treatment sludge | Most | Hydroxide or sulphide sludges. | Safe disposal, re-use<br>Re-use |
| Digestion | Alumina | Red mud | Safe disposal, re-use of liquor |

**Table 12: Overview of residues and available options for dealing with them**

Filter dusts can be recycled within the same plant or used for the recovery of other metals at other non-ferrous metal installations, by a third party or for other applications.

Residues and slags can be treated to recover valuable metals and render the residues suitable for other uses, e.g. as construction material. Some components can be converted into saleable products.

Residues from water treatment may contain valuable metals and can be recycled in some cases.

The regulator and operator should satisfy themselves that the recovery of residues by a third party is carried out to high environmental standards and does not cause negative cross-media effects.

- **Toxic Compounds**

Specific toxicity of some compounds that may be emitted (and their environmental impact or consequences) varies from group to group. Some metals have toxic compounds that may be emitted from the processes and so need to be reduced.

- **Energy recovery**

Energy recovery before or after abatement is applicable in the majority of cases but local circumstances are important, for example, where there is no outlet for the recovered energy. The BAT conclusions for energy recovery are:

1. Production of steam and electricity from the heat raised in waste heat boilers
2. The use of the heat of reaction to smelt or roast concentrates or melt scrap metals in a converter
3. The recovery of the heat content of hot process gases such as to preheat or dry feed materials, preheating of a furnace charge using the energy content of furnace gases or hot gases from another source to preheat the combustion air

4. The use of regenerative burners, recuperative burners or the preheating of combustion air
5. The use of CO produced as a fuel gas
6. The heating of leach liquors from hot process gases or liquors
7. The use of plastic contents in some raw materials as a fuel or reducing agent, provided that good quality plastic cannot be recovered and VOCs and PCDD/F are not emitted
8. The use of low-mass refractories where practicable.

## 6. BAT Conclusions from the individual sectors

In addition to the general conclusions there are specific conclusions about BAT for each of the sectors that comprise the non-ferrous metals industries and these are listed below.

- **Copper**

## 7. Degree of Consensus and Recommendations for Future Work

This BREF has met a high level of support from the TWG and participants at the 7th meeting of the Information Exchange Forum. Critical remarks have mainly related to information gaps and presentational aspects (calls for more BAT associated emission and consumption levels to be included in the Executive Summary).

It is recommended that this document be revised in 4 years time. The areas where additional efforts should be made to establish a sound basis of information include, above all, diffuse emissions and also specific emission and consumption data, process residues, waste water and aspects related to small and medium-sized companies. Chapter 2 contains further recommendations.

The EC is launching and supporting, through its RTD programmes, a series of projects dealing with clean technologies, emerging effluent treatment and recycling technologies and management strategies. Potentially these projects could provide a useful contribution to future BREF reviews. Readers are therefore invited to inform the European IPPC Bureau of any research results which are relevant to the scope of this document (see also the Preface of this document).

# PREFACE

## 1. Status of this document

Unless otherwise stated, references to 'the Directive' in this document means the codified IPPC Directive 2008/1/EC of the European Parliament and the Council. As the IPPC Directive applies without prejudice to Community provisions on health and safety at the workplace, so does this document.

This document is a working draft of the European IPPC Bureau. It is not an official publication of the European Communities and does not necessarily reflect the position of the European Commission.

## 2. Relevant legal obligations of the IPPC Directive and the definition of BAT

In order to help the reader understand the legal context in which this document has been drafted, some of the most relevant provisions of the IPPC Directive, including the definition of the term 'best available techniques', are described. This description is given for information only. It has no legal value and does not in any way alter or prejudice the actual provisions of the IPPC Directive.

The purpose of the IPPC Directive is to achieve integrated prevention and control of pollution arising from the activities listed in its Annex I, leading to a high level of protection of the environment as a whole. The legal basis of the Directive relates to environmental protection. Its implementation should also take account of other European Community objectives such as the competitiveness of the Community's industry thereby contributing to sustainable development.

More specifically, the Directive provides for a permitting system for certain categories of industrial installations requiring both operators and regulators to take an integrated, overall view of the potential of the installation to consume and pollute. The overall aim of such an integrated approach must be to improve the design, construction, management and control as well as decommissioning of industrial processes so as to ensure a high level of protection for the environment as a whole. Central to this approach is the general principle given in Article 3 of the Directive which states that operators should take all appropriate preventative measures against pollution, in particular through the application of the best available techniques enabling them to improve their environmental performance.

The term 'best available techniques' is defined in Article 2(12) of the Directive as 'the most effective and advanced stage in the development of activities and their methods of operation which indicate the practical suitability of particular techniques for providing in principle the basis for emission limit values designed to prevent and, where that is not practicable, generally to reduce emissions and the impact on the environment as a whole.' Article 2(12) goes on to clarify further this definition as follows:

1. 'techniques' shall includes both the technology used and the way in which the installation is designed, built, maintained, operated and decommissioned

2. 'available' techniques shall mean those developed on a scale which allows implementation in the relevant industrial sector, under economically and technically viable conditions, taking into consideration the costs and advantages, whether or not the techniques are used or produced inside the Member State in question, as long as they are reasonably accessible to the operator

3. 'best' shall means those most effective in achieving a high general level of protection of the environment as a whole.

Furthermore, Annex IV to the Directive contains a list of 'considerations to be taken into account generally or in specific cases when determining best available techniques... bearing in mind the likely costs and benefits of a measure and the principles of precaution and prevention'. These considerations include the information published by the Commission pursuant to Article 17(2) of the Directive.

Competent authorities responsible for issuing permits are required to take account of the general principles set out in Article 3 of the Directive when determining the conditions of the permit. These conditions must include emission limit values, supplemented or replaced where appropriate by equivalent parameters or technical measures. According to Article 9(4) of the IPPC Directive, these emission limit values, equivalent parameters and technical measures must, without prejudice to compliance with environmental quality standards, be based on the best available techniques, without prescribing the use of any technique or specific technology, but taking into account the technical characteristics of the installation concerned, its geographical location and the local environmental conditions. In all circumstances, the conditions of the permit must include provisions on the minimisation of long-distance or transboundary pollution and must ensure a high level of protection for the environment as a whole.

Member States have the obligation, according to Article 11 of the Directive, to ensure that competent authorities follow or are informed of developments in the best available techniques.

## 3. Objective of this document

Article 17(2) of the Directive requires the Commission to organise 'an exchange of information between Member States and the industries concerned on best available techniques, associated monitoring and developments in them', and to publish the results of the exchange.

The purpose of the information exchange is given in recital 27 of the Directive, which states that 'the development and exchange of information at Community level about best available techniques:

1. will help to redress the technological imbalances in the Community
2. will promote the worldwide dissemination of limit values and techniques used in the Community
3. will help the Member States in the efficient implementation of this Directive.'

The Commission (Environment DG) established an information exchange forum (IEF) to assist the work under Article 17(2) of the codified IPPC Directive 2008/1/EC and a number of technical working groups have been established under the umbrella of the IEF. Both IEF and the technical working groups include representation from Member States and industry as required in Article 17(2) of the Directive.

The aim of this series of documents, which will be continually reviewed and updated, is to reflect accurately the exchange of information which has taken place as required by Article 16(2) of the Directive and to provide reference information for the permitting authority to take into account when determining permit conditions. By providing relevant information concerning best available techniques, these documents should act as valuable tools to drive environmental performance.

## 4. Information sources

This document represents a summary of information collected from a number of sources, in particular, through the expertise of the groups established to assist the Commission in its work under Article 16(2) of the Directive, and verified by the Commission services. The work of the contributors and the expert groups is gratefully acknowledged.

## 5. How to understand and use this document

The information provided in this document is intended to be used as an input to the determination of BAT in specific cases. When determining BAT and setting BAT-based permit conditions, account should always be taken of the overall goal to achieve a high level of protection for the environment as a whole.

The rest of this section describes the type of information that is provided in each section of the document.

Chapter 1 provides general information on the industrial sector concerned. Chapter 2 provides information on the common industrial processes, abatement systems and general techniques that are used across the sector. Techniques to consider in the determination of BAT are reported in Chapter 2 unless they are the same as the applied techniques that are reported. Chapter 2 also concludes on BAT for process control, fume and gas collection, prevention and destruction of PCDD/F, sulphur dioxide removal, the removal of mercury, effluent treatment and water re-use and generally for other common processes. Chapters 3 to 12 give the applied processes, current emission and consumption levels, techniques to consider in the determination of BAT, the techniques that are considered to be BAT and emerging techniques for the metal groups that are represented by these chapters.

For each of the Chapters 3 to 12, data is provided for the group of metals in that chapter according to the following sections:

Section 1 describes the applied processes and techniques used for the particular group of metals.

Section 2 provides data and information concerning current emission and consumption levels reflecting the situation in existing installations.

Section 3 describes in more detail the emission reduction and other techniques that are considered to be most relevant for determining BAT and BAT-based permit conditions. This information includes the consumption and emission levels considered achievable by using the technique, some idea of the costs and the cross-media issues associated with the technique, and the extent to which the technique is applicable to the range of installations requiring IPPC permits, for example new, existing, large or small installations. Techniques that are generally seen as obsolete are not included.

Section 4 presents the techniques and the emission and consumption levels that are considered to be compatible with BAT in a general sense. The purpose is thus to provide general indications regarding the emission and consumption levels that can be considered as an appropriate reference point to assist in the determination of BAT-based permit conditions or for the establishment of general binding rules under Article 9([8]). It should be stressed, however, that this document does not propose emission limit values. The determination of appropriate permit conditions will involve taking account of local, site-specific factors such as the technical characteristics of the installation concerned, its geographical location and the local environmental conditions. In the case of existing installations, the economic and technical viability of upgrading them also should be taken into account. Even the single objective of ensuring a high level of protection for the environment as a whole will often involve making trade-off judgements between different types of environmental impact, and these judgements will often be influenced by local considerations.

Although an attempt is made to address some of these issues, it is not possible for them to be considered fully in this document. The techniques and levels presented in the BAT sections will therefore not necessarily be appropriate for all installations. On the other hand, the obligation to ensure a high level of environmental protection including the minimisation of long-distance or transboundary pollution implies that permit conditions cannot be set on the basis of purely local considerations. It is therefore of the utmost importance that the information contained in this document is fully taken into account by permitting authorities.

## 6. Dynamic nature of BAT and review of BAT reference documents (BREFs)

BAT is a dynamic concept because new techniques may emerge, technologies are still developing, or new environmental processes are being successfully introduced in the industry. Since the elements of BAT change over time and industry develops, BREFs have to be reviewed and updated as appropriate.

The original BREF on the non-ferrous metals industries was adopted by the European Commission in December 2001. This document is the result of the review of the NFM BREF.

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# Best Available Techniques Reference Document on the Non-Ferrous Metals Industries

## 3 PROCESSES TO PRODUCE COPPER AND ITS ALLOYS (INCLUDING TIN AND BERYLLIUM) FROM PRIMARY AND SECONDARY RAW MATERIALS ........ 284

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# SCOPE

This document addresses the industrial activities specified in Section 2.5 a) and b) of Annex I to the codified Council Directive 2008/1/EC (IPPC Directive):

*'2.5. Installations:*

*(a) for the production of non-ferrous crude metals from ore, concentrates or secondary raw materials by metallurgical, chemical or electrolytic processes;*
*(b) for the smelting, including the alloyage, of non-ferrous metals, including recovered products, (refining, foundry casting, etc.) with a melting capacity exceeding 4 tonnes per day for lead and cadmium or 20 tonnes per day for all other metals.'*

There are many similarities between primary and secondary production of non-ferrous metals and in some cases it is impossible to distinguish between the techniques used. In some cases, primary production of non-ferrous metal includes the integration of secondary raw material into common production processes to save energy, minimise production costs and recover important materials. Secondary production of non-ferrous metals includes the production of metal from secondary raw materials (including scrap and metal bearing materials) and the remelting and alloying processes. This BREF document covers the techniques for the production of both primary and secondary non-ferrous metals.

The production of carbon and graphite anodes (Section 6.8 of Annex I to the codified IPPC Directive) is included because of the similarity of part of the process to the production of anodes at some aluminium smelters as an integral part of the production process.

The production of 42 non-ferrous metals and the production of ferro-alloys were identified in countries who are obliged to implement IPPC. 10 groups of metals with similar production methods were identified. The study gathered data on the basis of these groups and this document is structured on this basis.

## The Metal Groups

The metal groups are:

- copper and its alloys, tin and beryllium
- aluminium and its alloys and the recycling of salt and aluminium from salt slags
- zinc, lead, cadmium, antimony and bisthmuth
- precious metals
- mercury
- refractory metals (e.g. Cr, W, V, Ta, Nb, Re, Mo)
- ferro-alloys (e.g. FeCr, FeSi, FeMn, SiMn, FeTi, FeMo, FeV, FeB)
- alkali and alkaline earth metals (e.g. Na, K, Li, Sr, Ca, Mg and Ti)
- nickel and cobalt
- carbon and graphite electrodes.

The production of radioactive metals is excluded from the document. The production of components such as semi-conductors is also excluded.

Installations under Section 2.1 of Annex I to the IPPC Directive – sintering and roasting – are covered by this document in two parts of the Annex:

a. those which are part of Section 2.5a) processes to produce the metal;
b. where roasting and sintering are carried out independently, for example the roasting of molybdenum sulphide.

There are interfaces with the chemicals sector but there are specific issues and differences that should be taken into account when these processes are associated with metal production, or when metal compounds are produced as by-products of the production of metal. The following processes are included in the scope of this work:

- The production of sulphur products such as elemental sulphur, sulphur dioxide and sulphuric acid when associated with the production of a non-ferrous metal. In the case of sulphuric acid, it is produced from the sulphur dioxide in gases emitted from various stages of the process. The gas concentration, temperature and trace contaminants influence process design and the choice of catalyst.
- The production of rhenium salts during the production of copper.
- The production of zinc oxide from fume during the production of other metals. *(Waelz kiln process?)*
- The production of nickel compounds from liquors produced during the production of a metal.
- The production of CaSi and Si which takes place in the same furnace as the production of ferro-silicon.
- The production of aluminium oxide from bauxite prior to the production of primary aluminium. *(is this realy included in this BREF?)* This is a pretreatment stage, which could be carried out at the mine or at the smelter. It is an integral part of the production of the metal when performed at the smelter and is therefore included in this document.

The rolling, drawing and pressing of non-ferrous metals, when directly integrated with the production of metal would be covered by a permit and are therefore included in this document. *(is this realy included in this BREF. See Sections 3.3.6.6 and 3.3.6.7. These sections contain no information)* Foundry processes are not included in this work and are covered in the BREF for the Smitheries and Foundries Industry [ 340, BREF - Smitheries and Foundries 2002 ].

In addition to basic manufacturing activities, this document covers the associated activities which could have an effect on emissions or pollution. Thus, this document includes activities from the preparation of raw materials to the dispatch of the finished products.

The main operations covered by the descriptions are:

- raw materials, storage and preparation
- fuels, storage and preparation
- the production processes, i.e. the pyrometallurgical and hydrometallurgical processes
- emission prevention and reduction techniques
- products, storage and preparation.

It should be noted that in 2000, for the industrial sectors covered by this document, data were collected for the EU-15. Furthermore in 2008, information and data have been updated for the EU-27 as far as possible.

## The structure of this document

Because of different products and processes involved, the structure of this document is described as follows:

Preliminary part: Executive Summary, Preface, Scope of the document
- Chapter 1: General description of the non-ferrous metal industries
- Chapter 2: General description of common processes and techniques used throughout the industries
- Chapter 3 to 12: General description of the metal groups described above
- supplementary part: References, Glossary, Annexes

Within Chapters 2 to 3, sections are built as described in the Preface.

## The use of other BREFs

The use of Energy Efficiency (ENE) [ 333, EC 2008 ], Common Waste Water and Waste Gas Treatment (CWW) [ 337, EC 2003 ], Large Volume Inorganic Chemicals - Ammonia, Acids and Fertiliser Industries (LVIC-AAF) [ 339, BREF LVIC-AAF 2007 ], General Principles of Monitoring (MON) [ 293, EC 2003 ] and other horizontal and vertical BREFs in conjunction with the Non-ferrous Metals Indistries BREF (NFM) is recommended within the procedure for applying or granting an IPPC permit.

The ENE BREF provides general guidance, and therefore may also provide information useful to other industries not covered by the IPPC Directive.

The CWW BREF was written for the chemical sector but there are also techniques that can be applicable to non-ferrous metals sector.

The LVIC-AAF BREF [ 339, BREF LVIC-AAF 2007 ]contains additional information about the manufacture of sulphuric acid.

Other horizontal BREFs should be considered within the procedure for applying or granting an IPPC permit:

- Industrial Cooling Systems (ICS) [ 342, European Commission 2001 ]
- Emissions from Storage (EFS) [ 290, EC 2006 ]
- General Principles of Monitoring (MON) [ 293, EC 2003 ]
- Economics and Cross-Media Effects (ECM) [ 336, EC 2006 ].

Other vertical BREFs might also need to be considered when the activities covered by them are operated on site or similar processes are used:

- Waste Treatments Industries (WT) [ 341, EC 2006 ]
- Waste Incineration (WI) [ 338, EC 2006 ]
- Large Combustion Plants (LCP) [ 343, EC 2006 ].

The steps shown in Figure 1 and elaborated below, need to be considered in order to ensure that the best use is made of information on (best available) techniques on issues which may be covered by this BREF and the other BREFs.

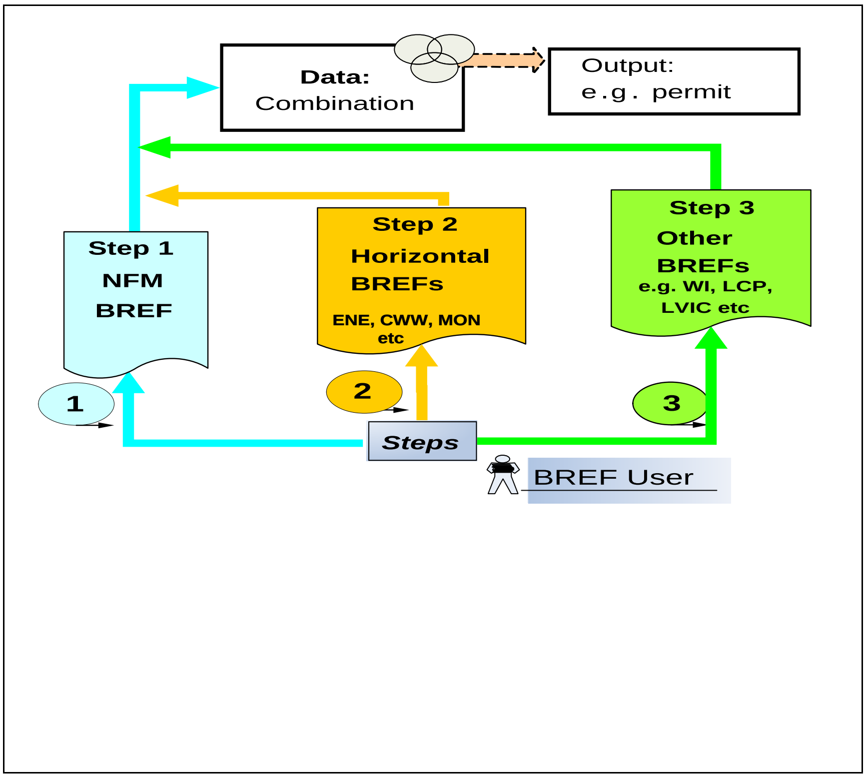


**Figure 1:** **Using NFM BREF with other BREFs**

**Step 1**: consult information from the NFM BREF

Identify appropriate techniques and BAT when preparing the permit. If there is insufficient information to determine the permit (or only partial information), then go to Step 2.

**Step 2**: consult information from Horizontal BREFs

This document may contain techniques to consider and BAT on activities which are not specifically covered (or only partly) by other BREFs.

Identify appropriate techniques and BAT in this document and use the BAT and supporting data when preparing the permit.

**Step 3**: identify, consult and add information from other relevant BREFs

Other vertical and horizontal BREFs may contain techniques and BAT on activities which are not covered at all, or not in enough detail by the NFM BREF (e.g. large combustion plants, waste incineration, emissions from storage).

# 1 GENERAL INFORMATION

## 1.1 Industry Overview

The European non-ferrous metals industry has an economic and strategic importance greater than its employment, capital and turnover statistics indicate. For example, high-purity copper is essential for electricity generation and distribution, and small amounts of nickel improve the corrosion resistance of steel.

Non-ferrous metals and their alloys therefore lie at the heart of modern life and many high technology developments, particularly in the energy generation, computing, electronic, telecommunications and transport industries depend upon them.

### 1.1.1 Non-ferrous metals and alloys

All the non-ferrous metals considered in this document have their own individual properties and applications. In several cases however, e.g. copper and aluminium, alloys are used in more applications than pure metals because they can be designed to have specific strength, toughness, etc. to meet the requirements of particular applications.

Metals are inherently recyclable and can be recycled time after time without losing any of their properties. They thus make a significant contribution to sustainable development. It is normally not possible to distinguish between refined metal that has been produced from primary or secondary raw materials and that produced from secondary raw materials (e.g. scrap).

### 1.1.2 Scope of the industry

The output of the industry is derived from a variety of primary and secondary raw materials. Primary raw materials are derived from ores that are mined and then further treated for example by washing and jigging to reduce waste material before they are metallurgically processed to produce crude metal. The treatment of ores is carried out close to the mines as, increasingly, is metal production. Secondary raw materials are indigenous scrap and residues.

In Europe, ore deposits that contain metals in viable concentrations have been progressively depleted and few indigenous sources remain. Most concentrates are thus imported into Europe from a variety of sources worldwide. The importance of using indigenous secondary raw materials such as scrap metal and other residues cannot be emphasised enough. Recycling constitutes an important component of the raw material supplies of the industry.

In the copper sector, secondary raw materials account for the production of about 45 % of EU copper but in some cases, such as brass rods, the product is made entirely from recycled copper and brass, with only a small input of primary zinc. When copper cathodes are produced from recycled materials there are savings of approximately 650000 t of $CO_2$ because specific direct emissions of secondary smelters are four times lower than those of primary smelters.

In the aluminium sector, the production and refining of secondary aluminium is also much less energy demanding, accounting for a consumption per kg of Al produced of about 5 % of the energy needed to produce primary aluminium.

The output of the industry is either refined metal or what is known as semis manufactures, i.e. metal and metal alloy cast ingots or wrought shapes, extruded shapes, foil, strip, rod, etc.

For this BREF document the non-ferrous foundries that produce cast metal products have not been included but are covered by the Smitheries and Foundries BREF document. The collection, sorting and supply of secondary raw materials for the industry lies within the metals recycling industry, which again is not considered in this document.

Although an apparent contradiction in terms, the production of ferro-alloys, which are mainly used as master alloys in the iron and steel industry, is considered part of the non-ferrous metals industry. Their alloying elements, i.e. refractory metals, chromium, silicon, manganese and nickel are all non-ferrous metals.

The precious metals sector is also considered part of the non-ferrous metals industry for the purposes of this document.

### 1.1.3 Structure of the industry

The structure of the industry varies by metal. There are no companies that produce all or even a majority of non-ferrous metals although there are a few pan-European companies producing several metals, e.g. copper, lead, zinc, and cadmium.

The size of the companies producing metals and metal alloys in Europe varies from a few employing more than 5000 people to a large number having between 50 and 200 employees.

Ownership varies between pan-European and national metals groups, industrial holdings groups, standalone public companies and private companies.

### 1.1.4 Economics of the industry

The key statistics of the European non-ferrous metals industry as defined for the purpose of this document are:

| | |
|---|---|
| output | 18 - 20 million tonnes |
| sales | EUR 40 - 45 billion |
| employees | more than 200000. |

Many refined non-ferrous metals are international commodities. The major metals (aluminium, copper, lead, nickel, tin and zinc) are traded on one of two future markets, the London Metal Exchange and Comex in New York. In addition to the New York Commodity Exchange (NYMEX), precious metals can also be traded on the London Bullion Market (LBMA), the Tokyo Commodity Exchange (TOCOM), the Zurich Gold Pool, the Dubai Multi Commodities Centre (DMCC) and the Bullion Vault. The collectively named ‘minor’ metals have no central market place; price levels are imposed by either producers or by merchants trading on the free markets. In most applications, a particular non-ferrous metal is in competition with other materials, notably ceramics, plastics and other ferrous and non-ferrous metals.

The profitability of each metal or metals group, and thus the economic viability of the industry both absolutely and on a short-term basis, depends upon a wide range of other economic factors such as the agreed treatment and refining charge rather than the metal price which often has no bearing on income.

The general economic rule applies however, i.e. the nearer a material or product approaches global market conditions and international commodity status, the lower is the return on the capital invested.

### 1.1.5 Environmental performance

There has been a steady improvement in the environmental performance and energy efficiency of the industry over the last twenty five years since the adoption of Directive 84/360/EEC ‘On the Control of Pollution from Industrial Plants’. The requirement to use best available techniques to minimise pollution is well understood by the industry in most Member States.

The recycling performance of the industry is very high. Metals are often produced at lower energy costs by using the recycling route. For example for copper; secondary smelting compared to primary smelting emits 4 times less carbon dioxide, consumes 3 times less electricity and 2.5 less fuel for combustion. Recycling of low quality, metal bearing residues however, requires higher efforts to protect the environment and improve energy-efficiency even further.

# 1.2 Copper and its alloys

## 1.2.1 General information

Copper has been used for many centuries; it has a very high thermal and electrical conductivity and is relatively corrosion-resistant. Used copper can be recycled without loss of quality. These properties mean that copper is used in diverse sectors such as electrical engineering, automobiles, construction, plumbing, machinery, shipbuilding, aircraft, and precision instruments. Copper is frequently alloyed with Zn, Sn, Ni, Al and other metals to make a range of brasses and bronzes [ 35, European Commission 1997 ].

Copper production is based on grade A copper cathodes, i.e. 99.95 % Cu. The grade A designation comes from the London Metal Exchange vocabulary for cathodes and refers to a British Standard. This has been replaced by a European CEN Standard EN 1978, where the quality is designated as Cu CATH1 or in the new European alphanumeric system CR001A.

The maximum tolerable impurities in percentages are as follows:

| | |
|---|---|
| Ag | 0.0025 |
| As | 0.0005 |
| Bi | 0.00020 |
| Fe | 0.0010 |
| Pb | 0.0005 |
| S | 0.0015 |
| Sb | 0.0004 |
| Se | 0.00020 |
| Te 0.00020 with As+Cd+Cr+Mn+P+Sb | 0.0015 |
| Bi+Se+Te | 0.0003 |
| Se+Te | 0.0003 |
| Ag+As+Bi+Cd+Co+Cr+Fe+Mn+Ni+P+Pb+S+Sb+Se+Si+Sn+Te+Zn | 0.0065 |

## 1.2.2 Sources of materials

Refined copper is produced from primary and secondary raw materials by a relatively small number of copper refineries; their product is copper cathode. This is melted, alloyed and further processed to produce rods, profiles, wires, sheets, strips, tubes, etc. This step may be integrated with the refinery but is frequently carried out at another site.

Important copper mine production can be found in Poland (KGHM Polska Miedź S.A. in Lubin, Polkowice-Sieroszowice and Rudna) with 512000 tonnes copper extracted in 2005. Other sizeable EU mining countries are Spain (startup of mining and hydrometallurgical production of copper cathodes at Las Cruces, ES in 2009 with a capacity of 72000 tonnes), Portugal (startup of mining at Neves Corvo, PT in 1989, with 90000 tonnes of copper in 2005), Sweden (102000 tonnes) and Bulgaria (95000 tonne).

With about 821000 tonnes of copper extracted from domestic ores in 2005, the EU-27 countries account for around 5.5 % of the total worldwide copper mine output. The former EU-15 total was 200000 tonnes (1.3 %).

### 1.2.3 Production sites

Annual refined copper production in the EU-27 reached 2.4 million tonnes in 2005, representing 14.5 % of worldwide production. The EU-15 accounted for 1.8 million tonnes (10.6 %). The largest facilities are located in Germany, Poland, Spain, Sweden, Finland, Belgium and Bulgaria. The final refinery products, copper cathodes, are made through electrolytic processes. These are often melted and cast on the premises into 'refinery shapes', referred to as billets and cakes. Some copper refiners also produce wire-rod, either at the refinery location or elsewhere [ 238, ECI Copper Installations 2008 ].

About 45 % of feed supplies to the EU-27 copper refineries are purchased on the international market in the form of copper concentrates, blister, anodes or scrap. (The EU-15 required 60 % imports). The remaining 55 % come from EU-produced copper concentrates, copper-bearing residue and scrap.

EU copper smelting and refining activity has been able to grow primarily by securing raw materials on the international market and by making use of 'domestic mining'. This consists of copper scrap and residues generated by consumers and processors, as well as by building demolition and end-of-life waste (e.g. vehicles and electric and electronic waste). Access to primary and secondary supplies has become increasingly difficult. This has partly been due to copper mining countries developing their own smelting and refining facilities, but mainly due to much stronger competition from countries such as China and India, seeking copper raw materials to meet the needs of their rapid industrialisation.

In 2007, there were fifteen major refineries in the EU-27, employing around 10000 people. There were eleven in the EU-15, and two were closed at the beginning of the 2000s, MKM in Germany and IMI in the UK.

The major changes have been [ 238, ECI Copper Installations 2008 ]:

- the inclusion of KGHM Poland
- the demerger of the Olen and Pirdop copper activities of Umicore (Union Minière) to the new company Cumerio
- the merger of Hüttenwerke Kayser into Norddeutsche Affinerie AG
- the merger of Norddeutsche Affinerie AG and Cumerio into Aurubis AG
- the merger of Outokumpu Harjavalta and Pori into New Boliden AB
- the merger of Krompachy into Montanwerke Brixlegg AG
- the closure of the secondary copper smelters of IMI Refiners and MKM.

The resulting structure of the European copper smelting and refining industry is as follows:

- Atlantic Copper S.A. in Huelva, Spain;
- New Boliden AB with sites in Harjavalta and Pori, Finland and Rönnskär, Sweden;
- Aurubis AG with sites in Hamburg, Germany; Lünen, Germany; Pirdop, Bulgaria and Olen, Belgium;
- KGHM Polska Mièdz S.A. with sites in Głogów (1 and 2) and Legnica, Poland;
- Metallo-Chimique N.V. in Beerse, Belgium with its daughter company Elmet S.L. in Berango, Spain;
- Montanwerke Brixlegg AG, Austria with its daughter company Krompachy, Slovakia;
- Umicore S.A. in Hoboken, Belgium.

Some of these are clear primary smelters (Atlantic Copper, KGHM, Pirdop, and Harjavalta) which use copper concentrates as their primary feedstock. Others are clear secondary smelters (Metallo-Chimique, Montanwerke Brixlegg, and Aurubis, Lünen), where the main feedstocks are scrap from the downstream value chain plus recycled products at their end of life. Some have the flexibility to process both primary and secondary feedstocks, like Boliden, Rönnskär and Aurubis AG, Hamburg.

New installations, facilities and technology innovations that have been developed since 2000 are [ 238, ECI Copper Installations 2008 ]:

- the KRS-smelter for secondary copper materials in Lünen;
- the ISA-Smelt-furnace in combination with a leaching and electrowinning plant in Hoboken;
- the house in house concept to capture diffuse emissions in Hamburg;
- chemical gypsum plant in primary smelting in a multi-stage process (Huelva and Pirdop);
- new fayalite slag tailings pond (Pirdop).

Two companies have capacities of around or over 500000 tonnes refined copper per year. KGHM, with three sites in Poland, Głogów I and II and Legnica; Aurubis AG with sites in Hamburg and Lünen (Germany) and Olen (Belgium) and Pirdop (Bulgaria).

Two others have capacities of around 300000 tonnes Boliden in Rönnskär (Sweden) and Harjavalta/Pori (Finland), bought from Outokumpu in 2003, and Atlantic Copper in Huelva (Spain).

Montanwerke Brixlegg in Brixlegg (Austria) and Krompachy (Slovakia) produces around 100000 tonnes and Metallo-Chimique at Beerse, in Belgium and at Elmet in Berango, Spain, account for less than 50000 tonnes (as cathodes but more than 100000 tonnes as anodes).

Umicore (formerly Union Minière) in Hoboken (Belgium), OMG in Kokkola (Finland) and Cyprus Copper, Cyprus also produce refined copper using a direct electrochemical route, with capacities of between 5000 and 50000 tonnes.

There are some other, smaller facilities in the new Member States (e.g. Baia Mare, Romania) and no information was made available.

Not all companies have balanced capacities between smelting and electrolytic refining. Some ship a large part of their anodes (>99 % copper) to refineries for final cathode (>99.9 % copper) production.

Depending on the sources of scrap, EU versus imports, EU copper smelting and refining capacities can meet less than half of end-user demand. This structural shortage of EU refined copper production is expected to continue, with the EU remaining a large net importer.

### 1.2.4 Production and use

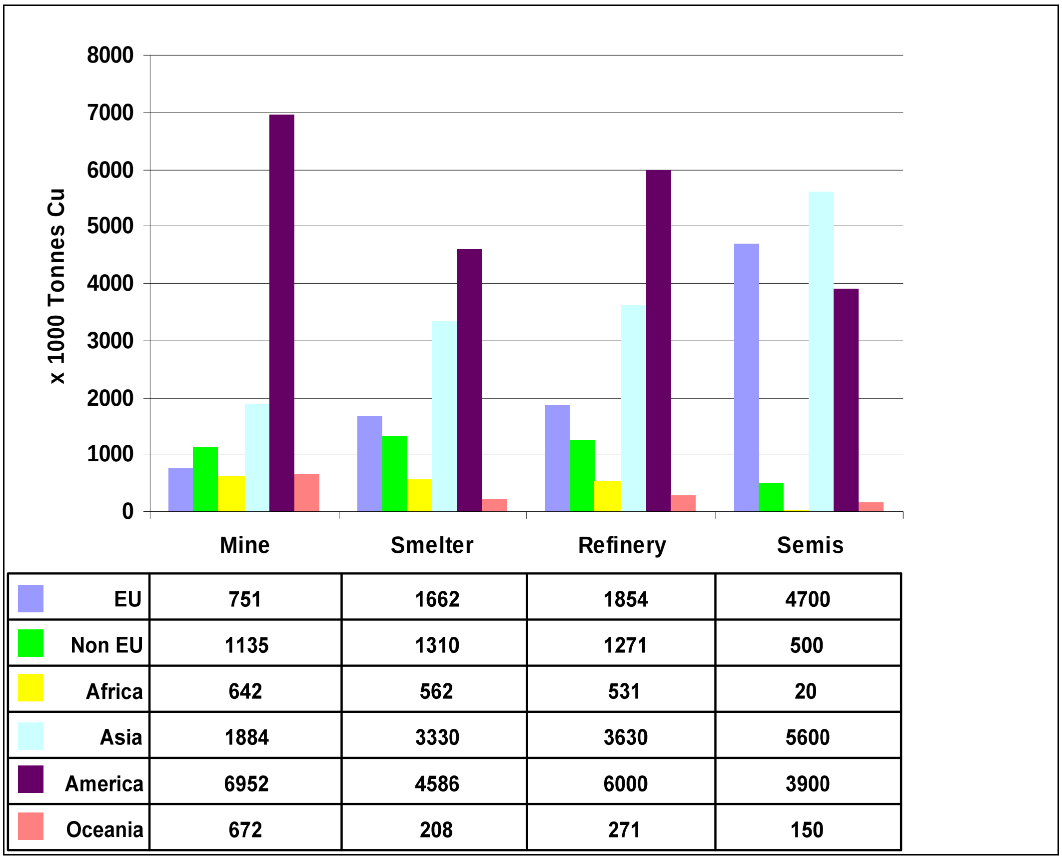
The products of the refineries are the major raw materials for the manufacturers of semi-fabricated products. With an output twice that of EU refinery output, the EU-27 semis manufacturers directly use a significant amount of scrap in the range of one million tonnes per year. They must also turn to the international market to secure adequate supplies of refined copper. It is estimated that around 60 % of their raw materials come from primary sources, the remaining 40 % from the direct use of scrap and other secondary materials [ 238, ECI Copper Installations 2008 ].

The 2005 output of the copper and copper alloy semis industry in the EU-27 exceeded 5.2 million tonnes (about 4.8 million tonnes copper equivalent). This represented more than one quarter of worldwide production. Despite this relatively large percentage, this was the lowest level this century, 10 % lower than the average of the past six years, and 20 % less than the peak in 2000. Germany, Italy and France account for about two thirds of EU-27 output. The range of products supplied by the semi manufacturers is very wide, consisting primarily of rods, profiles, wires, sheets, strips and tubes. Applications are equally diverse, and are used in sectors such as electrical engineering, automobiles, construction, machinery, shipbuilding, aircraft, precision instruments, watches and clocks, etc.

The production capacity of the EU semis industry exceeds demand. While recent figures from 2005 show the EU to be a net exporter of about 500000 tonnes per year, this over-capacity makes the industry, and its economic well-being, very sensitive to cyclical movements in demand.

The electrical wire-rod sector accounts for around half of semis production. Some 20 companies, employing around 3000 people in total, are involved in this sector. Whilst part of this is the integrated downstream output of copper refiners (e.g. KGHM and Aurubis AG), a significant part is upstream integration by wire and cable producers (e.g. Nexans and Prysmian) [ 238, ECI Copper Installations 2008 ].

Figure 1.1 shows the worldwide production of copper in 2005, semis include billets, cakes, ingots, plates as well as wire rods.



| | Mine | Smelter | Refinery | Semis |
|---|---|---|---|---|
| 🟪 EU | 751 | 1662 | 1854 | 4700 |
| 🟩 Non EU | 1135 | 1310 | 1271 | 500 |
| 🟨 Africa | 642 | 562 | 531 | 20 |
| 🟦 Asia | 1884 | 3330 | 3630 | 5600 |
| 🟪 America | 6952 | 4586 | 6000 | 3900 |
| 🟥 Oceania | 672 | 208 | 271 | 150 |

**Figure 1.1: Worldwide copper production in 2005**
**[ 238, ECI Copper Installations 2008 ],**

Far more companies participate in the other copper semis manufacturing industries. About 80 companies, employing some 35000 people throughout the EU-27, produce copper and copper alloy rods, bars, wires, sections, tubes, plates, sheet and strip. This sector is led by two large companies, KME Group SpA. (IT), with major manufacturing activities in France, Germany, Italy and Spain and Wieland Werke (DE) with operations in Austria, Germany and the UK. The semis activities of Boliden (SE) were acquired by Outokumpu (FL) in 2004. A major part of these were then demerged into a new company, Luvata, in 2006. Other large companies include Diehl (DE), Carlo Gnutti (IT), and Halcor (EL). About 30 companies in this sector have integrated foundries for the production of cakes, billets and other primary shapes for further processing. The others purchase these either from the smelters/refiners or from other semis manufacturers [ 238, ECI Copper Installations 2008 ].

Table 1.1 shows the copper production in the EU (and EAA) and Figure 1.2 and Figure 1.3 show the products.

| Country | Mine production | Primary cathode(anode) | Secondary cathode (anode) | Semis production |
|---|---|---|---|---|
| Austria | | | 77 | 58 |
| Belgium | | | 183 (126) | 392 |
| Bulgaria | 95 | 69 (208) | | |
| Denmark | | | | |
| Finland | 9 | 116 (171) | | 120 |
| France | | | | 616 |
| Germany | | 296 | 378 | 1406 |
| Greece | | | | 81 |
| Ireland | | | | |
| Italy | | 6 | 80 | 990 |
| Luxembourg | | | | |
| The Netherlands | | | | |
| Poland | 490 | 560 | | 229 |
| Portugal | 108 | | | |
| Spain | 37 | 229 (+61) | 63 (+28) | 268 |
| Sweden | 87 | 95 | 34 | 206 |
| UK | | 9 | 58 | 483 |
| Iceland | | | | |
| Norway | | 33 | | |
| Switzerland | | | | 70 |
| NB: Semis include billets, cakes, ingots, plates as well as wirerods.<br>Ore production in Europe accounts for ~30 % of primary feed | | | | |

**Table 1.1:** European production of copper and its alloys in thousand tonnes in 2007

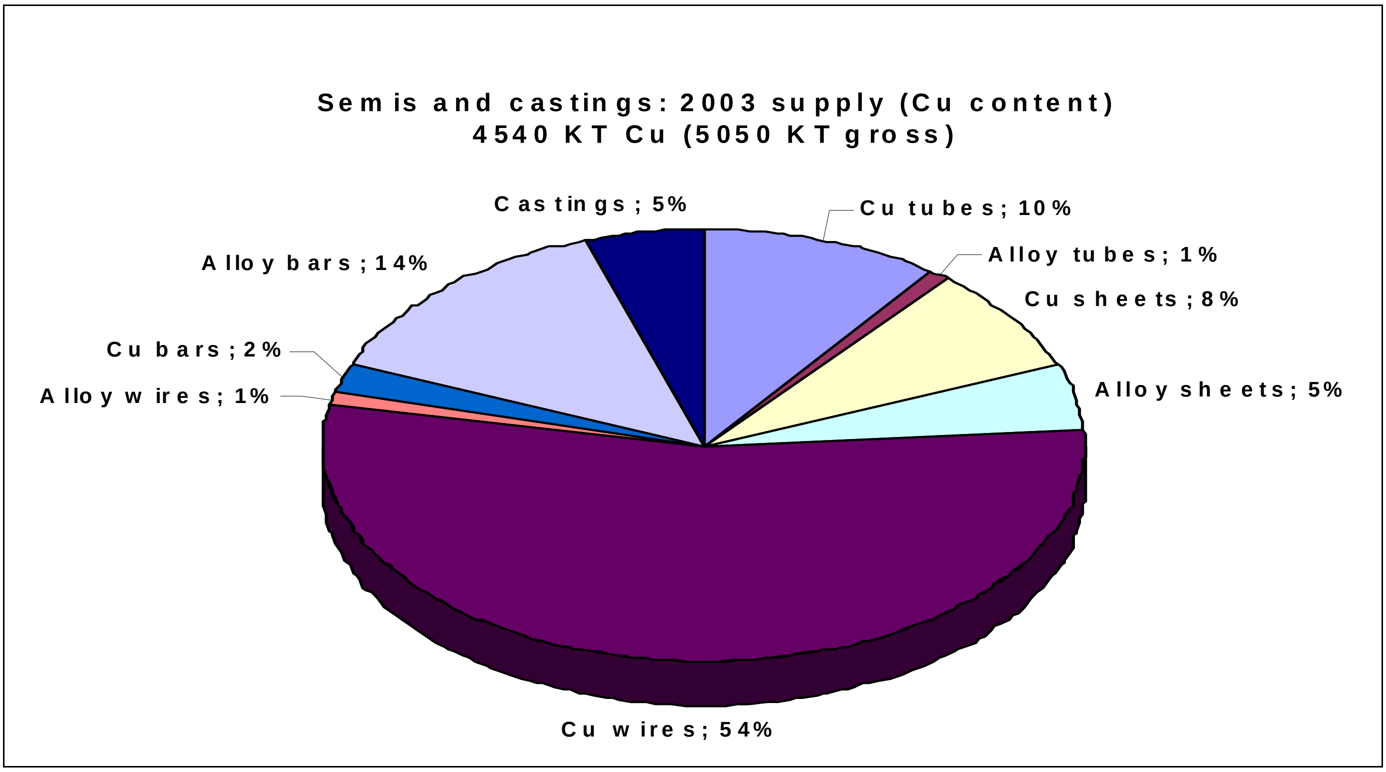


**Figure 1.2:** Copper Semis Products produced in 2003
[ 238, ECI Copper Installations 2008 ]

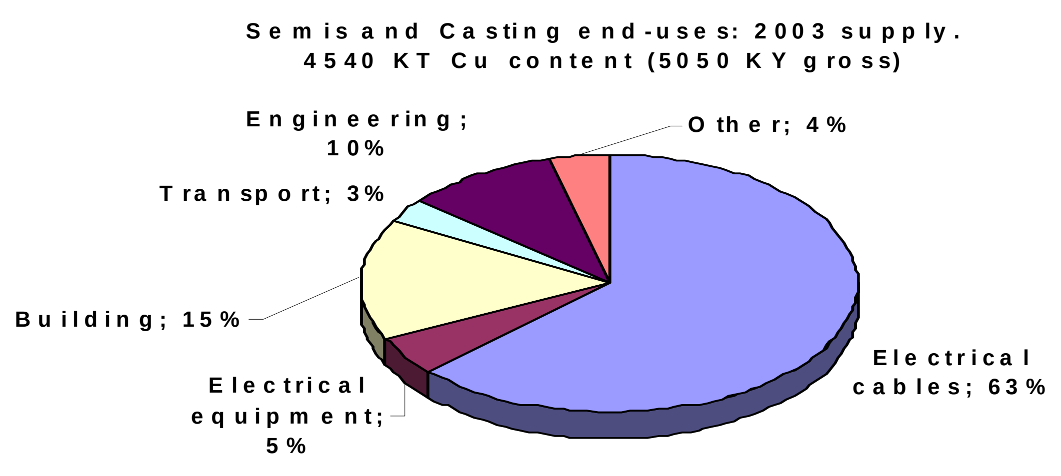


**Figure 1.3: End uses for semis produced in the EU in 2003**
**[ 238, ECI Copper Installations 2008 ].**

### 1.2.5 Environmental issues

Historically, the major environmental problem associated with the production of copper from primary sources were the emissions of sulphur dioxide to air from the roasting and smelting of sulphide concentrates. This problem has been effectively solved by the EU smelters who now achieve on average 98.9 % fixation of the sulphur and produce sulphuric acid and liquid sulphur dioxide.

The main environmental issues associated with the production of secondary copper are also related to the off-gases from the various furnaces in use. There is also the potential for the formation of PCDD/F due to the presence of small amounts of chlorine in the secondary raw materials and the destruction of PCDD/F is an issue that is being pursued [ 219, VDI (D) 2102 2007 ].

Diffuse or uncaptured emissions is also an issue that is becoming increasingly important for both primary and secondary production. Careful plant design and process operation is needed to capture process gases.

Recycling constitutes an important component of the raw material supplies of the copper refining and manufacturing facilities. Copper can be recovered from the major part of its applications and returned to the production process without loss of quality in recycling. Having very limited access to domestic primary sources of copper, the EU industry has traditionally given much attention to so-called 'surface mines', relying, to a large extent, on scrap feed to reduce the large deficit of its copper raw materials trade balance.

Almost 100 % of new or process copper scrap is recycled and, according to some studies, it has been estimated that 95 % of old copper scrap that becomes available is also recycled.

Overall, secondary raw materials account for the production of about 45 % of EU copper but in some cases, such as brass rods, the product is made entirely from recycled copper and brass, with only a small input of primary zinc.

The quality of secondary raw materials varies greatly and many sources of these materials are not suitable for direct use by the semis manufacturers. The scrap industry is relied upon to provide graded material of adequate cleanliness for the industry and although there are agreed specifications for scrap, wide variations are encountered. Additional treatment or abatement systems may be needed.

The EU copper industry has developed advanced technologies and made considerable investments to be able to process a wide range of copper scrap, including complex, low grade residues, and to comply at the same time with increasingly stringent environmental constraints.

The ability of the industry to increase this high recycling rate depends on a number of complex factors.

# 1.3 Aluminium

## 1.3.1 General information

Aluminium [ 35, European Commission 1997 ] is a material with a large range of applications, in the transportation, construction and packaging industries, the electricity sector, in all high-voltage electricity distribution systems, household appliances, and in the mechanical and agricultural sectors. It is light, has good electrical conductivity and forms a surface oxide layer when exposed to air that prevents further corrosion. Aluminium is highly reactive particularly in the form of powder and is used in aluminothermic reactions to produce a variety of other metals.

The aluminium industry is the youngest and largest of the non-ferrous metal industries; aluminium smelting only began about a century ago. The EU aluminium industry directly represents a workforce of about 250000 people and its annual turnover is in the order of EUR 38000 million in 2006.

## 1.3.2 Sources of materials

Primary aluminium is produced from bauxite that is converted into alumina. 100 tonnes of bauxite produces 40 to 50 tonnes of alumina (aluminium oxide) which then produces 20 to 25 tonnes of aluminium. Most of the bauxite is mined outside Europe but there are several alumina production facilities within Europe.

The secondary industry is dependent on sources of scrap. Scrap can be termed 'new scrap' that is generated during the production and fabrication of wrought and cast products or 'old scrap' that is recovered from articles at the end of their useful life. The recycling rate of 'new scrap' is 100 % of the amount produced.

## 1.3.3 Production and use

The European aluminium industry features mining and alumina production, primary and secondary smelting and metal processing into semi-finished products (e.g. bars, profiles, wires, sheets, foils, tubes, pipes) or speciality products (e.g. powders, special alloys). Table 1.2 shows the various materials produced by the aluminium sector in the EU-27.

| Material produced | EU-27 production (millions of tonnes) |
|---|---|
| **Metal production** | |
| Bauxite mining | 2.81 |
| Alumina refining | 6.9 |
| Primary metal production | 3.1 |
| Secondary metal production (refining + remelting) | 5.1 |
| **Semis** | |
| Rolled | 4.5 |
| Extruded | 3.2 |
| Other | 1 |
| **Total Semis** | 8.7 |
| Castings | 33 |

**Table 1.2: Production of aluminium in the EU-27 in 2007**

In 2007 the EU-27 accounted for about 8 % of the total world production of primary aluminium but is a net importer of aluminium. Table 1.3 shows the production and consumption in world areas.

| Area | Production (thousand tonnes) | Consumption (thousand tonnes) |
|---|---|---|
| Rest of Europe | 5151 | 8267 |
| EU-27 | 3093 | 7739 |
| US | 2560 | 5774 |
| Russia | 3949 | 1130 |
| Canada | 3083 | 742 |
| China | 12559 | 12100 |
| Australia | 1963 | 410 |
| Brazil | 1655 | 854 |
| India | 1223 | 1150 |
| Middle East | 1738 | NA |
| Rest of the world | 4154 | 7642 |
| Total World | 41128 | 45808 |

**Table 1.3: Primary aluminium production and consumption by country in 2007**

The following Table 1.4 shows the sources of imported primary aluminium to EU-27 as a percentage of the total imports.

| Area | Imports to EU-27 (% of total imports) |
|---|---|
| Asia | 3 |
| North America | 5 |
| Middle East | 6 |
| Latin America | 9 |
| Africa | 16 |
| Russia | 17 |
| Rest of Europe (without Russia) | 44 |

**Table 1.4: Imports of primary aluminium to EU-27 in 2007**

The EU-27 production of aluminium from secondary raw materials in 2007 represents about one third of the world secondary production.

### 1.3.4 Production sites

In 2007 a total of 25 primary aluminium smelters were operating in the EU-27, and a further 10 in the EEA. The number of companies is much smaller, and consists in Rio Tinto Alcan (UK, France and Iceland), Alcoa Europe (Spain, Italy and Iceland), Hydro Aluminium (Norway and Germany), Zalco (the Netherlands), Trimet (Germany), Alro (Romania), Slovalco (Slovakia), Talum (Slovenia), Mytilineos (Greece), Rusal (Sweden) and Century (Iceland). Some of these companies have subsidiaries or branches in other parts of the world, or are part of international corporations.

The situation is different for the secondary sector, in which over 130 companies produce more than 1000 tonnes per year of secondary aluminium each. There is a good integration of the rolling activity with the production processes but the extrusion industry is much less integrated, with about 300 production sites scattered over the EU territory. Many production activities are integrated, but a number of EU manufacturers focus their activity on one particular segment only, such as recycling and secondary smelting or semis fabrication.

### 1.3.5 Environmental issues

The main environmental issues for primary aluminium are the production of poly-fluorinated hydrocarbons and fluorides during electrolysis, the production of solid waste from the cells and the production of solid waste during the production of alumina. The production of $SO_2$ from the sulphur content of the anodes is an issue in the Netherlands. The industry has made progress to reduce these emissions, in particular by adopting for most of the smelters the Prebaked technology and upgrading the remaining Soderberg smelters in order improve their environmental and energy performances.

Emissions have been reduced over the last fifteen years by a factor of between four to ten, depending on the type of emissions and the process used ~~[ 312, VDI 2286 Aluminium Part 2 2008 ] [ 357, VDI 2286 Part 1 1998 ]~~ *This information is from the 10 years old BREF and not from [312]. For this reason these kind of statements can not simply be repeated and have to be checked about the situation in the last 10 years.*

Regarding the production of secondary aluminium, there are potential emissions of dust and PCDD/F from poorly operated furnaces and poor combustion and the production of solid wastes (salt slag, spent furnace linings, dross and filter dust).

The main cost of producing primary aluminium is electricity, and production tends to concentrate where low cost electricity is available, thus determining the geographical distribution of the production sites. The European aluminium industry has made considerable efforts to reduce its electricity consumption, reaching at present an average of 15 kWh per kg. The production and refining of secondary aluminium is much less energy demanding, accounting for a consumption per kg of about 5 % of the energy needed to produce primary aluminium.

There are many initiatives involved in improving the return of scrap aluminium and the industry is an active player in this area. The recycling of used beverage cans (UBCs) is an example of this. Collected material is recycled in a closed loop to produce more beverage cans to the same alloy specification. Much attention is paid by the secondary industry to produce the correct alloy composition and pre-sorting of scrap types is important. An example of this is the segregation of extrusion scrap to preserve the particular alloy.

# 1.4 Zinc, lead and cadmium

## 1.4.1 Zinc

### 1.4.1.1 General information

Zinc [ 35, European Commission 1997 ], [ 117, Krüger, J. 1999 ] has the third highest usage of non-ferrous metal, behind aluminium and copper. It has a relatively low melting point and is used in the production of a number of alloys such as brass. It can be easily applied to the surface of other metals such as steel (galvanising) and when it is used as a metal coating, zinc corrodes preferentially as a sacrificial coating. Zinc is also used in the pharmaceutical, nutrient, construction, battery and chemical industries. See Table 1.5

| Commercial use of zinc | Worldwide 1995 (%) | Worldwide 2000 (%) | Worldwide 2005 (%) | Europe 2005 (%) |
|---|---|---|---|---|
| Galvanising | 47.9 | 48.6 | 51.4 | 44.4 |
| Zinc alloying | 12.9 | 15.7 | 16.4 | 14.5 |
| Brass and bronze | 20.7 | 19.3 | 17.0 | 20.4 |
| Zinc semi-finished products | 6.5 | 6.2 | 5.7 | 12.6 |
| Chemicals | 8.5 | 7.0 | 6.1 | 6.5 |
| Zinc dust or powder | 0.5 | 0.2 | 0.2 | 0.2 |
| Miscellaneous | 3.1 | 3.0 | 1.4 | 1.4 |

**Table 1.5: World and European uses of zinc**
**[ 228, IZA plant data 2008 ]**

Zinc is supplied to the market in various qualities, the highest quality is special high grade (SHG) or Z1 which contains 99.995 % zinc while the lowest quality good ordinary brand (GOB) or Z5 is about 98 % pure. The sector produces extrusion products such as bars, rods and wires (mainly brass); rolling products such as sheets and strips; casting alloys; and powders and chemical compounds, such as oxides (see Table 1.6 and Table 1.7).

| Grade classification | Colour code | Nominal zinc content | 1 Pb max. | 2 Cd max. | 3 Fe max. | 4 Sn max. | 5 Cu max. | 6 Al max. | Total of 1 to 6 max. |
|---|---|---|---|---|---|---|---|---|---|
| Z1 | white | 99.995 | 0.003 | 0.003 | 0.002 | 0.001 | 0.001 | 0.001 | 0.005 |
| Z2 | yellow | 99.99 | 0.005 | 0.003 | 0.003 | 0.001 | 0.002 | - | 0.01 |
| Z3 | green | 99.95 | 0.03 | 0.005 | 0.02 | 0.001 | 0.002 | - | 0.05 |
| Z4 | blue | 99.5 | 0.45 | 0.005 | 0.05 | - | - | - | 0.5 |
| Z5 | black | 98.5 | 1.4 | 0.005 | 0.05 | - | - | - | 1.5 |
| Relevant standard EN 1179.2003. | | | | | | | | | |

**Table 1.6: Primary zinc grades**

| Grade | Nominal Zinc content | 1 Pb max. | 2 Cd max | 3 Fe max. | 4 Sn max. | 5 Cu max. | 6 Al max | Total of 1 to 6 max. | Remarks |
|---|---|---|---|---|---|---|---|---|---|
| ZSA | 98.5 | 1.3 | 0.02 | 0.05 | _ (1) | --- | 0.05 | 1.5 | Grades made mainly from Zinc bearing process scrap (e.g. Zn ashes) |
| ZS1 | 98.0 | 1.3 | 0.04 | 0.05 | 0.7 (1) | --- | 0.1 | 2.0 (2)<br>1.5 | Mainly by recycling of scrap |
| ZS2 | 97.5 | 1.5 | 0.05 | 0.12 | 0.7(1) | - - | - - | 2.5(2)<br>2.0 | Also used products |

Notes: Relevant standard EN 1179.2003.
(1) Sn max 0.3 % for brass making.
(2) For galvanising applications, EN ISO 1461: zinc bath must contain less than 1.5 % alloying elements (excluding. Fe & Sn) and 2.0 % (including Fe & Sn)

**Table 1.7: Secondary zinc grades**

End-uses include a wide range of applications, the most important being steel protection against rust for the automobile, appliance and building industries. Zinc alloys (e.g. brass, bronze, die casting alloys) and zinc semis are respectively the second and third major consumption areas with applications also in the building, appliance and car industries.

### 1.4.1.2 Sources of materials

Metal is produced from a range of zinc concentrates by pyrometallurgical or hydrometallurgical processes. Some concentrates contain high proportions of lead and these metals are also recovered. Zinc is also associated with cadmium and the concentrates are a source of this metal.

EU concentrates used to meet more than 45 % of the EU refinery requirements 20 years ago. This fell to 25 %, but they now account for 38 % of the requirements due to the accession of 12 new Member States. The deficit is filled in by increased imports, as mine production capacity is increasing in North America, Australia and some South American countries.

Secondary raw materials such as galvanising residues (ashes, skimmings, sludges, etc.), flue dust from steel plants are used. Brass processing and die-casting scrap, end-of-life roofing products are also sources of zinc. Metal production from secondary sources accounted for more than 8 % of the total EU refined zinc output in 1994. The recycling of zinc and zinc products is a key issue for the industry.

### 1.4.1.3 Production and use

The EU mine output is essentially accounted for by Ireland, Sweden and Poland and was 818000 tonnes of zinc concentrates in 2007. This increase from 400000 tonnes in 1998, is a result of process optimisation, opening of new mining operations and the accession of Poland. Metal production stepped back below the 1.8 million tonnes mark which it had overstepped in 1992, while consumption of refined zinc increased from 1640000 tonnes to 1770000 tonnes, accounting for 30 % of the demand for zinc in the market economy countries. See Table 1.8, Table 1.9 and Figure 1.4.

| | Production in 1995 (in 1000s of tonnes) | Production in 2000 (in 1000s of tonnes) | Production in 2005 (in 1000s of tonnes) | Production in 2007 (in 1000s of tonnes) |
|---|---|---|---|---|
| India | | | | 745 |
| Canada | 1121 | 1002 | 667 | 619 |
| Australia | 882 | 1380 | 1329 | 1402 |
| Peru | 692 | 910 | 1202 | 1444 |
| US | 644 | 852 | 748 | 787 |
| EU | 555 | 676 | 841 | 818 |

**Table 1.8: World production of zinc concentrates in 2007**
**[ 228, IZA plant data 2008 ]**

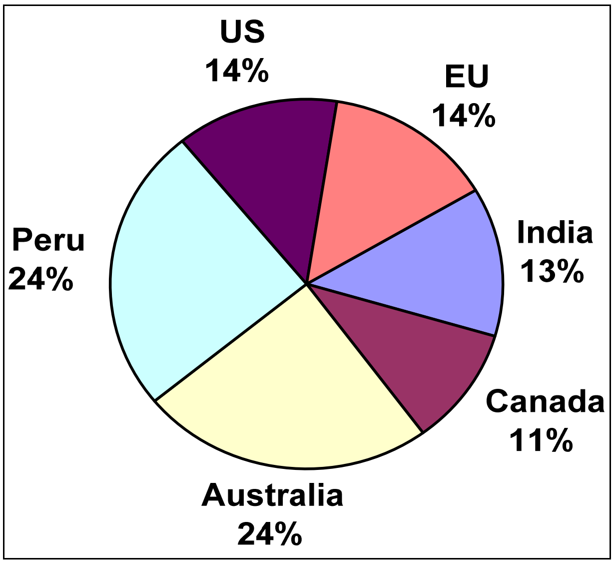


**Figure 1.4: World production of zinc from concentrates in 2007 excluding China**
[ 228, IZA plant data 2008 ]

After China, the EU stands as the second world leader in zinc production, far ahead of Canada and Japan, which rank third and fourth respectively. In 2007, the EU output was recorded at 2160000 tonnes of primary metal production, accounting for nearly 20 % of the market economy total of 11000000 tonnes. Also after China, the EU is the major consumer area for zinc among the market economy countries. The 2500000 tonnes zinc consumed in 2007 was 30 % below the reported Chinese market and more than double the third largest consumer market, the US.

| | Production in 1995 (in 1000s of tonnes) | Production in 2000 (in 1000s of tonnes) | Production in 2005 (in 1000s of tonnes) | Production in 2007 (in 1000s of tonnes) |
|---|---|---|---|---|
| China | No data has been reported | No data has been reported | No data has been reported | 3700 |
| EU | 1999 | 2016 | 2034 | 2160 |
| Canada | 720 | 780 | 724 | 802 |
| India | | | | 745 |
| Japan | 664 | 654 | 638 | 598 |
| US | 363 | 371 | 350 | 266 |
| Australia | 322 | 494 | 457 | 502 |
| CIS | 410 | 538 | 608 | 668 |

**Table 1.9: World production of refined zinc**
**[ 228, IZA plant data 2008 ]**

### 1.4.1.4 Production sites

Primary zinc is essentially produced by roast-leach-electrowinning processes (RLE) and by the Imperial Smelting Furnace (ISF) - distillation process. Table 1.10 shows the location and capacities of the sites in Europe.

| Country | Company | Location | Process | Capacity (t/yr) |
|---|---|---|---|---|
| Belgium | Nyrstar | Balen- Overpelt | RLE | 260000 |
| Bulgaria | KCM<br>OCK | Plovdiv<br>Karjali | RLE<br>RLE | 75000<br>45000 |
| Finland | Boliden | Kokkola | RLE | 305000 |
| France | Nyrstar | Auby | RLE | 130000 |
| Germany | Ruhr-Zink (1)<br>Xstrata | Datteln<br>Nordenham | RLE<br>RLE | 150000<br>140000 |
| Italy | Glencore | Porte Vesme (Sardegna) | RLE | 100000 |
| The Netherlands | Nyrstar | Budel-Dorplein | RLE | 240000 |
| Norway | Boliden | Odda | RLE | 165000 |
| Poland | ZGH Boleslaw<br>HC Miasteczko Slaskie | Boleslaw<br>Miasteczko | RLE<br>ISF | 90000<br>80000 |
| Romania | Mytilineos | Copsa Mica | ISF | 45000 |
| Spain | Xstrata<br>Española del Zinc | Sun Juan de Nieva<br>Cartagena | RLE<br>RLE | 490000<br>- |
| (1) Ruhr-Zinc ceased operation on 31 – 12 - 2008 | | | | |

**Table 1.10: Production of zinc metal in Europe from primary raw materials in 2007**
[ 228, IZA plant data 2008 ]

Zinc is recycled from end-of-life products such as sheets, brass and die casting parts which are remelted and re-used. It is also recycled from the remelting of scrap steel in electric arc furnaces (EAF) and the zinc reports to the dust which is captured and is treated in specialised facilities. Table 1.11 shows the location and capacities of the sites in Europe.

| Country | Company | Location | Process | Average production as Zn (kt/yr) |
|---|---|---|---|---|
| Bulgaria | KCM | Plovdiv | Waelz | 20 |
| France | Arcelor-Mittal<br>Recytech | Isbergues<br>Fouquières | MHF (1)<br>Waelz | 20<br>25 |
| Germany | Befesa<br>Befesa<br>Recylex | Duisburg<br>Freiberg<br>Gosslar | Waelz<br>Waelz<br>Waelz | 20<br>45<br>15 |
| Italy | Ponte Nossa, SpA.<br>Glencore | Pontenossa<br>Porto-Vesme | Waelz<br>Waelz | 20<br>20 |
| Luxemburg | Arcelor-Mittal | Waiver | MHF (1) | 25 |
| Norway | Eras Metal | Hoyanger | Plasma | 15 |
| Poland | Boleslaw recycling | Boleslaw | Waelz | 25 |
| Spain | Befesa | Bilbao | Waelz | 35 |
| (1) MHF = Multiple hearth furnace. | | | | |

**Table 1.11: Recycling units of zinc from end-of-life products in the EU (2007)**
**[ 228, IZA plant data 2008 ]**

### 1.4.1.5 Environmental issues

Historically, the major environmental problem associated with the production of zinc from primary sources were the emissions of sulphur dioxide to air from the roasting and smelting of sulphide concentrates. This problem has been effectively solved by the EU smelters who now achieve a high fixation of the sulphur and produce sulphuric acid and liquid sulphur dioxide.

The leaching of calcine and other material produces liquor that contains iron. The removal of iron results in the production of significant quantities of solid waste that contain a variety of metals. The disposal of this waste requires a very high standard of containment and monitoring. Efforts have been made over the past 10 years to minimise the amount of waste or to process it further to extract or valorise the metal content when technically and economically achievable. *This information is from the 10 years old BREF and not from [312]. For this reason these kind of statements can not simply be repeated and have to be checked about the situation in the last 10 years.*

Diffuse emissions from roasting and calcining are also very important and need to be considered for all of the process stages. The diffuse emissions of acid mists from the electrowinning of zinc is a particular example of this.

Zinc and zinc products can be largely recycled. Estimates based on historical consumption and product life cycles indicate that a recovery rate of 80 % of recoverable zinc has been reached. The recycling system of zinc is far advanced, not only as zinc metal but also in several different forms.

## 1.4.2 Lead

### 1.4.2.1 General information

Lead [ 35, European Commission 1997 ] is the most abundant metal in the earth's crust and has been used for many centuries. It is found in pure sulphide ores or in mixed ores where it is associated with zinc and small amounts of silver and copper. Lead is a soft metal, it has a low melting point and is resistant to corrosion. These properties give it great functional value, both in its pure form and as alloys or compounds.

Lead is classified in terms of the composition of the product. Table 1.12 shows the chemical composition of the grades of lead according to the new European Standard.

| Grade Designation | Pb min. | 1 Bi max. | 2 Ag max. | 3 Cu max. | 4 Zn Max. | 5 Ni max. | 6 Cd max. | 7 Sb max. | 8 Sn max. | 9 As max. | Total of 1 to 9 max. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **PB 990** | 99.990 | 0.010 | 0.0015 | 0.0005 | 0.0002 | 0.0002 | 0.0002 | 0.0005 | 0.0005 | 0.0005 | 0.010 |
| **PB 985** | 99.985 | 0.015 | 0.0025 | 0.0010 | 0.0002 | 0.0005 | 0.0002 | 0.0005 | 0.0005 | 0.0005 | 0.015 |
| **PB 970** | 99.970 | 0.030 | 0.0050 | 0.0030 | 0.0005 | 0.0010 | 0.0010 | 0.0010 | 0.0010 | 0.0010 | 0.030 |
| **PB 940** | 99.940 | 0.060 | 0.0080 | 0.0050 | 0.0005 | 0.0020 | 0.0020 | 0.0010 | 0.0010 | 0.0010 | 0.060 |
| NB: The German standard DIN 1719 is the basis for the new European Standard EN 12659, | | | | | | | | | | | |

**Table 1.12: the chemical composition of the grades of lead according to the new European Standard**

There have been major changes in the pattern of use of lead. The battery industry creates up to 70 % of the demand and is fairly stable but other uses for lead which include pigments and compounds, protection against radiation, rolled and extruded products for the building industry, cable sheathing, shots and petroleum additives are in decline (see Table 1.13).

| Commercial use | 1973 (%) | 1983 (%) | 1993 (%) | 1994 (%) |
|---|---|---|---|---|
| Batteries | 38 | 48 | 56 | 59 |
| Chemicals | 24 | 27 | 22 | 22 |
| Semi-finished products and casting | 17 | 17 | 16 | 16 |
| Cables | 15 | 5 | 2.5 | 2.0 |
| Alloys | 2 | 3 | 1.1 | 0.8 |
| Other | 4 | - | 1.6 | 0.2 |

**Table 1.13: Uses of lead worldwide**

### 1.4.2.2 Sources of materials

Refined lead is derived from primary material in the form of lead or mixed metal ores and concentrates, and secondary material in the form of scrap and residue. The balance between primary and secondary production has shifted since 1998 and in 2008, secondary sources accounted for more than 70 % of EU production.

Primary production requires the smelting of lead-bearing ores to produce lead bullion that is then refined. The economics of primary lead ore production is linked to the silver and zinc contents of the ore bodies. Lead metal production requires the sulphur content of the ores to be treated to produce sulphuric acid. Most primary lead smelters have a complex refining process associated with them and associated processes to recover the silver content as an silver-gold alloy. Primary refining is therefore linked to the economics of mining lead-zinc ore bodies. The increase in the value of lead in 2006 means that income does not depend on the zinc and silver content of the ores.

EU-27 countries produced 210000 tonnes of lead ore in 2006 compared to 350000 tonnes in 1996, the main producers being Ireland, Sweden and Poland. The main worldwide producers of lead ore are China, Australia, US, Peru, Mexico and Canada. Total world production in 2006 was 3500000 tonnes.

The secondary refining industry now supplies the majority of lead consumed. Lead acid accumulators in cars are the main source of scrap for secondary refining. The industry makes positive steps to encourage the recycling of these batteries; this proportion is increasing as the world car population increases and the return rate of old batteries increases. Secondary production also requires sulphur removal and other refining facilities as the secondary raw materials may contain unwanted compounds.

### 1.4.2.3 Production and use

EU-27 lead production has decreased to 1500000 (not consistant with table 1.14) tonnes in 2006, of which ~~>~~approximately 70 % was from secondary feed materials. The industry is responding to ecological concerns by recovering ever increasing amounts of lead so that primary production is steadily declining.

Lead consumption is linked to the manufacture and use of lead acid batteries and is estimated to account for 75 - 80 % of production. Other applications of lead are for roofing materials and radiation protection. The use of lead in certain applications is limited by several EU regulations. EU demand for lead is 1800000 tonnes and is therefore higher than the production capacity.

### 1.4.2.4 Production sites

There has been a major change in the processes used for lead production in the EU since 1998. All two-stage sintering/shaft furnace processes have now closed and all Imperial Smelting Furnaces have also closed except for one in Poland which is operated on a campaign basis to smelt sulphidic and then oxidic materials to recover lead and zinc. In 2008, there are only three direct smelting processes in use in the EU-27 with two in Germany and one in Italy. Lead production that is part of a complex metallurgical process to recover copper and precious metals remains unaffected. Table 1.14 gives the annual capacities for lead processes in the EU-27 for 2006.

| | **Primary or combined primary and secondary smelting (t/yr)** | **Secondary smelting** | | **Total lead** |
|---|---|---|---|---|
| | | **Shaft furnace (t/yr)** | **Rotary or other furnaces (t/yr)** | **Refining stage (t/yr)** |
| Austria | | | 32000 | 32000 |
| Belgium | 30000 | 50000 | 40000 | 120000 |
| Bulgaria | ???? | 30000 | | 100000 |
| Czech | | 35000 | | 35000 |
| France | | | 120000 | 120000 |
| Germany | 210000 | 50000 | 100000 | 360000 |
| Italy | 100000 | | 160000 | 260000 |
| The Netherlands | | | 20000 | 20000 |
| Poland | 35000 | | 55000 | 90000 |
| Portugal | | | 10000 | 10000 |
| Romania | 40000 | | | 40000 |
| Spain | 15000 | | 110000 | 125000 |
| Sweden | 65000 | 45000 | | 110000 |
| UK(1) | 180000 | | 85000 | 265000 |
| Other | 30000 | | 30000 | 60000 |
| Total | 775000<br>The sum is 705000 | 210000 | 762000 | 1747000<br>The crosssum is 1677000 |
| (1) Includes Non-EU bullion as primary smelting. | | | | |

**Table 1.14: Annual capacities for lead processes in EU-27 for 2006**

*(Where are these data from?)*

*In [522] and [523] the production figures are different. Try to find out what are the correct date and update.*

*The yellow highlighted figures are wrong. From [523] can be seen that the production in Bulgaria is higher.*

Production capacity has decreased by 500000 tonnes per year since 1997 *(Can not verify this statement. 13 times 500000 would be 6.5 million tonnes. This would mean that ghe production would be sero now)* and the remaining direct smelters take in more and more secondary raw materials to increase their capacities to between 50000 and greater than 100000 tonnes per year.

The secondary industry is characterised by a large number of smaller refineries, many of which are independent. There are approximately 30 secondary smelters/refiners in the EU producing from 5000 to 65000 tonnes per year. They recycle and refine scrap generated in their local area. The number of these refineries is decreasing as the large multinational companies, and the major battery manufacturing groups as well, acquire the smaller secondary facilities or set up their own recycling operations. Figure 1.5 shows the European lead refining capacity in 2007.

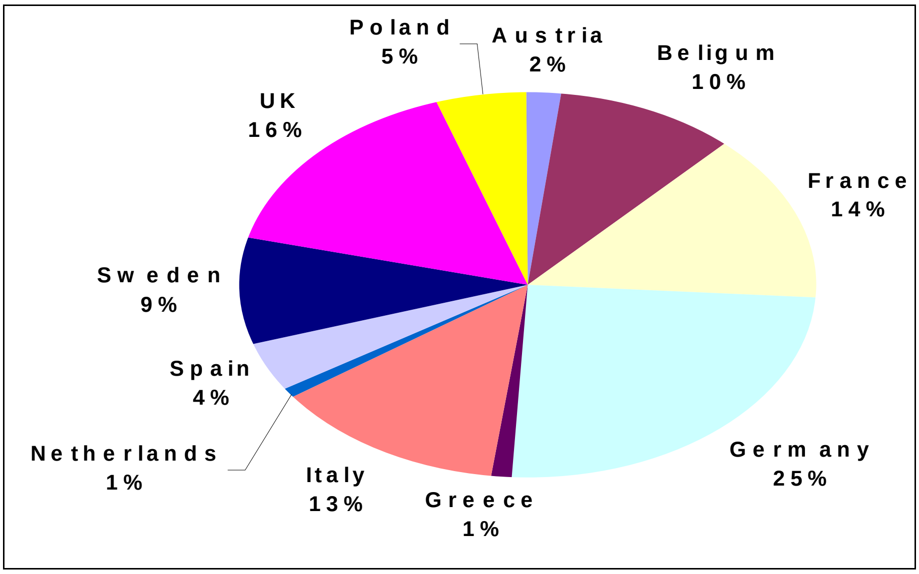


**Figure 1.5: European lead refining capacity in 2007**

The number of production sites has decreased and the total production capacity has fallen by 200000 tonnes per year since 1998.

### 1.4.2.5 Environmental issues

Historically, the major environmental problem associated with the production of lead from primary sources were the emissions of sulphur dioxide to air from the roasting and smelting of sulphide concentrates. This problem has been effectively solved by the EU smelters who now achieve a high fixation of the sulphur and produce sulphuric acid and liquid sulphur dioxide. Emissions of dust and metals from roads, storage areas and old waste deposits is also a potential problem. [ 254, VDI (D) 2597 2004 ].

The main environmental issues associated with the production of secondary lead are also related to the off-gases from the various furnaces in use. There is also the potential for the formation of PCDD/F due to the presence of small amounts of chlorine in the secondary raw materials and the destruction of PCDD/F is an issue that is being pursued [ 254, VDI (D) 2597 2004 ].

Lead is of great environmental concern and many lead compounds are classified as toxic. General policy is normally to restrict emissions to the lowest practicable levels given the state of technology, and recycling is normally conducted whenever appropriate and economic. Most control measures are concerned principally with human and animal exposure. Measures to protect children living in the vicinity of smelting plants are of particular significance. Environmental legislation requires investment to reduce lead in air emissions. In recent years several new technologies have been developed and implemented which offer more efficient methods of smelting lead concentrates. These processes have also reduced emissions to the environment. Existing processes have been improved by using state of the art control and abatement systems.

Batteries, which created more than 70 % of lead consumption in the EU in 2006, are recycled with very high efficiency. The EU battery Directive 2006/66 of September 2006 encourages high collection rates, prohibits disposal of lead batteries and prescribes from 2010 onwards a recovery rate of 65 % of the average weight of lead acid batteries. Regulations for end-of-life vehicles (2000/~~52~~53/EC) and electric and electronic goods (2002/~~95~~96/EC) limit the use of lead in certain articles.

Regulations affecting lead fall into four main categories: occupational exposure, emissions (ambient air quality), controls on food and water and on products. ~~Occupational exposure is addressed under EU Directive 96/62/EC~~*(this is the old air quality directive which do not address occupational health of workers)* ~~on the protection of workers from risks related to exposure to metallic lead and its ionic compounds at work. This directive sets limits on the level of lead in air in the workplace and on certain biological indicators which reflect the level of exposure of individual workers~~. The limit values are complemented by rules on the protection of the workforce by providing the use of protective clothing, respirators, washing facilities or specifying rules on eating, drinking, smoking, etc.

Lead in the general atmosphere is limited by the ~~under~~ Directive 2008/50/EC on ambient air quality and cleaner air for Europe~~Directive 82/844/EEC~~*(this is old. And succeeded by the new air quality directive)* ~~of December 3, 1982,~~ which sets a limit for levels of lead in air throughout the EU. These limit values are being revised. Levels of lead in water are also controlled in a number of directives relating to water depending on its type and use, e.g. water intended for human consumption, water for bathing, fishing waters and on material in contact with food and drinking water.

### 1.4.3 Cadmium

#### 1.4.3.1 General information

Cadmium belongs to the zinc subgroup of the periodic table and was discovered by Frierich Strohmeyer in 1817 during an investigation into $ZnCO_3$. It is associated with zinc in minerals at a ratio of 1:300 Cd to Zn. It is physically similar to zinc but is more dense and softer and can be polished. Unlike zinc it is also resistant to alkalis. Cadmium is also a good absorber of neutrons and is therefore often used in nuclear reactors. In its compounds it has an oxidation state of 2+. Cadmium is widely distributed worldwide with a content between 0.1 and 1 ppm in the topsoil.

#### 1.4.3.2 Source of materials

There are only a few cadmium-specific minerals, such as greenockite (CdS) or otavite ($CdCO_3$) and as CdO. None of these minerals are industrially important. Zinc minerals, which contain cadmium as an isomorphic component at concentrations of about 0.2 % have economic significance for cadmium recovery. In addition, lead and copper ores may contain small amounts of cadmium.

#### 1.4.3.3 Production and use

Unlike other metals, cadmium has been refined and utilised only relatively recently; production and use have risen only during the last 40 to 50 years. The main uses today are:

- electroplated cadmium coatings
- nickel-cadmium batteries
- some pigments and stabilisers for plastics
- alloys for specialised thermal and electrical conductivity applications, electrical contact alloys and nuclear control rods
- small amounts are used for solar cells.

Since 1988, the world cadmium production decreased fairly constantly from 20000 to 18000 t/yr. The use of cadmium in various applications has varied since 1970 and has been affected by technical, economic and environmental factors. This has influenced the metal prices. Metal prices in the seventies reached USD 3 per lb, and in the eighties varied between USD 1.1

and 6.9 per lb. Since that time the cadmium price fell to USD 1 per lb and even went as low as USD 0.45 per lb, which is equivalent to the zinc price level.

The main cadmium producer and user countries are shown in Table 1.15.

| Country | Production (t/yr) (Cd and Cd compounds) | Use (t/yr) (Cd and Cd compounds) |
|---|---|---|
| Korea | 3704 | 100 |
| China | 3000 | 5407 |
| Canada | 1388 | 107 |
| Japan | 1934 | 2210 |
| Belgium | 0 | 4799 (as CdO) |
| Mexico | 1584 | 140 |
| United States | 700 | 441 |
| Germany | 575 | 666 |
| France | 300 | 268 |

**Table 1.15: Main cadmium producers and users in 2007**

Cadmium is recovered:

- from pyrometallurgical Pb-Cu recovery in the flue dust from the smelting operation
- from pyrometallurgical Pb-Zn recovery in the flue dust from the sinter/roast operation and from crude zinc
- from hydrometallurgical extraction from zinc in the cadmium cementate produced in electrolyte purification.

Flue dusts are generally leached with $H_2SO_4$ to separate the cadmium which is afterwards precipitated as $CdCO_3$ or reduced to cadmium sponge with more than 90 % cadmium. The sponge may be either smelted under NaOH, vacuum distilled, or dissolved and electrolysed.

Crude zinc may be distilled in New Jersey columns to produce pure zinc and a Cd-Zn-alloy with more than 60 % cadmium. The Cd-Zn alloy from the New Jersey distillation operation should be distilled twice, before pure cadmium is produced.

Cements are usually dissolved and electrolysed to produce cadmium of high purity (≥ 99.99 % cadmium).

In the 1990s several EU operations ceased activity. Cadmium is still extracted from the main zinc processes under controlled conditions and the residue is safely deposited according to the waste legislation. Recycling takes place, but only very few companies take part. Mainly used batteries are recycled to recover cadmium and nickel (see Table 1.16).

| Country | Company | Location | Process | Capacity (t/yr) |
|---|---|---|---|---|
| Bulgaria | KCM | Plovdiv | RLE | 320 |
| | OCK | Kardjall | | 100 |
| France | SNAM | Viviez | Recycling | 300 |
| Germany | Xstrata | Nordenham | RLE | 475 |
| | Accurec | Mülheim | Recycling | 100 |
| Italy | Glencore | Porto Vesme | RLE | 450 |
| The Netherlands | Nyrstar | Budel | RLE | 575 |
| Norway | Boliden | Odda | RLE | 100 |
| Poland | H.C. Miasteczko Sl. | Miasteczko Slą | ISF | 350 |
| Sweden | SAFT | Oskarshamn | Recycling | 300 |

| | | | | |
|---|---|---|---|---|
| Romania | Mytilineos | Copsa Mica | ISF | 100 |

**Table 1.16: Main European primary and secondary cadmium producers in 2007**

#### 1.4.3.4 Environmental issues

The status of legislation of cadmium compounds has a significant impact on emissions. Cadmium is listed in the EU Water Framework Directive 2000/60/EC. A technical working group under Directive 2008/50/EC on ambient air quality and cleaner air for Europe ~~Directive 96/62/EC Air Quality Assessment and Management~~ has developed a target value for cadmium in ambient air. These factors need to be taken into account.

A typical zinc production process can produce 600 tonnes per year of cadmium. Cadmium production is closely controlled to prevent diffuse emissions and remove dust to a very high standard. Less than 2 % of the exposure of general population to cadmium is due to potential emissions to the environment from cadmium-bearing products in their total life cycle.

In many applications, cadmium alloys are essential and cannot be substituted with other materials. Similarly the use of cadmium in rechargeable batteries can also be an environmental benefit.

The critical effect of cadmium in human beings is renal tubular dysfunction. The tubular damage is irreversible at given, progressed stages, so prevention is more important than diagnosis. The long biological half-life of cadmium can lead to a continuous increase in renal levels over many years and so past exposure is often more important than present exposure. In that perspective, most of the EU operations apply risk prevention and risk management measures contained in the EMI/CdA guidance document updated in 2006.

# 1.5 Precious metals

## 1.5.1 General

Precious metals [ 35, European Commission 1997 ] include such well-known metals as gold and silver as well as the six platinum group metals (PGMs): platinum, palladium, rhodium, iridium, ruthenium and osmium. They are termed precious metals because of their rarity and corrosion resistance.

The EU has the largest refining and fabricating capacity for precious metals in the world, even though its actual mineral resources of such metals are limited. The recycling of precious metals from scrap and industrial residues has always been an important raw material source for the EU precious metals industry.

Consumption of gold in the EU is mainly for jewellery, with smaller amounts used in electronics and other industrial and decorative applications. The principal users of silver are the photographic and jewellery industries. The platinum group metals are used extensively as catalysts and the imposition of emission limits on vehicles sold in the EU has stimulated demand for their use in catalytic converters.

## 1.5.2 Sources of materials

Mines in all parts of the world consign large quantities of precious metals, in crude ore or by-product forms, to the EU refineries. Refineries with significant precious metal capacities are found in Belgium, Germany, Sweden, Finland and the United Kingdom. Bulgaria, Poland and Romania have considerable mining activities either in precious metals or base metals with precious metal content. These activities typically recover precious metals from lead and zinc, copper or nickel ores, as well as low grade scrap materials of all kinds, and they supply the pure metals in bars or plates, grain or sponge.

There are small deposits of precious metal ores in Europe; Table 1.17 shows the primary resources in 2005. Poland is the world's second largest producer of silver after Mexico. These resources account for approximately 25 % of the world's primary silver, 1.1 % of world's primary gold and 0.08 % of world's primary PGMs. Deposits of gold are being developed in Greece and their contribution will be significant in coming years.

| Country | Silver (t/yr) | Gold (t/yr) | PGMs (t/yr) |
|---|---|---|---|
| Finland | 15.0 | 0.5 | 0.1 |
| France | 1.0 | 3.5 | |
| Greece | 25 | | |
| Ireland | 4.0 | | |
| Italy | 5.0 | | |
| Poland | 1244 | 0.71 | 0.07 |
| Portugal | 24 | | |
| Romania | 20 | 0.5 | 0.01 |
| Spain | 5.0 | 5.4 | |
| Sweden | 268 | 6.3 | |

**Table 1.17: Precious metal primary resources in 2005**

Europe has a number of companies that specialise in the collection, preprocessing and trading of scrap and secondary materials before the actual assay and refining stages take place. Typical items are discarded catalysts, printed circuit boards, obsolete computers, old photographic film, X-ray plates and solutions, spent electroplating baths, etc.

### 1.5.3 Production and use

The cost of recovery and recycling is more than justified by the high intrinsic value of the precious metals contained in these scrap and residues. It is not just the economic aspects that encourage the recycling of precious metals but also the environmental issues where stricter limits on the tolerable metal content of waste materials sent for dumping are being set.

The refining of gold, silver and the platinum group metals in the EU takes place either at the specialist precious metal refining and fabricating companies or at base metal refineries. The total precious metal refining capacity of the EU firms is the largest in the world (see Table 1.18).

| Country | Silver (t/yr) | Gold (t/yr) | PGMs (t/yr) |
|---|---|---|---|
| Austria | 190 | 70 | 1 |
| Belgium | 2440 | 60 | 45 |
| France | 1520 | 135 | 12 |
| Germany | 2700 | 193 | 92 |
| Italy | 1050 | 115 | 15 |
| Netherlands | 130 | 15 | 1 |
| Poland | 1500 | 3 | |
| Romania | | | |
| Spain | 830 | 30 | 5 |
| Sweden | 250 | 15 | 1 |
| U K | 2320 | 300 | 100 |
| Switzerland | 620 | 565 | 14 |
| Other EU Countries | 50 | 10 | 5 |

**Table 1.18: Annual capacities of European refineries (tonnes) 2006**

The refinery capacity is approximately double the amount actually processed so that a rapid turn round of processed metal can be maintained.

Most of the precious metals are fairly easily fabricated either as pure metals or as alloys. Gold in particular is usually turned into specific alloys for jewellery or dental purposes in order to improve its wear-resistance or colour. Because of the high intrinsic value and the wide range of forms and alloys required, such metals are usually fabricated or processed in relatively small quantities compared with base metals. One of the few precious metal products manufactured in tonnage quantities is silver nitrate for the photographic industry.

European demand for precious metals is high. The jewellery trade has the highest consumption of gold and the photographic trade for silver. The highest consumption of platinum is in the production of auto catalysts. Other principal uses are in chemicals, dentistry and investment such as coinage. The demand in 2006 for precious metals is shown in Table 1.19 below.

| Total Demand | Silver (t/yr) | Gold (t/yr) | PGMs (t/yr) |
|---|---|---|---|
| European | 5710 | 881 | 85 |
| World | 26142 | 3692 | 488 |

**Table 1.19: Precious metal demand 2006**

### 1.5.4 Production sites

The principal precious metals refiners and fabricators of the EU operate on an international scale and are world leaders in their field. Prominent names are Umicore and Heraeus in

Germany and Johnson Matthey in the United Kingdom. The US precious metals firm, Engelhard Corporation, has been operating in the EU for a number of years and in late 1994 announced a joint venture with the French precious metals company CLAL which no longer exists. There is now a company called Cookson-CLAL.

Major EU base metal refiners with significant precious metal involvement include Umicore in Belgium, Aurubis in Germany, Norilsk Nickel in Finland, KGHM Polska Miedz in Poland and New Boliden in Sweden.

### 1.5.5 Environmental issues

The EU precious metal refineries form a technically advanced, high performance industry that is very strongly focused on research and development. The processes often use hazardous reagents such as HCl, $HNO_3$, $Cl_2$ and organic solvents. Advanced processing techniques are used to contain these materials and the small scale of production allows these techniques to be used effectively to minimise and abate potential emissions. This encompasses not merely new uses for the precious metals but also the discovery of techniques for economising the quantities of precious metals used in existing applications. The raw materials are subject to intensive sampling and assay and any process wastes are analysed to the same standard.

The recovery of these metals from secondary raw materials is particularly important and many of these materials are classified as wastes from other industries.

## 1.6 Mercury

### 1.6.1 General information

Mercury is the only metal that is liquid at room temperature and has the lowest fusion and boiling point of all metals. It also has a high electrical conductivity and these features are used in a variety of applications such as electrical switch-gear and battery production. Mercury forms alloys easily with a number of other metals and these are known as amalgams, which are extensively used in dentistry. The major use of mercury is as a flowing cathode in the chlor-alkali process. This process exploits the high conductivity of mercury and the formation of an amalgam with sodium. This process however is being phased out and demand for mercury has declined.

Regulation EC 1102/2008 classifies mercury and mercury compounds produced during the production of non-ferrous metals as waste with effect from 15 March 2011.

Mercury is characterised by the toxicity of the metal and its vapour and the extreme toxicity of some of its compounds. The result is that mercury is being replaced by alternative materials in many of its uses and so the demand and production of mercury has declined rapidly. There are implications in the future as it is likely that some existing inventories of mercury will come on the market or may even become wastes.

### 1.6.2 Sources of materials

Mercury appears in nature in the form of cinnabar (sulphide of mercury), which is associated with very hard gangues such as the quartzite and the basalts. It is also present in the form of other compounds such as oxides, sulphates, chlorides or selenides. These are rare and are always associated with the cinnabar and generally have a low relevance. There are exceptions such as livingstonite (HgSbS), which has been used in Mexico. The quality of primary ores varies considerably from 0.1 to more than 3 % mercury (see Table 1.20).

| Source | Mercury content in the ore (%) |
|---|---|
| Almaden, Spain | >3 |
| Mc Dermitt, US | 0.5 |
| Nikitovska, Ukraine | 0.1 |

**Table 1.20: Sources of mercury**

Other sources of mercury are the ores and concentrates of other metals such as copper, lead and zinc, etc. Mercury is produced from the purification of gases emitted during the production of these metals. Mercury is also recovered from secondary materials such as dental amalgam and batteries and it is also obtained from the refining of oil.

### 1.6.3 Production and use

The decomposition of the cinnabar is complete at temperatures of 600 ºC shown by the formula below.

$$HgS + O_2 \rightarrow Hg + SO_2$$

Mercury metal is condensed at room temperature. The heating can be carried out in either Herreshoff, muffle or rotating furnaces. The last two are not frequently used.

In EU-27 the production of mercury from cinnabar has now ceased.

Mercury production from the production of other non-ferrous metals in Europe for 1997 is estimated at 350 tonnes. These processes generally produce mercury or calomel in the range 0.02 to 0.8 kg of mercury per tonne of metal produced depending on the mercury content of the concentrate.

The decline in mercury production can be seen in the European production for 1960, 1970 1980 and 2008, See Table 1.21.

| Year | Production (t/yr) |
|---|---|
| 1960 | 4250 |
| 1970 | 3700 |
| 1980 | 1100 |
| 2008 | 0 |

**Table 1.21: Primary production of mercury in Western Europe**

### 1.6.4 Environmental issues

The toxicity of mercury and its compounds is a significant factor in environmental impact. Mercury in the environment can interact with various organic compounds to produce very toxic organo-mercury compounds. Legislation at the time of writing (2010) is therefore imposing more stringent standards on the industry to prevent emissions, to curtail its use in various processes and to remove mercury from the environment.

## 1.7 Refractory Metals

### 1.7.1 General information

The term "refractory metals" refers to a group of metals (in some cases rare earth metals) that can mostly be characterised by the same physical properties. These properties are, for the majority of refractory metals:

- a high melting point
- high density
- special electrical characteristics
- inertness and in particular
- the ability to confer exceptional increases in physical performance by small additions to steel and other metals.

Selected physical properties of some refractory metals are shown in Table 1.22 below.

| Metal | Symbol | Atomic number | Atomic mass | Melting point (ºC) | Boiling point (ºC) | Density (g/cm$^3$) |
|---|---|---|---|---|---|---|
| Chromium | Cr | 24 | 51.99 | 1857 | 2672 | 7.19 |
| Manganese | Mn | 25 | 54.94 | 1220 | 2150 | 7.44 |
| Tungsten | W | 74 | 183.85 | 3410 | 5900 | 19.3 |
| Vanadium | V | 23 | 50.94 | 1929 | 3450 | 6.11 |
| Molybdenum | Mo | 42 | 95.94 | 2610 | 5560 | 10.22 |
| Tantalum | Ta | 73 | 180.95 | 2996 | 5425 | 16.65 |
| Titanium | Ti | 22 | 47.88 | 1725 | 3260 | 4.5 |
| Niobium | Nb | 41 | 92.90 | 2468 | 4927 | 8.57 |
| Rhenium | Re | 75 | 186.2 | 3180 | 5900 | 21.02 |
| Hafnium | Hf | 72 | 178.4 | 2230 | 4602 | 13.09 |
| Zirconium | Zr | 40 | 91.22 | 1857 | 3580 | 6.5 |

**Table 1.22: Physical properties of refractory metals**

Refractory metals and hard metal powders are used for a wide range of industrial applications. Chromium metal is important in steel alloying and as a metal coating in the galvanic industry. Among a variety of other uses like steel alloying, manganese is the key component of certain widely used aluminium alloys and is used in oxide form in dry cell batteries [ 171, Jones, T.S. 1997 ]. The largest use of tungsten is as cemented carbides, which are also called hard metals. Cemented carbides are wear resistant materials used by the metalworking, mining and construction industries. Tungsten metal wires, electrodes, and/or contacts are used in lighting, electronic, heating and welding applications [ 172, Shedd, K.B. 1997 ]. Molybdenum finds significant usage as a refractory metal in numerous chemical applications, including catalysts, lubricants, pigments, ribbons and wires in the lighting industry, semiconductor base plates in the electronics industry, melting electrodes in the glass industry and furnace hot zones and sputter targets in the coating technologies industries [ 173, Blossom, J.W. 1997 ]. Tantalum and its twin element niobium are used as tantalum and niobium powder and carbides. Tantalum powder is mainly used for the production of tantalum capacitors.

Niobium and columbium are synonymous names for the same element. Columbium was the first name given, and niobium was the name officially designated by the International Union of Pure and Applied Chemistry in 1950 [ 169, Cunningham, L.D. 1997 ]. As a metal, titanium is well known for corrosion resistance and for its high strength-to-weight-ratio. Rhenium is used as a component of nickel-based super alloys for aircraft engines and in petroleum-reforming catalysts for the production of high-octane hydrocarbons, which are used in the production of lead-free petrol [ 173, Blossom, J.W. 1997 ].

Zirconium is the 18th most abundant element in the Earth's crust with an average crystal abundance of 165 parts per million. Martin-Heinrich Klaproth discovered the element in 1789 by analysing zircon. Hafnium-free zirconium is used as cladding for nuclear fuel rods. Commercial grade zirconium, unlike nuclear grade, contains hafnium and is used in the chemical process industries because of its excellent corrosion resistance. Hafnium is a bright silver, ductile, lustrous metallic element with a very high melting point. Hafnium metal was first produced in 1925 by Anton Eduard van Arkel and Jan Hendrik de Boer by passing hafnium tetrachloride over a tungsten filament. Hafnium is used in nuclear control rods because of its high thermal neutron absorption cross-section [ 176, Hedrick, J.B. 1997 ]. Other applications of refractory metals include the use as mixing elements for the production of ceramics that contain metal.

Due to their refractory nature, the metals are sometimes processed in different ways from more common metals. The production generally requires hydrometallurgical methods for extraction and purification [ 7, St. Barbara Consultancy Services 1993 ] and hydrogen reduction and carburisation for the production of hard metal powder and hard metal carbides. The crude refractory metals and metal powders often need powder metallurgical techniques in order to produce finished or semi-finished products.

Processes for the manufacturing of refractory metals that include the production of hard metal powder and metal carbides will cover the metals chromium, manganese, tungsten, vanadium, molybdenum, titanium, tantalum, niobium, rhenium as well as the production of zirconium and hafnium.

### 1.7.2 Sources of materials

Refractory metals can be produced from a wide range of primary and secondary raw materials. Refractory metals are produced from primary raw materials by the hydrometallurgical treatment of oxidic and sulphide ores and concentrates, hydrogen reduction and carburisation in order to produce cemented carbides.

The production from secondary raw material is normally based on hard metal scrap and residues from other production processes like spent catalysts. The fact that recycling plays an important role can be demonstrated by the point that about 30 % of the world tungsten supply is produced from secondary raw materials. The tungsten processing industry is able to treat almost every kind of scrap that contains tungsten and waste to recover tungsten and, if present, other valuable constituents.

Table 1.23 gives an overview of the most important primary and secondary raw materials that are used for the production of refractory metals. It also provides information about the mineral deposits within the European Union.

A number of other raw materials such as coke, coal, charcoal, silicon, aluminium, calcium and magnesium as reducing agents are also used. Different chemicals are needed, e.g. sulphuric acid for leaching, purification, precipitation, ion exchange and electrolytic operations.

| Metal | Primary raw material (Resources)(1) | | | | Secondary raw material |
|---|---|---|---|---|---|
| | Minerals | Content | Other metals | Deposits within the EU | |
| Chromium | Chromite | Cr <50 % | Fe, Mg, Al | Finland and Greece | Chromium scrap |
| Manganese | Pyrolusite<br>Braunite<br>Manganite<br>Psilomelane | Mn 63 %<br>Mn 66 %<br>Mn 62 %<br>Mn 45 - 60 % | Si<br>Ba | Greece (2) and Italy (2) | |
| Tungsten | Wolframite<br>Scheelite<br>Ferberite<br>Hübnerite | $WO_3$ 76 %<br>$WO_3$ 80 %<br>$WO_3$ 76 %<br>$WO_3$ 76 % | Fe, Mn<br>Ca<br>Fe<br>Mn | Austria, France, Portugal and UK | Tungsten scrap (grinding wheel swarf and dust)<br>Hard metal scrap |
| Vanadium | Titanomagnetite (3)<br>Montroseite<br>Corvusite<br>Roscoelite | V 1.5 %<br>V 45 %<br>V 40 %<br>V <14 % | Fe, Al, Ti, Cr<br>Fe<br>Al, Si | | Boiler residues<br>Fly ashes from incinerators<br>Spent catalysts from the petrochemical and chemical industry<br>Waste salts from the production of alumina |
| Molybdenum | Molybdenite<br>Wulfenite<br>Powelite<br>Ferrimolybdite<br>Chalocopyrite(4) | | Re<br>Pb<br>Ca, W<br>Fe<br>Cu | | Spent catalysts from petroleum refining that contain Mo |
| Titanium | Rutile<br>Ilmenite<br>Leucoxene<br>$TiO_2$-rich slag from ilmenite | $TiO_2$ 94 %<br>$TiO_2$ <70 %<br>$TiO_2$ 80 % | | | Titanium scrap mostly from the production of semi-finished products<br>Titanium swarf |
| Tantalum | Tantalite<br>Wodginite<br>Microlite<br>Columbite<br>Cassiterite(5) | $Ta_2O_5$ 42 - 84 %<br>$Ta_2O_5$ 60 - 70 %<br>$Ta_2O_5$ 1 - 40 % | Fe, Mn, Nb<br>Nb,Sn,Mn,Fe<br>Na,Ca,Nb<br>Fe,Mn,Nb | | Unoxidised metallic tantalum scrap<br>Tantalum anodes<br>Capacitors<br>Sintered pellets<br>Oxidised tantalum scrap related with other oxidised metals<br>Tantalum anodes coated with oxidised manganese |
| Niobium | Tantalite<br>Columbite<br>Microlite | $Nb_2O_5$ 2 - 40 %<br>$Nb_2O_5$ 40 - 75 % | Fe, Mn, Ta<br>Fe, Mn, Ta<br>Na, Ca, Ta | | Hard metal scrap |
| Rhenium | Molybdenite<br>Copper concentrate | 5 to 20 ppm | Mo | Poland | Platinum-rhenium catalysts used in the petroleum industry |
| Zirconium | Zircon (6) | | Hf | | |
| Hafnium | Zircon (6) | | Zr | | |

(1) The list does not contain all possible raw materials, it only provides an overview of the most important material sources.
(2) The manganese deposits in Greece and Italy contain low grade minerals and have only been used from time to time.
(3) The vanadium-bearing titanomagnetite deposits are of magmatogenic origin and occur in many parts of the world [ 104, Ullmann's Encyclopaedia 1996 ]. From the titanomagnetite ore a vanadium slag can be produced, which is the first source to produce vanadium compounds.
(4) A copper-molybdenum sulphide concentrate which is used as a secondary ore.
(5) The production of tin from cassiterite ore led to a slag that contains tantalum and niobium, which is a main raw material source of tantalum and niobium production.
(6) Zirconium and hafnium sometimes are by-products from heavy sand deposits, which always contain titanium and other rare earth metals.

**Table 1.23: Primary and secondary raw materials for the production of refractory metals**

### 1.7.3 Production and use

The European refractory metal production and market is very sensitive to the political and economic situation of the raw material producing countries. The world consumption of primary tungsten for instance was strong in 1997 and remained well above world mine production. An estimated one third of world supply was from tungsten mineral released from stockpiles in Russia and Kazakhstan. The stockpile emissions have maintained an oversupplied market and have kept the price of primary tungsten below the operating cost of most mines. As a result, many mines have closed, and world tungsten production capacity has fallen to around 75 % of world consumption. Also China continues to be a strong competitor in case of increasing their refractory metal production. However, due to the advantageous properties of refractory metals and the growing understanding of how to use refractory metals, the production will increase at least on a long-term basis. For future consumption of tungsten cemented carbides for instance, the largest end-use sector is estimated to increase by more than 5 % on the 1998 basis [ 172, Shedd, K.B. 1997 ]. The world production of chromium metal is presented in Table 1.24.

| Country | Production capacity (t/yr) |
|---|---|
| ~~Brazil~~ | ~~500~~ |
| China | 64000 |
| France | 7000 |
| Germany | 1000 |
| India | 500 |
| Japan | 1000 |
| Kazakhstan | 2~~1~~000 |
| Russia | 16~~3~~000 |
| United Kingdom | ~~10000~~7000 |
| United States | 3000 |

**Table 1.24: World chromium metal production capacity**
~~[ 170, Papp, J.F. 1997 ]~~
[170, Papp, J.F. 2001]

### 1.7.4 Production sites

*(Rewrite this section by just giving the European producers and the production figures for the world and Europe).*

The production of refractory metals in the European Union is based on a limited number of companies for instance chromium metal is mainly produced by two major companies. These are London and Scandinavian Metallurgical Co. Limited who operate a new modern chromium plant built in 1997, and Delachaux in France who have just reported the completion of its chromium metal plant in Valenciennes. *(check whether this is correct. In [523] France is not mentioned as a chromium producer.*

The following companies, Kennametal Hertel AG, Widia GmbH and HC Starck GmbH in Germany, Ceratizit SA (check whether this is correct: Ceratizit produces in Austria/Reutte. Do they also produce in Luxembourg?) in Luxembourg, Treibacher Industrie AG and Plansee Metall ~~Gmbh~~ GmbH in Austria, Sandvik and Seco Tools in Sweden and Eurotungstène Poudres in France [ 179, ITIA 1999 ] are producing tungsten metal powder and carbides in Europe.

The companies mentioned above for the production of tungsten metal powder produce some other refractory metals. *(What does this mean? Do they produce tungsten powder and other metals or only other metals? In tjis case the message of the aforementioned paragraph is wrong!)* An overview of the world's largest producers of tantalum and niobium and their products is shown in Table 1.25. Unfortunately there is no information on Chinese producers available. *(Check [523]. Maybe there is some information. )*

*This should be included in the text:*

| | | |
|---|---|---|
| *Estonia* | *Silmet* | *Nb oxide/metal* |

| Country | Company | Products (1) |
|---|---|---|
| Austria | Treibacher Industrie AG | Nb and Ta oxide/carbide, FeNb, NiNb |
| Brazil | Cia. Brasileira de Metalurgia e Mineração (CBNM) | Nb oxide/metal, FeNb, NiNb |
| | Cia. Industrial Fluminense (2) | Nb and Ta oxide |
| | Mineração Catalão de Goiás S.A. (Catalão) | FeNb |
| Canada | Cainbior Inc., and Teck Corp. (Niobec) | FeNb |
| Estonia | Silmet | Nb oxide/metal |
| Germany | Gesellschaft Fur Electrometallurgie GmbH (GFE) (2)<br>H.C. Starck GmbH & Co. KG | FeNb, NiNb<br>Nb and Ta oxide/metal/carbide, K-salt, FeNb, NiNb<br>Ta capacitor powder |
| Japan | Mitsui Mining & Smelting Co. | Nb and Ta oxide/metal/carbide |
| | Showa Cabot Supermetals (3) | Ta capacitor powder |
| | H.C. Starck-V Tech Ltd. (4) | Ta capacitor powder |
| Kazakstan | Ulba Metallurgical | Ta oxide/metal |
| | Irtysh Chemical & Metallurgical Works | Nb oxide/metal |
| Russia | Solikamsk Magnesium Works | Nb and Ta oxide |
| Thailand | H.C. Starck (Thailand) Co. Ltd. (4) | K-salt, Ta metal |
| United States | Cabot Corp. | Nb and Ta oxide/metal, K-salt, FeNb, NiNb |
| | | Ta capacitor powder |
| | H.C. Starck Inc. (5) | Nb and Ta metal, Ta capacitor powder |
| | Kennametal, Inc. | Nb and Ta carbide |
| | Reading Alloys, Inc. | FeNb, NiNb |
| | Shieldalloy Metallurgical Corp. (2) | FeNb, NiNb |
| | Wah Chang (6) | Nb oxide/metal, FeNb, NiNb |
| | H.C. Starck-TTI, Inc. (4) | Ta capacitor powder |

(1) Nb = niobium; Ta = tantalum; FeNb = ferroniobium; NiNb = nickel niobium; K-salt = potassium fluotantalate; oxide, pentoxide.
(2) A wholly owned subsidiary of Metallurg Inc., New York.
(3) A joint venture between Showa Denko and Cabot Corp.
(4) A subsidiary of H.C. Starck GmbH & Co. KG.
(5) Jointly owned by Bayer US and H.C. Starck GmbH & Co. KG.
(6) A subsidiary of Allegheny Teledyne Inc.

**Table 1.25: Principal world producers of niobium and tantalum producers**
[ 169, Cunningham, L.D. 1997 ]

*From the information in [509] can be seen that only tungsten is produced at Treibacher Industry AG. Ta oxide is not produced at all. The others such as FEV, FeMo, FeNb, FeW are produced but should be included in chapter 9 Ferro-alloys. The table seems to be partly misleading.*

### 1.7.5 Environmental issues

The main environmental impact from the production of refractory metals is dust and hard metal powder which are potentially toxic as well as fumes from the smelting processes for instance by producing chromium metal. Dust emissions occur from the storage and handling of raw materials and products and the furnace operation, where both stack and diffuse emissions play an important role.

The use of hydrogen as a reducing agent presents the possible risk fire hazards. Hydrogen fluoride, which is used in several processes, is highly toxic and therefore should be handled very carefully to avoid any health problems for the plant staff. Another environmental impact of the production of hard metals is the high radioactive level of some raw materials (e.g. pyrochlore), and the toxicity of metal compounds such as cobalt and nickel.

Process residues and by-products are slag, sludge that contains metal, filter dust and spent refractories. These materials are already recycled and re-used to a large extent where it is possible. Due to the radioactive levels of several raw materials, residues of such metal processes might be radioactive.

Water emissions are produced from cooling, granulation, other process and other site-related effluents.

It is very important to collect, filter and recycle as much as possible from an economic point of view. The treatment of small off-gas volumes is also less difficult because high performance fabric filters for instance, may advantageously be used.

## 1.8 Ferro-alloys

### 1.8.1 General information

Ferro-alloys are master alloys that contain some iron and one or more non-ferrous metals as alloying elements. Silicon metal is produced in the same metallurgical process as ferro-silicon and is therefore considered as a ferro-alloy. Ferro-alloys are used as deoxidising element in steelmaking and enable alloying elements such as chromium, silicon, manganese, vanadium, molybdenum, etc. to be safely and economically introduced into metallurgical processes, thus giving certain desirable properties to the alloyed metal, for instance to increase the corrosion resistance, hardness or wear resistance.

The importance of ferro-alloys increased with the progress of steel metallurgy which demanded diversified alloying elements to achieve better controlled quantities, in purer and more advanced steel qualities. The ferro-alloy industry became a key supplier to the steel industry.

Silicon metal is used as an alloying element in aluminium and in chemical and electronic industry, solar cells, etc.

Ferro-alloys are usually classified in two groups:

- bulk ferro-alloys basic specification_(ferro-chrome, ferro-silicon together with silicon metal, ferro-manganese and silico-manganese), which are produced in large quantities in electric arc furnaces
- special ferro-alloys (ferro-titanium, ferro-vanadium, ferro-tungsten, ferro-niobium, ferro-molybdenum, ferro-boron, alloyed or refined ferro-silicon, silicon metal and ternary/quaternary alloys) which are produced in smaller quantities, but with growing importance.

Bulk ferro-alloys are used mainly in steelmaking and steel or iron foundries. The uses of special ferro-alloys are far more varied, and the proportion used in steelmaking has diminished over recent years in favour of those used in the aluminium and chemical industries, especially silicon products.

### 1.8.2 Sources of material

The raw materials (alloying elements) for the production of ferro-alloys are either main products (quartzite for silicon, chromite for chrome, etc.) or by-products of mining production (molybdenite from copper mining). Of course the two sources can exist simultaneously. In most cases for FeCr and FeMn production, the iron part is also received from ore and no iron is added.

They can also be recovered from scrap, which is most often the case for the iron share of the composition, which comes from iron and steel scrap, but also for the alloying element itself titanium for example. Residues from steel mills like electric arc furnace and converter filter dust, as well as shot blasting and grinding dust is an important secondary raw material which has increasing significance. The main raw material sources and mineral deposits for the alloying elements are given below:

- Chromite that is concentrated in two large deposits, which are mainly located in South Africa and Kazakhstan. Smaller deposits are found in other places in the world such as India, Brazil and Europe (Finland, Turkey, Albania and Greece).
- Raw material for producing ferro-silicon and silicon metal is available everywhere in the world, although not all sources allow the production, under economic and quality conditions, of all the ranges of silicon alloys.

- Ore that contains manganese is mainly found in South Africa, Ukraine, Gabon and Australia. Smaller occurrences are found in Brazil, India, Mexico and Myanmar. The quality (content of manganese and level/nature of the impurities) of the ore can influence greatly the economics of the ferro-alloy production.
- The special alloying elements are very often concentrated in few countries (molybdenum in North America, Chile and China; niobium in Brazil) and prices and availability are very sensitive to economic conditions.
- Rich slags are also a significant raw material and come from FeMn processes and battery recovery.

### 1.8.3 Production and use

From around 1978, the world pattern of the ferro-alloy market has changed significantly. The consumption in developing countries has vastly increased with the development of their steel production i.e. because they have taken a growing share of the traditional markets of the industrialised countries, where steel production was stagnant or growing at a slow rate. The ferro-alloy industry is facing a growing proportion of imports, at first the new industrialised countires and in recent years from the countires of East Europe, the CIS and China.

As a consequence, EU ferro-alloy production has been submitted to a difficult competition that results in a decreasing trend of the total amount of ferro-alloys produced. The actual total European production of bulk ferro-alloys split into the different alloys and the countries where they are being produced can be seen in Table 1.26. While the world production of ferro-alloys increased since 2003 from 22.6 million tonnes to 31.8 million tonnes (see Table 1.27) the European ferro-alloy production decreased from 3 billion tonnes to 2.1 million tonnes. The leading ferro-alloy producing countries in 2007 were, in descending order of production, China, South Africa, Ukraine, Russia, and Kazakhstan. These countries account for 78 % of world Ferro-alloy production.

What can also be seen from Table 1.26 is, that the last European blast furnace used for the bulk ferro-alloys production was closed down in 2003 and nowadays all bulk ferro-alloys in Europe are produced in electric furnaces.

| **Production of ferro-alloys (tonnes)** | | **1998** | **1999** | **2000** | **2001** | **2002** | **2003** | **2004** | **2005** | **2006** |
|---|---|---|---|---|---|---|---|---|---|---|
| Austria *(electric furnace)* | Ferro-molybdenum | 4900 | 4900 | 4700 | 4900 | 4930 | 4400 | 4700 | 5000 | 5000 |
| | Ferro-nickel | 3300 | 2600 | 3300 | 2600 | 2150 | 2000 | 1900 | 2500 | 2500 |
| | Ferro-vanadium | 5900 | 6400 | 5900 | 5800 | 5500 | 5300 | 5800 | 6250 | 6250 |
| Belgium *(electric furnace)* | Ferro-manganese | 13843 | | | | | | | | |
| | Ferro-silico-manganese | 5035 | | | | | | | | |
| | Ferro-molybdenum and ferro-vanadium (2) | 11356 | 6659 | | | | | | | |
| Bulgaria *(electric furnace)* | Ferro-silicon (1) | 8000 | 8000 | 8000 | 8000 | 8000 | 8000 | 8000 | 8000 | 8000 |
| Czech Republic *(electric furnace)* | Ferro-vanadium (1) | 2000 | 2000 | 2500 | 2500 | 3000 | 3000 | 3500 | 2700 | 2800 |
| Finland *(electric furnace)* | Ferro-chrome | 230906 | 256290 | 260605 | 236000 | 248000 | 250000 | 264492 | 234881 | 243350 |
| France *(electric furnace(3))* | Ferro-manganese & spiegeleisen (1) | 438212 | 419672 | 409169 | 414200 | 416569 | 356192 | 110072 | 109111 | 139533 |
| | Ferro-silico-manganese (1) | 57000 | 55000 | 32773 | 65248 | 66215 | 107000 | 64000 | 65000 | |
| | Ferro-silicon | 106000 | 110000 | 110000 | 100000 | 100000 | 100000 | 100000 | 100000 | 100000 |
| | Other ferro-alloys | 55000 | | | | | | | | |
| | Silicon metal (1) | 70082 | 80000 | 94127 | 89896 | 84768 | 85000 | 85000 | 85000 | 85000 |
| Germany *(electric furnace)* | Ferro-chrome | 20879 | 16960 | 21600 | 19308 | 20018 | 18318 | 24857 | 22672 | 26710 |
| | Other ferro-alloys (1) | 30000 | 30000 | 30000 | 30000 | 30000 | 30000 | 30000 | 30000 | 30000 |
| | Silicon metal | 19200 | 21855 | 27119 | 27739 | 25257 | 27870 | 28773 | 29349 | 29865 |
| Greece *(electric furnace)* | Ferro-nickel | 62673 | 59545 | 81662 | 88755 | 96000 | 90000 | 91000 | 96000 | 89000 |
| Iceland *(electric furnace)* | Ferro-silicon | 67784 | 70100 | 108288 | 112935 | 118810 | 117171 | 119389 | 114844 | 113798 |
| Italy *(electric furnace)* | Ferro-chrome | 11487 | | | | | | | | |
| | Ferro-manganese (1) | 49000 | 19000 | 40000 | 40000 | 40000 | 25000 | 38000 | 32000 | 13000 |
| | Ferro-silico-manganese (1) | 119675 | 112358 | 100000 | 100000 | 100000 | 100000 | 100000 | 100000 | 96600 |
| | Ferro-silicon | 19909 | | | | | | | | |
| | Silicon metal | 8 094 | 6257 | 9590 | | | | | | |
| Norway *(electric furnace)* | Ferro-chrome | 174 678 | 159714 | 153500 | 82600 | 61100 | | | | |
| | Ferro-manganese (1) | 153089 | 124000 | 150585 | 111823 | 126960 | 130000 | 130000 | 130000 | 130000 |
| | Ferro-silico-manganese (1) | 206749 | 235000 | 198671 | 277938 | 252723 | 50000 | 260000 | 290000 | 310000 |
| | Ferro-silicon | 357293 | 354281 | 450364 | 427590 | 359944 | | 389599 | | |

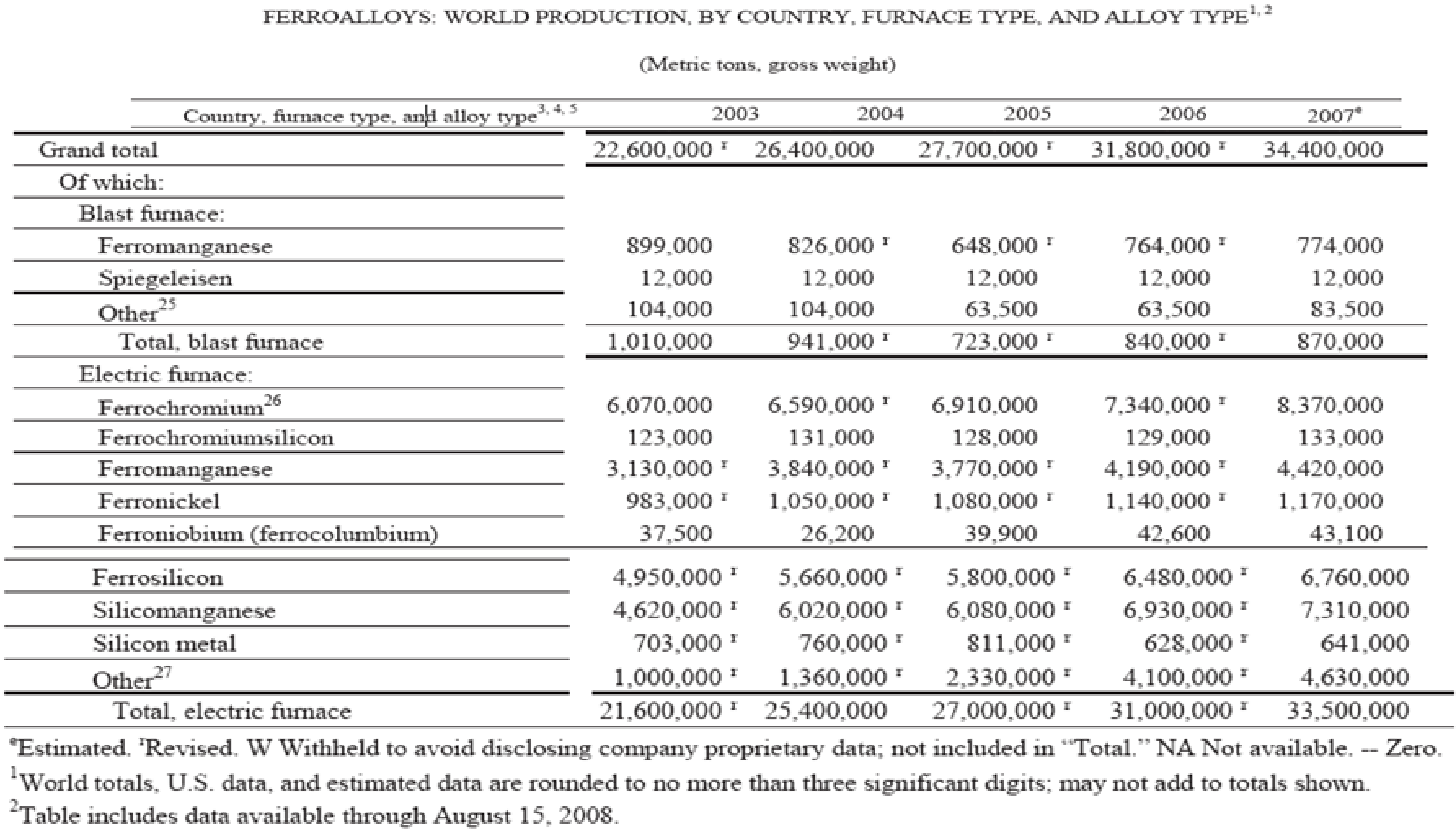
| Production of ferro-alloys (tonnes) | | 1998 | 1999 | 2000 | 2001 | 2002 | 2003 | 2004 | 2005 | 2006 |
|---|---|---|---|---|---|---|---|---|---|---|
| | Other ferro-alloys (1) | 38130 | 49000 | 54639 | 47600 | 48500 | 50000 | 60000 | 60000 | 60000 |
| | Silicon metal (1) | 132309 | 153120 | 138139 | 134958 | 152981 | 150000 | 193566 | 178572 | 150000 |
| Poland *(electric furnace)* | Ferro-chrome | 4212 | | | | 106 | 188 | | | |
| | Ferro-manganese | 50152 | 57 | 0 | 497 | 602 | 979 | 46898 | 7782 | 4089 |
| | Ferro-silico-manganese | 15100 | 10000 | 18997 | 20007 | 7500 | 5000 | 29600 | 10242 | 3310 |
| | Ferro-silicon | 74991 | 62481 | 55969 | 48608 | 41759 | 92687 | 83552 | 65118 | 13034 |
| | Other ferro-alloys | 13300 | 2700 | 4174 | 4039 | 4200 | | 1419 | 3663 | 4848 |
| Romania *(electric furnace)* | Ferro-chrome | 873 | | | | | | | | |
| | Ferro-manganese | 4 170 | 25 | 1989 | 384 | | | 191 | 18625 | 3777 |
| | Ferro-silico-manganese | 83617 | 550 | 62320 | 71921 | 84720 | 141899 | 194754 | 100957 | 66476 |
| | Ferro-silicon | 5553 | | 8309 | 5823 | | | | | |
| | Silicon metal (1) | 150 | | | | | | | | |
| Slovakia *(electric furnace)* | Ferro-chrome | 11715 | 6986 | 17658 | 5968 | 5695 | 1924 | 1784 | 867 | 19 |
| | Ferro-silico-manganese | 46627 | 37000 | 52141 | 46288 | 62084 | 52733 | 64862 | 47843 | |
| | Ferro-silicon | 49963 | 70000 | 59443 | 55577 | 35920 | 41539 | 34684 | 16512 | |
| | Other ferro-alloys | 54672 | | 50508 | 46357 | 24657 | 44589 | 68096 | 48161 | |
| Slovenia *(electric furnace)* | Ferro-chrome | 10621 | 560 | | | | | | | |
| | Ferro-silicon (1) | 10000 | 8000 | 9000 | 9000 | 9000 | 12000 | 18000 | 11000 | 8000 |
| Spain *(electric furnace)* | Ferro-chrome | 1145 | 935 | 905 | | | | | | |
| | Ferro-manganese (1) | 18360 | 10000 | 26815 | 24804 | 33218 | 35000 | 35000 | 35000 | 35000 |
| | Ferro-silico-manganese (1) | 107952 | 95000 | 128197 | 102110 | 103494 | 100000 | 100000 | 100000 | 100000 |
| | Ferro-silicon (1) | 39115 | 42000 | 50071 | 53427 | 56994 | 60000 | 60000 | 60000 | 60000 |
| | Silicon metal (1) | 18424 | 28000 | 28215 | 29114 | 26071 | 25000 | 25000 | 25000 | 25000 |
| Sweden *(electric furnace)* | Ferro-chrome | 115534 | 128269 | 106399 | 107036 | 118800 | 106100 | 127300 | 127500 | 136400 |
| | Ferro-silicon | 20356 | 21440 | 18948 | 21197 | 21500 | 17100 | 18500 | 9800 | 4600 |
| Total | | 3052143 | 2886714 | 3195289 | 3082547 | 3007745 | 2445989 | 3022288 | 2389949 | 2105959 |

(1) Estimate (either for the full period or for some years)
(2) Confidential
(3) A blast furnace used for the production of ferro-managanese was shut down in 2003.
*Source*: BGS

~~(1) Estimate (either for the full period or for some years)~~
~~(2) Confidential~~
~~*Source*: BGS~~

**Table 1.26: European production of bulk ferro-alloys from 1998 to 2006 in tonnes per year**
www.**bgs**.ac.uk/downloads/start.cfm?id=1389
*British Geological Survey. 2010. European mineral statitics 2004 – 2008*

Clarify if we can use this.



FERROALLOYS: WORLD PRODUCTION, BY COUNTRY, FURNACE TYPE, AND ALLOY TYPE[1, 2]

(Metric tons, gross weight)

| Country, furnace type, and alloy type[3, 4, 5] | 2003 | 2004 | 2005 | 2006 | 2007[e] |
|---|---|---|---|---|---|
| Grand total | 22,600,000 [r] | 26,400,000 | 27,700,000 [r] | 31,800,000 [r] | 34,400,000 |
| Of which: | | | | | |
| Blast furnace: | | | | | |
| Ferromanganese | 899,000 | 826,000 [r] | 648,000 [r] | 764,000 [r] | 774,000 |
| Spiegeleisen | 12,000 | 12,000 | 12,000 | 12,000 | 12,000 |
| Other[25] | 104,000 | 104,000 | 63,500 | 63,500 | 83,500 |
| Total, blast furnace | 1,010,000 | 941,000 [r] | 723,000 [r] | 840,000 [r] | 870,000 |
| Electric furnace: | | | | | |
| Ferrochromium[26] | 6,070,000 | 6,590,000 [r] | 6,910,000 | 7,340,000 [r] | 8,370,000 |
| Ferrochromiumsilicon | 123,000 | 131,000 | 128,000 | 129,000 | 133,000 |
| Ferromanganese | 3,130,000 [r] | 3,840,000 [r] | 3,770,000 [r] | 4,190,000 [r] | 4,420,000 |
| Ferronickel | 983,000 [r] | 1,050,000 [r] | 1,080,000 [r] | 1,140,000 [r] | 1,170,000 |
| Ferroniobium (ferrocolumbium) | 37,500 | 26,200 | 39,900 | 42,600 | 43,100 |
| Ferrosilicon | 4,950,000 [r] | 5,660,000 [r] | 5,800,000 [r] | 6,480,000 [r] | 6,760,000 |
| Silicomanganese | 4,620,000 [r] | 6,020,000 [r] | 6,080,000 [r] | 6,930,000 [r] | 7,310,000 |
| Silicon metal | 703,000 [r] | 760,000 [r] | 811,000 [r] | 628,000 [r] | 641,000 |
| Other[27] | 1,000,000 [r] | 1,360,000 [r] | 2,330,000 [r] | 4,100,000 [r] | 4,630,000 |
| Total, electric furnace | 21,600,000 [r] | 25,400,000 | 27,000,000 [r] | 31,000,000 [r] | 33,500,000 |

[e]Estimated. [r]Revised. W Withheld to avoid disclosing company proprietary data; not included in "Total." NA Not available. -- Zero.

[1] World totals, U.S. data, and estimated data are rounded to no more than three significant digits; may not add to totals shown.

[2] Table includes data available through August 15, 2008.

¶

Table 1.27: Ferroalloys world production by country, furnace type and alloy type from 2003 to 2007 in tonnes per year

Due to the technical and metallurgical developments and changes in the iron and steel production, the consumption pattern of ferro-alloys has also changed, especially in industrialised countries:

- carbon steel production is increasingly produced in electric arc furnaces from scrap, which allow recovery of the alloying elements, reducing the relative consumption of ferro-alloys;
- a more efficient carbon steel production (continuous casting, for example) and a more advanced metallurgy led to a significant drop of the specific consumption of manganese (from 7 kg/tonne of steel, to 5 kg/tonne in 20 years) and of ferro-silicon (from 5 kg/tonne of steel, to 3.5 kg/tonne in 20 years);
- a growing need for metallurgically sophisticated alloying elements (niobium, molybdenum), and for treatment elements (calcium), led to an increased consumption of special alloys;
- an increasing production of stainless steel led to a significant increase of the consumption of chromium alloys (mainly high carbon ferro-chrome).

Western Europe consumption, has been more or less stagnant, around 4.2 millions tonnes/year, and its production went down from 4 millions tonnes to 3 millions tonnes since 1988.

### 1.8.4 Production sites

There are a number of companies producing different ferro-alloys in about 60 industrial production sites in Europe. The largest European ferro-alloy producing countries are Norway for the production of bulk ferro-alloys and France and Spain especially for the production of manganese and silicon alloys. Finland is a major producer of ferro-chrome from a local chrome ore mine. In Sweden, mainly ferro-chrome and ferro-silicon is produced. Special ferro-alloys like ferro-molybdenum, ferro-vanadium and ferro-titanium are produced in the UK, Belgium, Austria and Germany.

### 1.8.5 Environmental issues

Production of ferro-alloys generally involves the use of electric arc furnaces and reaction crucibles into which natural products (e.g. quartz, lime, various ores, wood) with relatively fluctuating physical compositions are loaded. Due to this, the main environmental impacts by producing ferro-alloys are the emission of dust and fume from the smelting processes. Dust emissions also occur from the storage, handling and pretreatment of raw materials where diffuse dust emissions play an important role. Depending on the raw material and the process used, other emissions to air are $SO_2$, $NO_X$, CO, $CO_2$, polycyclic aromatic hydrocarbons (PAH), volatile organic compounds (VOCs), and metals such as Hg, As and Cr. The formation of PCDD/F in the combustion zone and in the cooling part of the off-gas treatment system (de novo synthesis) may be possible ~~[ 255, VDI (D) 2576 2008 ]~~.[226]

Significant process residues and by-products are slag, filter dust and sludge and spent refractories. These materials are already recycled and re-used to a large extent where it is possible. Rich slag, meaning slag with a relatively high proportion of metal oxides, is used as raw material in the production of other ferro-alloys. For instance, rich slag from the production of ferro-manganese is one of the most important raw materials for the production of silico-manganese. Water emissions and site related effluents are produced from cooling, granulation and other processes.

The ferro-alloys industry, whose basic tool is an electric arc furnace in which metal oxides are reduced by carbon, is a major consumer of energy and a producer of carbon dioxide ($CO_2$). It has therefore, always regarded the reduction of energy consumption as a vital priority. The laws of thermodynamics, which govern the reactions used, limit the possible reduction of energy necessary for the smelting process. ~~[ 255, VDI (D) 2576 2008 ].~~ The reduction of the overall energy consumption is therefore in most cases only possible by using an efficient energy recovery system. The recovered energy can be transferred into electrical energy or used as heat for various purposes. CO-rich off-gas from closed furnaces can also be used as secondary fuel or as a raw material for chemical processes. The recovery of energy reduces the use of other natural energy resources and therefore the impact of global warming.

# 1.9 Alkali and Alkaline Earth Metals

## 1.9.1 General information

Alkali metals, which belong chemically to group one of the periodic table of the elements and include metals such as lithium, sodium, potassium, as well as the extremely rare radioactive substance, francium. Alkali metals are characterised by their low melting point and density. They have a silvery-white colour and are softer than other metals. Alkali metals have only one single, highly mobile electron in the outermost shell. Due to this fact, alkali metals are highly reactive especially with oxygen or water where they can also react violently by producing gaseous hydrogen and heat.

Alkaline earth metals resemble alkali metals in several ways but they react less vigorously with water. Alkaline metals are elements in the second group of the periodic table. In order of their increasing atomic number and their metallurgical and technical importance, they are magnesium, calcium and strontium.

## 1.9.2 Sources of materials

Sodium as sodium compounds and metal are widely used in industry for manufacturing chemicals and pharmaceuticals, in metallurgical processes and in a variety of other everyday products. Sodium metal is commonly produced by the electrolysis of fused sodium chloride.

Lithium metal is produced in a very similar way to sodium metal using the electrolysis of a molten eutectic mixture of lithium chloride and potassium chloride at about 450 °C in a Downs cell.

Potassium, which was discovered in 1807 by the English chemist Humphry Davy, occurs in many silicate rocks and minerals where the major commercial source is salt deposits. Potassium metal is silvery-white in colour and was the first metal to be isolated by electrolysis. Potassium metal will only be produced on an industrial scale by the reduction of potassium chloride with sodium metal.

Humphry Davy also discovered magnesium as a metallic element in 1808. It is a silvery-white ductile chemically active metal and belongs to the group of alkaline metals. Magnesium can be produced either by the electrolysis of magnesium chloride based on raw material such as seawater, dolomite, magnesite, carnallite or brines. It is also from dolomite by thermal reduction using ferro-silicon and/or aluminium. Magnesium is also recovered from a wide range of residues that contain magnesium and magnesium scrap.

The majority of magnesium is used in aluminium alloys. The fastest rate of growth in the use of magnesium alloys is in the die casting of parts for use wherever the light weight is of importance, e.g. in the automotive industry. Another major application is steel desulphurisation using magnesium powder. The increasing use of secondary magnesium residues for steel desulphurisation is reducing the growth in the production of primary magnesium powder. The world use of magnesium metal in the different markets is shown in Figure 1.6 below [ 1, Davy Consultants UK 1993 ].

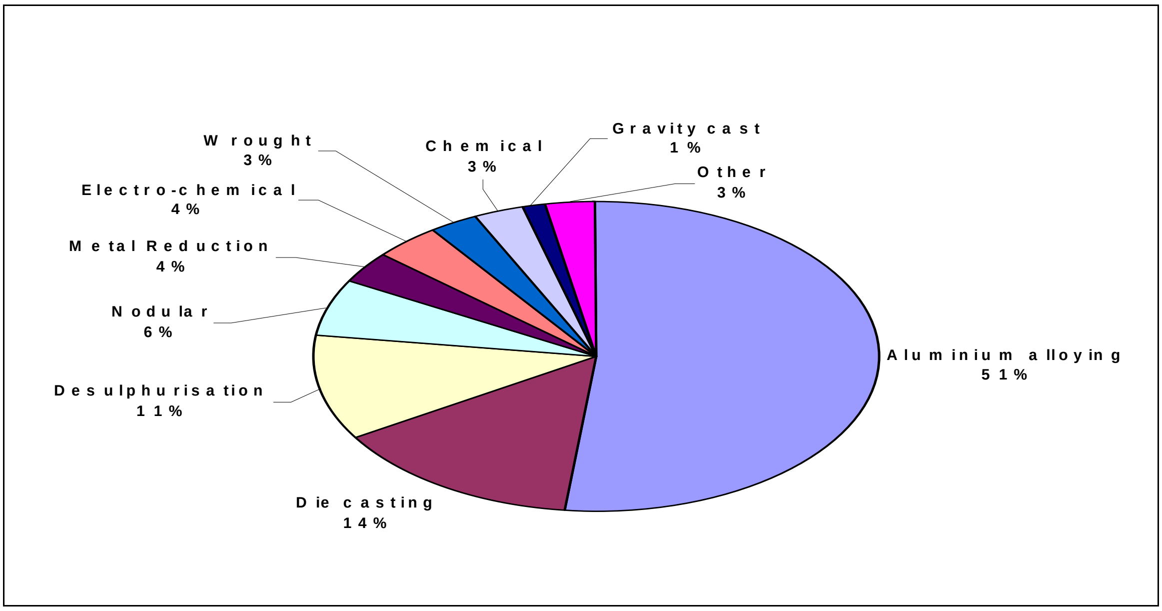


**Figure 1.6: World use of magnesium metal**

Calcium and strontium metal are used for a variety of purposes. Calcium as an alloying element improves the quality of steels, especially the mechanical properties like formability, drawing and machinability. Because of its strong ability to form oxides and sulphites, calcium is important in the production of ultraclean steel. Calcium metal may also be used for lead debismuthising. Strontium metal is needed in aluminium refining as well as for the rafination of steel slag.

### 1.9.3 Production and use

The production of alkali- and alkaline metals especially for the production of sodium, lithium, calcium and strontium metal is associated with only a few companies.

| **Continent and country** | **Capacity** | **Number of producers** |
|---|---|---|
| North America: | | |
| Canada | 49000 | 2 |
| United States | 80000 | 2 |
| Europe: | | |
| France | 17000 | 1 |
| Kazakhstan (1) | 10000 | 1 |
| Norway | 35000 | 1 |
| Russia (1) | 45000 | 2 |
| Serbia and Montenegro | 5000 | 1 |
| Ukraine (1) | 24000 | 1 |
| Others | | |
| China | ~150000 - 200000 | ~200 |
| India | 900 | 1 |
| Brazil | 10000 | 1 |
| Israel | 27500 | 1 |
| World total | 503400 – 55340 | ~214 |
| (1) Excluding magnesium production capacity that is used exclusively for titanium production. | | |

**Table 1.28: World primary magnesium production capacity by country**
**[ 186, Kramer, D. 1997 ]**

The world capacity for primary magnesium production is in the order of about 400000 tonnes per year, where the European production is about 57000 tonnes per year. Table 1.28 and Table 1.29 give an overview about the primary magnesium production capacity and the worldwide produced amounts of primary and secondary magnesium by country.

| **Country** | **1993** | **1994** | **1995** | **1996** | **1997** (e) |
|---|---|---|---|---|---|
| Primary production: | | | | | |
| Brazil (e) | 9700 | 9700 | 9700 | 9000 | 9000 |
| Canada (e) | 23000 | 28900 | 48100 | 54000 | 57700 |
| China (e) | 11800 | 24000 | 93600 | 73100 (r) | 92000 |
| France | 10982 | 12280 | 14450 | 14000 (e) | 12000 |
| Israel | - | -- | - | - | 8000 |
| Japan | 7471 | 3412 | - | -- | -(3) |
| Kazakstan (e) | 2000 | - (3) | 9000 (r) | 9000 (r) | 8972 (3) |
| Norway | 27300 | 27635 | 28000 (e) | 28000 (r) (e) | 28000 |
| Russia (e) (4) | 30000 | 35400 | 37500 | 35000 | 39500 |
| Serbia and Montenegro | - (e) | - | 2560 | 2500 (e) | 2500 |
| Ukraine (e) | 14900 | 12000 | 10000 (r) | 10000 (r) | 10000 |
| United States | 132000 | 128000 | 142000 | 133000 | 125000 (3) |
| Total | 269000 | 282000 | 395000 (r) | 368000 [r] | 392000 |
| Secondary production: | | | | | |
| Brazil (e) | 1600 | 1600 | 1600 | 1600 | 1600 |
| Japan | 13215 | 19009 | 11767 | 21243 (r) | 22797 (3) |
| Former USSR (e)(5) | 6000 | 5000 | 6000 | 6000 | NA |
| United Kingdom (e)(6) | 1000 | 1000 | 1000 | 1000 | 1000 |
| United States | 58900 | 62100 | 65100 | 70200 (r) | 80200 (3) |
| Total | 80700 | 88700 | 85500 | 100000 (r) | 106000 |

(1) World totals and estimated data are rounded to three significant digits; may not add to totals shown.
(2) Table includes data available through 22 July, 1998.
(3) Reported figure.
(4) Includes secondary raw materials.
(5) Dissolved in December. 1991; however, information is inadequate to formulate reliable estimates for individual countries of the former USSR.
(6) Includes alloys.
(r) Revised
(e) Estimated

**Table 1.29: Produced amounts of primary and secondary magnesium in tonnes per year**

## 1.9.4 Production sites

There are only a few production sites of sodium, lithium and potassium within the European Union. Sodium metal is produced by Associated Octel, a company located in the United Kingdom and a company which operates a sodium production plant in France. For the production of primary magnesium there are two companies in Europe. Hydro Magnesium (NHM) operates an electrolytic magnesium plant in Porsgrunn, Norway, based on dolomite and seawater as the raw material. Pechiney Électrométallurgie (PEM) operates a thermal reduction plant in Merignac in France, based on the Magnatherme process and is a process developed by PEM. There are some mostly smaller companies within the European Union producing secondary magnesium. In the European Union only one plant each produces calcium and strontium metal. Both plants are operated by Pechiney Électrométallurgie (PEM) in its factory at La Roche de Rame in France.

### 1.9.5 Environmental issues

The main environmental issues from the production of alkali and alkaline metals are air and water emissions. The generation of air emissions is due to the dusty nature of some processes and unit operations that are used in the alkali and alkaline metal production. For instance the unloading, crushing and calcining of raw materials are all related to the generation of dust. Other main environmental issues are the emissions of chlorine and chlorine-related compounds like chlorinated hydrocarbons and PCDD/F. Chlorinated hydrocarbons and PCDD/F are mainly emitted in the chlorination process that is used in the electrolysis of magnesium. These pollutants need to be removed from the off-gas, which can be done by using a wet-cleaning system. This consequently results in polluted washing water that itself needs an efficient waste water treatment. Emissions to water are also produced by washing the filter cake from a sodium process. To prevent the magnesium metal from re-oxidation by the surrounding air, sulphur-hexafluoride ($SF_6$) is used in the casting equipment, where it is also emitted to the atmosphere.

# 1.10 Nickel and Cobalt

## 1.10.1 Nickel

### 1.10.1.1 General information

Nickel [ 35, European Commission 1997 ], [ 92, Laine, L. 1998 ] is a silver white metal with typical metallic properties. Although it was only discovered as a metal in 1751 its alloys have been used for several centuries, e.g. the Chinese had been making "white copper" which resembled silver in appearance. Between 1870 and 1880, nickel's use in alloy steels was demonstrated and electrolytic nickel plating was successfully developed.

The great importance of nickel lies in its ability, when alloyed with other elements, to increase a metal's strength, toughness and corrosion resistance over a wide temperature range. Nickel is therefore an extremely important commercial element. Given these beneficial properties, nickel is used in a wide variety of products. Most primary nickel is used in alloys; the most important of which is stainless steel. Other uses include electroplating, foundries, catalysts, batteries, coinage, and other miscellaneous applications. Nickel is found in transportation products, electronic equipment, chemicals, construction materials, petroleum products, aerospace equipment, durable consumer goods, paints and ceramics. Nickel is a vital metal to industrialised societies.

Chemically, nickel resembles iron and cobalt, as well as copper. Nickel can form several compounds, e.g. sulphate, chloride, oxide, and hydroxide. One property of nickel is its ability to react directly with carbon monoxide to form a binary carbonyl complex that is volatile at ambient temperatures. At moderate temperatures, nickel is corrosion resistant against air, seawater, and non-oxidising acids. Another property of nickel is its corrosion resistance to alkalis. In contrast, nickel is attacked by aqueous ammonia solutions.

### 1.10.1.2 Sources of materials

Nickel is a naturally occurring element that exists in nature mainly in the form of sulphide, oxide, and silicate minerals. The deposits are of two main types:

- Nickel sulphides often occur together with economically recoverable amounts of copper, cobalt, gold, silver, platinum group metals and several other metals. The most important occurrences are in Africa, Australia, Canada and Siberia.
- Nickel laterites are products of the weathering of ultra basic rocks that originally contained very small amounts of nickel. Over time impurities are washed out of the deposits and nickel is present as a complex oxide of silicon, iron and magnesium. Cobalt and iron are commonly associated with nickel, but laterites do not contain other valuable constituents. The most important occurrences are in the tropical areas in Southeast Asia, Australia, South America, the Caribbean Ocean and the Balkans area especially Greece, which are the only sources of nickel ore in Europe at the time of writing (2010).

The complex metallurgy of nickel is reflected in the wide range of extraction and refining processes in operation. Every plant presents a unique set of process features and environmental issues. The nickel content of sulphide ores usually can be concentrated several times by relatively economical ore-dressing techniques before the concentrate is smelted and refined to nickel products.

Laterite ores, in contrast, are amenable to only limited benefication by physical methods, e.g. magnetic or heavy media techniques, and therefore almost the entire volume of ore must go directly to metallurgical plants. Thus, laterite processing tends to be more cost-intensive, but mining costs are usually much lower than for sulphide ores. These differences, plus the availability of by-product value, can have an important influence on the viability of a specific deposit and whether refined metal or ferro-nickel is produced from it.

#### 1.10.1.3 Production and use

Nickel products can be divided into three groups based in the Industry classification that is recognised internationally:

- Class I - refined nickel, nickel content of 99 % or more. The group includes electrolytic nickel, pellets, briquettes, granules, rondelles and powder/flakes.
- Class II - charge nickel, nickel content of less than 99 %. The group includes ferro-nickel, nickel oxide sinter and utility nickel.
- Class III - chemicals: nickel oxides, sulphate, chloride, carbonate, acetate, hydroxide, etc.

The world production of nickel remained below 1000 tonnes per year until 1876. Global primary nickel production in 2005 was approximately 1.3 million tonnes and the production capacity approximately 1.45 million tonnes. In Europe the production capacity was approximately 229000 tonnes and the consumption is approximately 410000 tonnes in 2005 (see Figure 1.7). The actual production in total from the sites given in Table 1.30 was around 279000 tonnes for 2008 compared to 182000 tonnes for 2000.

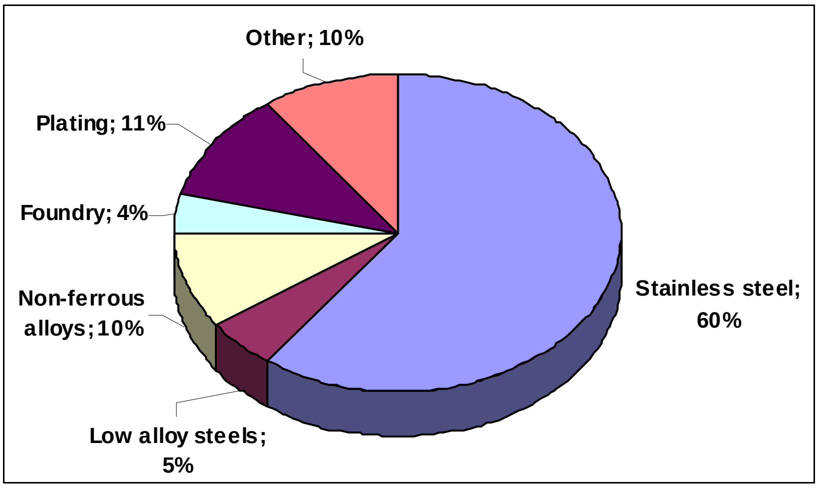


**Figure 1.7: Western world uses of nickel in 2005**

Growth in primary nickel use in Western Europe between 1950 and 2005 (4.7 % yearly) exceeded the increase in global use but the rise since 2000 was very subdued (slightly below 1 % yearly). The share of Western Europe in global primary nickel use is gradually declining from its peak in 1998 (38 %) to 33 % in 2005.

#### 1.10.1.4 Production sites

Table 1.30 and Figure 1.8 show the sites where nickel is produced in Europe.

| Producer | Source of raw materials | Production capacity (t/yr Ni) | By-products |
|---|---|---|---|
| Boliden, Finland and Norilsk Nickel, Finland | Finland, Brazil and Australia | 66000 | Cu precipitate<br>Sulphuric acid<br>Co sulphate solution<br>Ni sulphate<br>Ni hydroxycarbonate |
| Eramet, France | New Caledonia | 16000 | Cobalt Chloride<br>Ferric Chloride |
| Xstrata, Norway | Canada and Botswana | 86000 | Cu, Co, Sulphuric acid |
| Vale INCO, United Kingdom | Canada(1) | 41000 | Nickel metal |
| Treibacher, Austria | Secondary raw materials | <1000 | FeNi |
| Larco, Greece | Greece, Turkey | 25000 | FeNi |
| Total | - | 235000 | |
| (1) nickel in matte~~.~~ | | | |

**Table 1.30: Nickel production sites in Europe (2006)**
[reference??]

~~The actual production in total from the sites given in Table 1.29 was around 279000 tonnes for 2008 compared to 182000 tonnes for 2000.~~

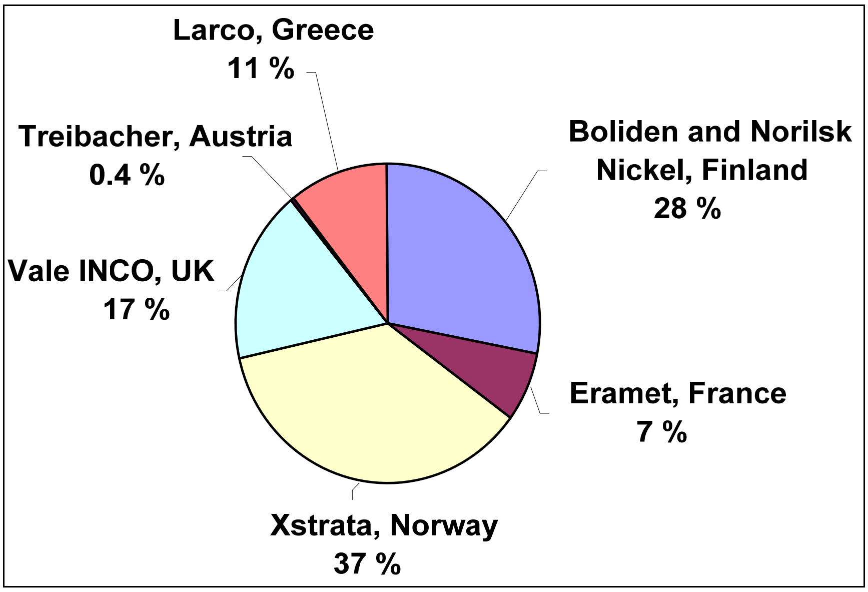


**Figure 1.8: European nickel production (2006)**
*(Change the figure to make it consistant: Either give the countires or the producers but be consistant with the Cobalt section and others.).*

### 1.10.1.5 Environmental issues

The emission of sulphur dioxide to air from the roasting and smelting of sulphide concentrates is a potentially serious environmental issue. This problem has been effectively solved by the EU smelters who now achieve on average 98.9 % fixation of the sulphur and produce sulphuric acid and liquid sulphur dioxide. Diffuse emissions of dust, metals and solvents are also an issue and need to be prevented and controlled. The use of chlorine in some processes is coupled with robust leak prevention measures and alarms.

The main environmental issues associated with the production of secondary nickel are also related to the off-gases from the various furnaces in use. These gases are cleaned in fabric filters and so can reduce the emissions of dust and metal compounds such as lead. There is also the potential for the formation of PCDD/F due to the presence of small amounts of chlorine in the secondary raw materials and the destruction of PCDD/F is an issue that is being pursued.

Nickel is a sustainable commodity. Stainless steel and other nickel-bearing alloys are the primary sources of secondary nickel. It is estimated that around 80 per cent of the nickel is recycled from new and old stainless steel scrap and returns to that end use. Other nickel-bearing materials such as precipitates and residues are recycled to primary production.

In many applications, nickel alloys are essential and cannot be substituted with other materials. The use of nickel in applications where its properties of strength, corrosion resistance, high conductivity, magnetic characteristics, and catalytic properties are exploited is seen as a positive environmental benefit. Similarly the use of nickel in rechargeable batteries is also of environmental benefit.

## 1.10.2 Cobalt

### 1.10.2.1 General information

Cobalt [ 35, European Commission 1997 ], [ 92, Laine, L. 1998 ] is a silver-white metal with typical metallic properties and was first isolated in 1735. Pure metallic cobalt has few applications, but its use as an alloying element for heat or wear resistant applications and as a source of chemicals makes it a strategically important metal.

Although very little cobalt metal was used until the 20th century, its ores have been used for thousands of years as blue colouring agents for glass and pottery, e.g. on Egyptian pottery around 2600 BC and on Chinese pottery at around 700 AD. The use of cobalt as metal dates from 1907 when E. Haynes patented a series of cobalt-chromium alloys named stellites that were the forerunners of modern superalloys. The ability of cobalt to enhance the properties of permanent magnets was shown in 1930.

Cobalt is used in alloys including superalloys for aircraft engines, magnetic alloys for powerful permanent magnets, hard metal alloys for cutting tool materials, cemented carbides, wear- or corrosion-resistant alloys, and electro-deposited alloys to provide wear and corrosion-resistant metal coatings. Its use in rechargeable batteries has been a fast-growing application over the last few years.

Cobalt chemicals are used in rechargeable batteries; as pigments in the glass, ceramics and paint industries; as catalysts in the petroleum industry; as paint dryers; and as trace metal additives for agricultural and medical use.

### 1.10.2.2 Sources of materials

From the beginning of the 20th century the world's main supply of cobalt moved from Europe to Africa, Australia, Russia and Canada. Production in 2007 was around 60000 t/yr.

Cobalt is produced mainly as a by-product of the mining and processing of copper and nickel ores. Silver, gold, lead and zinc ores may also contain considerable amounts of cobalt but their processing does not always lead to recovery. The sources of ores are:

- the copper-cobalt deposits in the Congo and Zambia
- the nickel sulphide ore bodies in Australia, Canada, Finland and Russia
- the nickel oxide ore bodies in Cuba, New Caledonia, Australia and Russia.

Recovery from secondary sources can occur through the introduction of the recycled material at an appropriate stage in a primary refining or transformation process, depending on its technical and economical capabilities. Additional or pretreatment steps may be necessary. The final products can be cathodes, powders, oxides, salts or solutions.

Production comes from the following sources:

| | |
|---|---|
| nickel industry | 43 % |
| copper industry & other | 32 % |
| primary cobalt operations | 25 %. |

#### 1.10.2.3 Production and use

Primary cobalt always occurs associated with other metals, particularly copper and nickel, and these are usually predominant. Depending on the feed material, several processes have been developed which can involve pyrometallurgical as well as hydrometallurgical steps. These steps produce either:

- a cobalt-rich solution in integrated plants;
- a cobalt-rich sulphide, hydroxide or carbonate if further refining is done elsewhere;
- a cobalt-rich alloy.

Further refining is hydrometallurgical, although the final stage, the production of a commercial product, can be a high temperature process; especially when the product is a powder and the refining activity is integrated in the transformation process. Worldwide production of refined cobalt in 2008~~7~~ was approximately 56.2000 tonnes in 2008~~7~~.

Cobalt has a number of important applications which are summarised in Table 1.31.

| Uses | Breakdown of the total cobalt production |
|---|---|
| Batteries | 25 % |
| Superalloys | 22 % |
| Catalysts | 9 % |
| Hard metals | 12 % |
| Pigments | 10 % |
| Tyre adhesives/soaps/driers | 6 % |
| Magnets | 6 % |
| Others | 10 % |

**Table 1.31: Breakdown of the total cobalt production to the different sectors of use**

The worldwide apparent demand for cobalt in 2007 was around 55500 t/year and may be broken down on a regional basis as follows:

| | |
|---|---|
| Africa | <1 % |
| Asia | 39 % |
| Europe | 19 % |
| China | 21 % |
| Americas | 18 % |
| Oceania | <1 % |
| Other | 1 %. |

The chemicals sector is the largest consumer of cobalt accounting for about 50 % of total usage. The main application is in rechargeable batteries, a sector which has grown considerably in recent years. Other uses include cobalt for catalysts, paint/ink driers, pigments and colours, electroplating, rubber adhesives, animal supplements and medical applications. Because cobalt confers both strength and surface stability to the metallic form, it plays an important part in superalloys, which account for about 22 % of cobalt consumption. These alloys are found in the turbine section of jet engines as they have properties which make them resistant to the conditions found in hostile environments, particularly when associated with heat and oxidation. Up until 2007, this was the largest single use sector for cobalt, having now been overtaken by rechargeable batteries. Cobalt is also used to produce industrial cutting tools (high speed steels and diamond tools) and special metallic applications where resistance to wear is required. Cobalt is also an important constituent in the special surgical alloys used to make prosthetic hip and knee joints. The metal also has remarkable magnetic and paramagnetic qualities and is used in this application to a limited extent and also in magnetic tapes, though this application is now not so important.

### 1.10.2.4 Production sites

Cobalt production is particularly associated with sites that produce nickel and also sites where copper is found. The most significant source of cobalt can be found in the Democratic Republic of Congo and Zambia. Significant cobalt abundance is also found in association with the nickel operations in Canada and Russia. Finland, Norway, Belgium and China show significant production of refined cobalt, but this results from the processing of mainly imported ore and concentrate.

The worldwide production of cobalt is shown in Table 1.32.

| Source | Refined cobalt production (%) |
|---|---|
| Africa | 14.3 % |
| Australia | 6.8 % |
| Belgium(1) | 5.3 % |
| Brazil | 2.3 % |
| Canada | 10.6 % |
| China | 25.0 % |
| Finland | 17.1 % |
| France | 0.6 % |
| India | 1.8 % |
| Japan | 2.0 % |
| Norway | 7.4 % |
| Russia | 6.8 % |
| (1) Includes refined production from Umicore's Chinese plant. | |

**Table 1.32: Worldwide cobalt production (2007)**

### 1.10.2.5 Environmental issues

The status of some cobalt compounds has a significant impact on the assessment of emissions, and cobalt is listed in the Water Framework Directive 2000/60/EC. There are potential dust and metal emissions from grinding operations, and to a lesser extent from hydrometallurgical operations; chlorine in electrowinning and VOCs in solvent extraction; metals in effluents of hydrometallurgical purification and recovery operations; solid waste from purification and effluent treatment. The industry endeavours to work in a sustainable manner and uses a variety of techniques to recover and produce cobalt depending on the raw materials and end-products mix essentially, and the actual occurrence and significance of these issues is therefore site-specific.

# 1.11 Carbon and Graphite

## 1.11.1 General information

~~There is a vast range of carbon and graphite products that are in use. They range from large electrodes to small bushes and bearings. Other specialist products such as carbon fibres and carbon composites are also made for high technology industries that require the very high strength and low weight of these materials.~~

~~Carbon exists in three allotropic forms – diamonds, graphite and amorphous carbon. The difference between the allotropes is essentially the structure of the carbon atoms and the structure determines the properties of the resulting material. Carbon and graphite products are applied in multiple applications because they can be designed to have specific strength, toughness, electrical and mechanical properties and are especially highly pure and chemically resistant under oxygen free conditions [ 203, Fundación Entorno, Empresa y Medio Ambiente 1999 ] [ 116, VDI (D) 3467 1998 ].~~

Carbon and graphite materials are mainly applied for the conduction of electrical power (cathodes and graphite electrodes) and as chemical reducing agents in the aluminium industry (anodes).

Carbon and graphite products can basically be divided into five product groups:

1. Green mix and paste: mainly used in the aluminium, ferro-alloy and in the steel industry.
2. Anodes, mostly used in the aluminium industry as a reducing agent.
3. Carbon and graphite, mostly used for the recycling of steel in the arc steel furnace and as cathodes in the aluminium industry.
4. Speciality carbon and graphite: a wide range of products ranging from very high purity to very high mechanical strength and thermal resistance.
5. Calcined anthracite and petroleum coke used as a re-carburiser in steel production.

The application of carbon specialities can roughly divided into

- high purity carbon and graphite
- highly mechanical and thermal applications
- engineered products like carbon and graphite fibres
- graphite foils and process equipment.

Carbon or graphite electrodes and furnace linings are produced for a variety of ferrous and non-ferrous metal production processes and are consumed during the production of the metals. More than 2000 other products of varying sizes, shapes and properties are produced for other applications. Carbon and high purity graphite materials are essential for the production of semi-conductors and microchips, graphite electrodes for the recycling of steel scrap and highly chemical resistant carbon and graphite are used for the recovery of residuals and the treatment of pollutants.

## 1.11.2 Sources of materials

The production of carbon and graphite materials are mainly based on petroleum coke and coal (anthracite) and a highly annealed coke based on coal tar. Petroleum pitch and coal tar pitch are used as a binder material, which is finally converted to inert solid carbon, coke or graphite during calcination, manufacture or use. Resin-based binder systems are used, which are cured before application.

The quality of coke and coal (anthracite) varies depending on the source but the most important factor is the sulphur content of the coke as this will be emitted as sulphur dioxide during calcination, manufacture or use. Normally, petroleum-based cokes or coal of a low or medium sulphur content are used for the major products like paste, anodes and electrodes.

The properties of the raw materials should be very consistent and are controlled by physical and chemical tests. New raw materials are tested in production trials to check their suitability and to adjust the production parameters to the new material. The final quality of raw materials is only based on the performance and acceptance of the manufactured carbon and graphite product.

Other materials are used in the production of specialist carbons and include metal and metal powders and a variety of resins.

### 1.11.3 Production and use

Coke, coal (anthracite) or carbon is usually bound with pitch (14 - 18 % by weight) to produce a green paste. For electrode paste production, calcined anthracite or petroleum coke is bound with pitch (20 - 30 % by weight). This paste then undergoes a number of shaping, baking, impregnation and graphitising stages to produce the final product. Green paste is also used directly for Søderberg electrodes. The baking process results in a loss in weight of ~ 5 % of the mass of the material. Packing coke is used in certain furnaces and in these cases is consumed at the rate of ~14 kg per tonne of product.

Carbon, calcined anthracite and graphite are mostly consumed during their application and converted into carbon dioxide (i.e. anodes for aluminium and steel electrodes). Steel production consumes electrodes at the rate 1.5 to 3 kg per tonne of steel. Due to the significant reduction of the consumption rates in some industries, the quantities of carbon and graphite used for the production of aluminium and steel has been reduced.

The processing stage and size of the process varies according to the product. The aluminium industry is by far the largest user of carbon materials as prebaked anodes, Søderberg paste and cathode blocks. Generally the specialist graphite products are smaller in scale than electrode products. ~~Table 1.32 shows the size of the various production areas.~~

| ~~**Product type**~~ | ~~**Capacity (t/yr)**~~ |
|---|---|
| ~~Green mix for Søderberg electrodes or paste~~ | ~~410000~~ |
| ~~Anodes for primary Al~~ | ~~1380000~~ |
| ~~Electrodes~~ | ~~420000~~ |
| ~~Speciality carbon and graphite~~ | ~~25000~~ |

~~**Table 1.32: Annual production capacities of carbon and graphite in the EU and Norway**~~

*I don't see why this table is needed.*

### 1.11.4 Production sites

Carbon and graphite products are made at 88 sites in Europe with an annual capacity of ~ 2 million tonnes (see Table 1.33).

| Country | Green mix paste | Anodes | Cathodes | Graphite electrodes (large shape) | Carbon and graphite specialities |
|---|---|---|---|---|---|
| Austria | >20 | 0 | 0 | >20 | <5 |
| France | 300 | 200 | >50 | >35 | 2 |
| Germany | 380 | 220 | <20 | 80 | 178 |
| Italy | 200 | 0 | 0 | 30 | NR |
| The Netherlands | 0 | 650 | 0 | 0 | NR |
| Norway | 400 | 300 | 0 | 0 | 18 |
| Poland | 150 | 0 | >20 | <20 | >40 |
| Spain | 150 | 0 | 0 | 100 | NR |
| Sweden | 80 | 0 | 0 | 0 | NR |
| UK | 200 | 160 | 10 | 0 | NR |

NR: No data has been reported

**Table 1.33: Carbon and graphite production in Europe for 2006 (data in thousand tonnes)**

~~Figure 1.9 shows the distribution of the Industry throughout Europe.~~

~~**Figure 1.9: European production sites for carbon and graphite**~~

*This figure is outdated. It includes figures for the production of each of the product types which do not fit to table 1. Delete!!*

There is a strong tendency to close on-site anode production and to switch to an off site supply. Some of the larger on-site producers with capacities of up to 150000 t/yr also supply smaller primary aluminium smelters with anodes. The biggest carbon-producing plant in Europe and probably in the world is located in the Netherlands with a production capacity of 565000 t/yr. Nevertheless, the major quantities of anodes are still produced in numerous on-site units.

A few companies only produce cathodes due to the fact that there is a very high lifetime cycle demanded by the aluminium industry. The life cycle of a cathode block ranges from 6 to 10 years. The properties have to guarantee a very good performance with respect to lifetime, electrical resistance and abrasion.

*This section should be overworked by a competent industry representative.*

### 1.11.5 Environmental issues

The main environmental impacts of these processes are the impacts of emissions to air of tars and PAH from the complex mixtures of binder and impregnation pitches, sulphur dioxide from coke and fuels and VOCs from impregnating agents. A variety of new abatement processes have been developed to destroy tars and PAH using novel afterburning systems. [ 116, VDI (D) 3467 1998 ]

The pitches release polynuclear (polycyclic?) hydrocarbon compounds while being carbonised. Benz(a)pyrene or the PAH are used as an guideline substances to monitor the character of the emissions. Emissions occur during the storage of pitch, mixing and shaping, while carbonising in the baking furnaces and during impregnation.

If cokes with an increased sulphur content or sulphur additives are used during the production of carbon speciality products, sulphur dioxide might be formed and released.

Dust or particulate emissions are potentially significant. Fine-grained materials are normally not used for paste, anode and electrode production, but are for other products.

~~The progress in the applied techniques to control the impact on the environment has been significant.~~

Water pollution is, in general, a minor issue of the carbon industry. Production processes are dry and generally use contained cooling water systems. Exceptionally, surface water for cooling may be used where it is suitable due to local conditions, ~~[ 116, VDI (D) 3467 1998 ]~~.*This information is from the 10 years old BREF and not from [116].*

Most successful are the efforts of the carbon and graphite industry in recycling carbon materials (used and unused) and to open new fields of applications of these materials, replacing other natural sources.

# 2 COMMON PROCESSES AND TECHNIQUES/EQUIPMENT

## 2.1 Organisation of the chapter

There are many processes, variations in equipment and techniques that are used for the production of non-ferrous metals. These processes and variations need to be treated in a logical manner to allow the information to be presented clearly. Many of the techniques and individual stages of the production processes are common for most of the non-ferrous metals produced and these common stages can be described together to avoid too much repetition. These common stages can be divided as follows:

- management systems
- emission measurement and the use of emission data
- diffuse emissions
- process control techniques
- receipt, storage and handling of raw materials
- preprocessing and pretreatment of raw materials and transfer to production processes
- metal production processes and furnace types
- air abatement and recovery techniques
- PCDD/F
- sulphur dioxide
- water re-use and effluent treatment
- prevention, minimisation, recycling and treatment of process residues (including by-products and waste)
- energy and waste heat recovery
- cross-media issues
- noise and vibration
- odour
- safety aspects
- decommissioning.

Techniques for reducing diffuse emissions, fumes, PCDD/F and sulphur dioxide are reported individually because of their importance in this industry.

BAT conclusions are drawn for:

- environmental management systems (EMSs)
- material handling and storage
- process control
- fume and gas collection
- the prevention and the destruction of PCDD/F
- sulphur dioxide removal
- the removal of mercury
- effluent treatment and water re-use
- energy efficiency
- intermediate products, process residues and wastes
- emission monitoring.

Techniques for reducing the environmental impact of an installation can be described in three categories:

1. management techniques: relating to the systems and procedures for designing and operating a process and for training operators and other staff;
2. process-integrated techniques: relating to the use of techniques to prevent or reduce emissions from activities such as storage, reaction, separation and purification;
3. energy reduction and abatement techniques: relating to end-of-pipe techniques to reduce emissions to air, water and land.

This chapter briefly describes the common techniques covering these three categories that are used in this sector. An indication is given (where possible) of the techniques that are able to prevent or reduce emissions to each environmental media. This chapter also indicates where these techniques can be used in the various process stages to improve existing processes. This theme is developed in the metal-specific chapters that follow.

The metallurgical production processes for the 10 groups, identified by the Technical Working Group, are covered in Chapters 3 to 12 respectively. The techniques to consider in the determination of BAT in these chapters include more detailed process descriptions, examples and diagrams. They also provide more detail of how the integrated process operates and where the variations in the techniques to consider in the determination of BAT described in Chapter 2 are used, e.g. the way furnaces differ from the generic description. This approach has been used to minimise repetitive descriptions and to allow the transfer of information and techniques across the 10 groups.

Best available techniques are not specified for all of the common processes described in this chapter but the various common processes and techniques will contribute to the best available techniques described in Chapters 3 to 12. Additionally, the techniques described in this chapter are also suitable for reducing overall emissions and will therefore influence the way existing plants are improved.

Chapter 2 should be used in conjunction with Chapters 3 to 12 to give the complete production cycle, e.g. Chapters 2 and 3 will give the overall ranges for the production of copper and its alloys.

### 2.1.1 Installations that produce a number of metals or have associated processes on-site

A significant number of installations produce a number of metals from different groups or may have associated processes integrated with them. Examples are the processing of bauxite at an aluminium smelter, the presence of an anode production plant at an aluminium smelter or the production of a range of different metals from complex raw materials in particular copper, lead, zinc and precious metals.

The elements of integrated plants may be found in different parts of the BREF, e.g. anode slime details in precious metals; prebaked anode details in Chapter 12 and other metals within their metal-specific chapter. The chapter describing the main metal will contain some references to these processes, e.g. anode slime production in Chapter 3 and the presence of an anode plant in Chapter 4. Table 2.1 shows processes that may form integrated installations and explains where these sections and chapters are and so show how a complex plant can be approached.

| **Materials produced in the same installation** | **Chapters that contain process and other details** | **Chapters that contain overview of the processes** | **Comment** |
|---|---|---|---|
| Alumina from bauxite in an Al smelter | Chapter 4 | Chapter 4 | Integrated with a few installations |
| Prebaked anodes produced in an aluminium smelter | Chapter 12 | Chapter 4 | Factors of common storage and mixing techniques taken into account |
| Lead, zinc or precious metals with the production of copper | Chapters 5 and 6 | Chapter 3 | Some duplication between Chapter 3 and the other chapters |
| Nickel, cobalt and copper | Chapters 3 and 11 | Chapter 11 | |
| Mercury during the production of other metals | Chapter 7 and Chapter 2 | Chapters 3 and 5 | Mercury removal from smelter gases before acid plant |
| FeCr, FeSi, FeMn, etc. | Chapter 9 | Chapter 9 | Factors of common abatement techniques. Common energy recovery techniques. |
| Refractory metals | Chapter 8 | Chapter 8 | |
| Ferro-alloys and refractory metals | Chapters 8 and 9 | Chapters 8 and 9 | |

**Table 2.1: Processes that may form integrated installations**

### 2.1.2 Standard information for techniques to consider in the determination of BAT

*This section should appear prior to a section "General techniques to consider in the determination of BAT". Here it can not be identified to have any relation to the technique to consider in the determination of BAT section. Those section appear in the following from time to time, having all the same title even if they contain different aspects. I propose to have a few blocks as described in section 2.5.*

The sections of this document entitled 'Techniques to consider in the determination of BAT' set out techniques considered generally to have potential for achieving a high level of environmental protection in the industries within the scope of the document. The techniques are described in each of Chapters 2 to 10 and include management systems, process-integrated techniques and end-of-pipe measures, but a certain amount of overlap exists between these three when seeking the optimum results.

Prevention, control, minimisation and recycling procedures are considered as well as the re-use of materials and energy.

Techniques may be presented singly or as combinations to achieve the objectives of the IPPC Directive. Annex IV to this Directive lists a number of general considerations to be taken into account when determining BAT and techniques within this chapter will address one or more of these considerations. As far as possible, a standard structure is used to outline each technique, to enable comparison of techniques and an objective assessment against the definition of BAT given in the IPPC Directive.

The content is not an exhaustive list of techniques and others may exist or be developed which may be equally valid within the framework of IPPC and BAT.

The standard structure used to outline each technique is shown in Table 2.2.

| Type of information considered | Type of information included |
|---|---|
| Description | Technical description of the technique (including drawings, schematics if necessary) |
| Achieved environmental benefits | Main environmental benefits (including energy, water, raw material savings, as well as production yield increases, energy efficiency, etc.) addressed by the technique |
| Cross-media effects | Main environmental side effects and disadvantages to other media caused by using the technique. Details of the environmental effects of the technique in comparison with others |
| Operational data | Data on consumption and emission levels from operational plants using the technique (including any reference conditions and monitoring methods used). Any other relevant information on how to operate, maintain and control the technique |
| Applicability | Indication of the type of plants in which the technique may be applied, considering, e.g. plant age (new or existing), plant size (large or small), techniques already installed and type or quality of product |
| Economics | Information on costs (both investment and operational) and any possible savings (e.g. reduced raw material or energy consumption, waste charges) or revenues including details on how these costs/savings or revenues have been calculated/estimated |
| Driving force for implementation | Local conditions or requirements which lead to, or may stimulate, implementation. Information on reasons other than environmental ones for implementation (e.g. increase in productivity, safely) |
| Example plants | Reference to (a) plant(s) in which the technique is applied and from which information has been collected and used in writing the section |
| Reference literature | Literature or other reference material (e.g. books, reports, studies, websites) that was used in writing the section and that contain more details on the technique |

**Table 2.2: Information breakdown for each technique described in this chapter**

Best available techniques are influenced by a number of factors in this sector and a methodology was needed to examining the techniques. The approach that was used is given below:

1. First of all, the choice of process depends strongly on the raw materials that are available to a particular site. The most significant factors are the composition, the presence of other included metals, their size distribution (including the potential to form dust) and the degree of contamination by organic material. There may be primary materials available from single or multiple sources, secondary raw materials of varying quality or a combination of primary and secondary raw materials.
2. Secondly, the process should be suitable for use with the best gas collection and abatement systems that are available. The fume collection and abatement processes used will depend on the characteristics of the main processes, for example some processes avoid ladle transfers and are therefore easier to seal. Other processes may be able to treat recycled materials more easily and therefore reduce the wider environmental impact by preventing disposal.
3. Finally, the water and waste issues have been taken into account, in particular the minimisation of wastes and the potential to re-use residues and water within the process

or by other processes. Energy used by the processes and abatement is also a factor that is taken into account in the choice of processes.

The conclusion on BAT is therefore complicated and depends on the above factors. The varying requirements mean that BAT is influenced mainly by the raw materials available to the site and the required throughput of the plant, the issues are therefore site-specific. There are advantages for some primary process that are capable of accepting some secondary materials.

Several production process and pollution abatement combinations can be operated to the highest environmental standards. The processes vary in the throughput that can be achieved and the materials that can be used and so several combinations are included. All of the processes maximise the re-use of residues and minimise emissions to water. The economics of the processes vary. Some need to operate at a high throughput to achieve economic operation, while others are not able to achieve high throughputs.

As indicated in the Preface to this document, this section concludes on techniques and associated emission and consumption levels that are considered to be compatible with BAT in general. The purpose is to provide general indications of the emission and consumption levels that might be considered an appropriate benchmark of BAT-based performance in the copper sector. This is done by quoting achievable levels in ranges that are generally applicable to both new and upgraded plants. Conditions may be present in existing installations, such as space or height limitations, that prevent the full implementation of BAT.

Emission and consumption levels at a given plant will also vary with time depending on the specific condition of the equipment, its maintenance and the process control of the abatement plant. The operation of the source process will also influence performance of the abatement plant as there are likely to be variations in temperature, gas volume and even the characteristics of the material emitted during the operation of a process or batch. The achievable emissions are therefore only a basis from which actual plant performance can be judged. Process dynamics and other site-specific issues need to be taken into account at a local level.

# 2.2 Management systems

Effective management is important in achieving good environmental performance. It is an important component of BAT and forms part of the definition of techniques given in Article 2 of the Directive.

The work undertaken in preparing this document has shown that there are many significant differences between the environmental performance of a process that is managed and operated well and an identical process that is managed and operated poorly. Management and communication systems are some of the most significant factors in this difference.

Achievement of a good performance requires commitment at all levels within a company starting at board or policy level and includes the site management, supervisors and operators. The system should establish objectives, set targets and communicate instructions and results. Environmental management systems such as ISO14001 and EMAS, management systems for occupational health and safety such as OHSAS 18001 or a quality management system such as ISO 9000 can assist by formalising the system.

Although they are not a requirement of the IPPC Directive, an installation should consider the benefits that can arise from adopting such a system. The techniques used can also improve economic performance by improving operating efficiency, reducing costs such as energy or disposal costs and improving metal yields. These techniques are therefore essential factors for a modern installation.

## 2.2.1 Management policy and commitment

An effective management system can include the following factors below:

- Identification of all health, safety and environmental impacts of activities, products and processes, e.g. OHSAS 18001.
- A commitment to develop and implement the measures identified.
- The communication of the policy to employees and contractors to ensure that they are aware of the commitment and are involved in its delivery.
- The use of a clear structure for managing environmental issues that is fully integrated with the wider company and site decision making systems.
- The environmental performance of the process is highly dependent on the attention and awareness of the process operator. Awareness of this and their role in the environmental performance is important.
- The overall environmental performance can be monitored on a regular basis and the results can form part of the management assessment process. Environmental performance indicators can be devised and disseminated to operators and feedback from operators can be obtained and used.
- Contingency plans can be prepared which identify the potential types of incident that can occur and provide clear guidance on how they will be managed and who is responsible. Procedures can be prepared to identify, respond to and learn from all complaints and incidents.
- Where new processes are being commissioned, or where existing processes are being recommissioned after alterations, a commissioning plan can be prepared that clearly identifies the issues and the person(s) responsible for the environmental performance of the process during the commissioning period.

### 2.2.2 Design and maintenance

The IPPC Directive requires the achievement of 'a high level of protection of the environment as a whole'. Design and maintenance have the main influence on fulfilling this requirement by assessing the effect of existing plants and any new or substantially changed processes on the degree of protection of air, water and land. An adequate supply of important equipment for security and for the environment should be kept to minimise accidental emissions and their impact. Several companies specialise in design and maintenance.

This requirement can be achieved as follows:

- The environmental implications (including noise) of a new or substantially modified process or raw material should be considered at the earliest stages of the project and should continue to be reviewed at regular intervals thereafter. This is the most cost-effective time to introduce improvements in overall environmental performance. An audit trail of the design and decision-making process is a useful method to show how various process and abatement options were considered. Commissioning issues should be planned for new or modified plants.
- Potential diffuse emissions should be considered at all stages.
- A programme of preventive maintenance should be used and recorded. It should be coupled with diagnostic testing where appropriate.
- Important equipment for security and environment should be held as spare parts [ 243, French comments on MnFe alloys 2008 ].
- Local extraction systems should be examined regularly and defects or damage repaired promptly.
- All staff should be made aware of the role they can play by maintaining vigilance, for example, in relation to damage to hoods and duct work or plant failures. Appropriate procedures should be used to encourage staff involvement and respond to reports.
- An internal procedure should be used to authorise modifications and to undertake checks after modifications before a process starts up.

### 2.2.3 Training

Training is an important factor and the following points should be included in training schedules:

- All staff should be aware of the implications to the environment of the process and their work activities.
- There should be a clear statement of the skills and competencies required for each job.
- Training given to staff involved in a process operation should include the environmental implications of their work and the procedures for dealing with incidents.
- Records of the training given to process operation staff can be very useful in ensuring progressive and complete training.
- Training of other departments about the environmental issues and the consequences that can affect the installation can also be effective in preventing conflicts that affect environmental performance. For example, finance and sales teams can have significant influences on environmental performance. Full accounting measures can identify excess raw material usage and can identify true energy and disposal costs for process stages; unplanned deliveries and sales can lead to production short cuts and cause incidents.

### 2.2.4 Techniques to consider in the determination of BAT

The sections of this document entitled 'Techniques to consider in the determination of BAT' set out techniques considered generally to have potential for achieving a high level of environmental protection in the industries within the scope of the document. The background to the way the techniques are described is given in Section 2.1.2 and Table 2.2.

#### 2.2.4.1 Environmental management tools

**Description**

The best environmental performance is usually achieved by the installation of the best technology and its operation in the most effective and efficient manner. This is recognised by the IPPC Directive's definition of 'techniques' as *"both the technology used and the way in which the installation is designed, built, maintained, operated and decommissioned"*.

For IPPC installations an Environmental Management System (EMS) is a tool that operators can use to address these design, construction, maintenance, operation and decommissioning issues in a systematic, demonstrable way. An EMS includes the organisational structure, responsibilities, practices, procedures, processes and resources for developing, implementing, maintaining, reviewing and monitoring the environmental policy. Environmental Management Systems are most effective and efficient where they form an inherent part of the overall management and operation of an installation.

All effective EMSs contain the notion of continuous improvement meaning that environmental management is a process, not a project which eventually comes to an end. There are various process designs, but most environmental management systems are based on the plan-do-check-act cycle (which is widely used in other company management contexts). The cycle is a re-iterative dynamic model, where the completion of one cycle flows into the beginning of the next, see Figure 2.1.

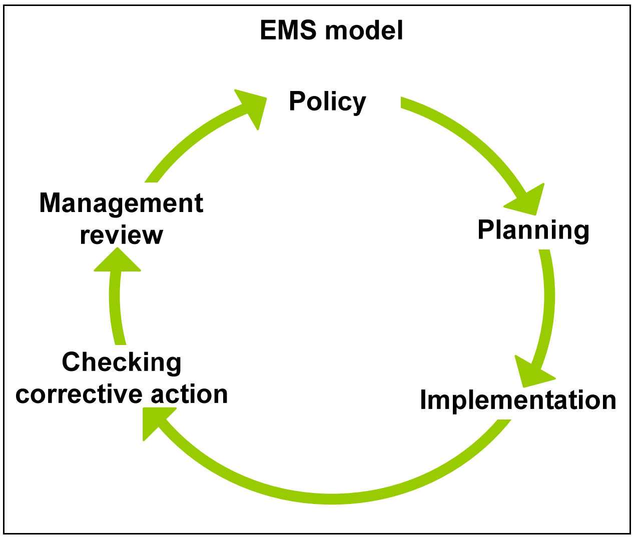


**Figure 2.1: Continuous improvement in an EMS model**

Within the European Union, many organisations have decided on a voluntary basis to implement environmental management systems based on EN ISO 14001:2004 or the EU Eco-Management and Audit Scheme (EMAS). EMAS includes the management system requirements of EN ISO 14001, but places additional emphasis on legal compliance, environmental performance and employee involvement. It also requires external verification of the management system and validation of a public environmental statement (in EN ISO 14001 self-declaration is an alternative to external verification). There are also many organisations that have decided to put in place non-standardised EMSs.

While both standardised systems (EN ISO 14001:2004 and EMAS) and non-standardised (‘customised’) systems in principle take the *organisation* as the entity, this document takes a narrower approach, not including all activities of the organisation, e.g. with regard to their products and services, due to the fact that the regulated entity under the IPPC Directive is the *installation* (as defined in Article 2 of the Directive).

An Environmental Management System (EMS) for an IPPC installation can contain the following components:

(a) commitment of top management
(b) definition of an environmental policy
(c) planning and establishing objectives and targets
(d) implementation and operation of procedures
(e) checking and corrective action
(f) management review
(g) preparation of a regular environmental statement
(h) validation by a certification body or an external EMS verifier
(i) design considerations for end-of-life plant decommissioning
(j) development of cleaner technologies
(k) benchmarking.

These features are explained in somewhat greater detail below. For detailed information on components (b) to (h), which are all included in EMAS, the reader is referred to the reference literature indicated below.

(a) Commitment of top management:

The commitment of top management is the precondition for a successful EMS. It is important that top management:

- place environmental management high on the company agenda, make it visible and give it credibility
- identify one top manager with responsibility for environmental management
- help create an environmental management culture and create the necessary driving forces for implementation
- define a strategy (long term visions) to achieve environmental objectives
- set company targets to achieve these environmental objectives
- define short and medium term concrete actions to achieve the long term vision
- provide the platform to integrate decision-making in order to achieve integrated pollution prevention and control, particularly for when planning new installations or significant upgrading
- guide the company to make investment and purchasing decisions that achieve integrated pollution prevention and control on a continuing basis. Integrated pollution prevention and control is achieved through integrated decision-making and actions, including the buying of utilities and capital equipment, planning, production, and maintenance as well as environmental management
- define an environmental policy, see (b) below.

(b) Definition of an environmental policy:

Top management are responsible for defining an environmental policy for an installation and ensuring that it:

- is appropriate to the nature, scale and environmental impacts of the activities

- includes a commitment to pollution prevention and control including the efficient use of raw materials, energy and water
- includes a commitment to comply with all relevant applicable environmental legislation and regulations, and with other requirements to which the organisation subscribes
- provides the framework for setting and reviewing environmental objectives and targets
- is documented and communicated to all employees
- is available to the public and all interested parties.

(c) Planning and establishing objectives and targets:

It is important to have:

- procedures to identify the environmental aspects of the installation, in order to determine those activities which have or can have significant impacts on the environment, and to keep this information up-to-date
- procedures to evaluate proposals for new processes, units and equipment, change in raw and auxiliary materials or fuels, upgrades, rebuilds and replacements in order to identify the environmental aspects and to influence the planning and purchasing to optimise the environmental performance of the installation with regard to the objectives of the IPPC Directive
- procedures to authorise the modifications indicated above and to undertake checks after modifications have been implemented and before the process starts up
- procedures to identify and have access to legal and other requirements to which the organisation subscribes and that are applicable to the environmental aspects of its activities
- establishing and reviewing documented environmental objectives and targets, taking into consideration the legal and other requirements to which the organisation subscribes and the views of interested parties
- establishing and regularly updating an environmental management programme, including designation of responsibility for achieving objectives and targets at each relevant function and level as well as the means and timeframe by which they are to be achieved
- carrying out audits to review, e.g. the efficient use of energy, water, raw and auxiliary materials.

(d) Implementation and operation of procedures:

It is important to have systems in place to ensure that procedures are known, understood and complied with, therefore effective environmental management includes:

(i) structure and responsibility:

  - defining, documenting, reporting and communicating roles, responsibilities and authorities, which includes appointing one specific management representative (in addition to a top manager (see (a) above)
  - providing resources essential to the implementation and control of the environmental management system, including human resources and specialised skills, technology and financial resources

(ii) training, awareness and competence:

  - defining, documenting and communicating skills and competencies required for each job
  - identifying training should ensure that all personnel whose work may significantly affect the environmental impacts of the activity have received appropriate training for all modes of operations they can encounter, i.e. preparation, start-up, routine operation, shutdown and abnormal conditions

(iii) communication

- establishing and maintaining procedures for internal communication between the various levels and functions of the installation, as well as procedures that foster a dialogue with external interested parties and procedures for receiving, documenting and, where reasonable, responding to relevant communication from external interested parties

(iv) employee involvement

- involving employees in the process aimed at achieving a high level of environmental performance by applying appropriate forms of participation such as the suggestion book system or project-based group works or environmental committees

(v) documentation

- establishing and maintaining up-to-date information, in paper or electronic form, to describe the core elements of the management system and their interaction and to provide direction to related documentation

(vi) efficient process control

- adequate control of processes and equipment (including pollution prevention and control equipment) under all modes of operation, i.e. preparation, start-up, routine operation, shut-down and abnormal conditions
- identifying the key performance indicators (e.g. flow, pressure, temperature, composition, quantity) and methods (e.g. weighting systems, metering systems, calculations, sampling and analysis) for measuring and controlling these parameters
- documenting and analysing abnormal operating conditions to identify the root causes and then addressing these to ensure that abnormal events do not recur (this can be facilitated by a ‘no-blame’ culture where the identification of causes is more important than apportioning blame to individuals)

(vii) maintenance programme

- establishing a structured programme for maintenance (including preventive and corrective maintenance) based on technical descriptions of the equipment, norms, etc. as well as any equipment failures and consequences of the failures
- identifying from routine maintenance, breakdowns and/or abnormalities, possible decreases in environmental performance, or where environmental performance could be improved
- supporting the maintenance programme by appropriate record keeping systems and diagnostic testing
- clearly allocating responsibility for the planning and execution of maintenance

(viii) emergency preparedness and response

- establishing and maintaining procedures to identify the potential for and response to accidents and emergency situations, and for preventing and mitigating the environmental impacts that may be associated with them

(e) Checking and corrective action (see also benchmarking (e)):

(i) monitoring and measurement

- establishing and maintaining documented procedures to monitor and measure, on a regular basis, the key characteristics of operations and activities that can have a significant impact on the environment. This includes the recording of information for tracking performance, relevant operational controls and conformance with the installation's environmental objectives and targets *(see also the Reference Document on the General Principles of Monitoring* [ 293, EC 2003 ]
- establishing and maintaining a documented procedure for periodically evaluating compliance with relevant environmental legislation and regulations

(ii) corrective and preventive action
  - establishing and maintaining procedures for defining responsibility and authority for handling and investigating non-conformance with permit conditions, other legal requirements and commitments as well as objectives and targets
  - taking action to mitigate any impacts caused by abnormal events and for initiating and completing corrective and preventive actions that are appropriate to the magnitude of the problem and commensurate with the environmental impact encountered

(iii) records
  - establishing and maintaining procedures for the identification, maintenance and disposition of legible, identifiable and traceable environmental records, including training records and the results of audits and reviews

(iv) audit
  - establishing and maintaining a programme (or programmes) and procedures for periodic environmental management system audits. Such a programme (or programmes) includes discussions with personnel, inspection of operating conditions and equipment and reviewing of records and documentation. Each audit results in a written report, to be carried out impartially and objectively by employees (internal audits) or external parties (external audits), covering the audit scope, frequency and methodologies, as well as the responsibilities and requirements for conducting audits and reporting results, in order to determine whether or not the environmental management system conforms to planned arrangements and has been properly implemented and maintained
  - completing the audit or audit cycle, as appropriate, at intervals of no longer than three years, depending on the nature, scale and complexity of the activities, the significance of associated environmental impacts, the importance and urgency of the problems detected by previous audits and the history of environmental problems – more complex activities with a more significant environmental impact are audited more frequently
  - having appropriate mechanisms in place to ensure that the audit results are followed up

(v) periodic evaluation of legal compliance
  - reviewing compliance with the applicable environmental legislation and the conditions of the environmental permit(s) held by the installation
  - documentation of the evaluation.

(f) Management review:

- reviewing, by top management, at intervals that it determines, of the environmental management system, to ensure its continuing suitability, adequacy and effectiveness
- ensuring that the necessary information is collected to allow management to carry out this evaluation
- documentation of the review.

(g) Preparation of a regular environmental statement:

- preparing an environmental statement that pays particular attention to the results achieved by the installation against its environmental objectives and targets. It is regularly produced – from once a year to less frequently depending on the significance of emissions, waste generation, etc. This statement considers the information needs of relevant interested parties and it is publicly available (e.g. in electronic publications, libraries etc.). When producing a statement, the operator may use relevant existing environmental performance indicators, making sure that the indicators chosen:

   i. give an accurate appraisal of the installation's environmental performance
   ii. are understandable and unambiguous
   iii. allow for year on year comparison to assess the development of the environmental performance of the installation
   iv. allow for comparison with sector, national or regional benchmarks as appropriate
   v. allow for comparison with regulatory requirements as appropriate.

(h) Validation by a certification body or an external EMS verifier:

- having the management system, audit procedure and environmental statement examined and validated by an accredited certification body or an external EMS verifier can, if carried out properly, enhance the credibility of the system.

(i) Design considerations for end-of-life plant decommissioning:

- giving consideration to the environmental impact from the eventual decommissioning of the installation at the stage of designing a new plant, as forethought makes decommissioning easier, cleaner and cheaper
- decommissioning poses environmental risks for the contamination of land (and groundwater) and generates large quantities of solid waste. Preventive techniques are process-specific but general considerations may include:
   i. avoiding underground structures
   ii. incorporating features that facilitate dismantling
   iii. choosing surface finishes that are easily decontaminated
   iv. using an equipment configuration that minimises trapped chemicals and facilitates drain-down or cleaning
   v. designing flexible, self-contained units that enable phased closure
   vi. using biodegradable and recyclable materials where possible.

(j) Development of cleaner technologies:

- environmental protection should be an inherent feature of any process design activities carried out by the operator or its contractors, since techniques incorporated at the earliest possible design stage are both more effective and cheaper. Giving consideration to the development of cleaner technologies can, for instance, occur through R&D activities or studies. As an alternative to internal activities, arrangements can be made to keep abreast with – and where appropriate – commissioned work by other operators or research institutes active in the relevant field.

(k) Benchmarking:

- carrying out systematic and regular comparisons with sector, national or regional benchmarks, including for energy efficiency and energy conservation activities, choice of input materials, emissions to air and discharges to water (using for example the European Pollutant Emission Register, EPER), consumption of water and generation of waste.

**Standardised and non-standardised EMSs**

An EMS can take the form of a standardised or non-standardised ('customised') system. Implementation and adherence to an internationally accepted standardised system such as EN ISO 14001:2004 can give higher credibility to the EMS, especially when subjected to a properly performed external verification. EMAS provides additional credibility due to the interaction with the public through the environmental statement and the mechanism to ensure compliance with the applicable environmental legislation. However, non-standardised systems can, in principle, be equally effective provided that they are properly designed and implemented.

### Achieved environmental benefits

Implementation of, and adherence to, an EMS focuses the attention of the operator on the environmental performance of the installation. In particular, the maintenance of, and compliance with, clear operating procedures for both normal and abnormal situations and the associated lines of responsibility should ensure that the installation's permit conditions and other environmental targets and objectives are met at all times.

Environmental management systems typically ensure the continuous improvement of the environmental performance of the installation. The poorer the starting point is, the more significant short term improvements can be expected. If the installation already has a good overall environmental performance, an EMS helps the operator to maintain the high performance level.

### Cross-media effects

Environmental management techniques are designed to address the overall environmental impact of the installation, which is consistent with the integrated approach of the IPPC Directive.

### Operational data

All significant consumptions (including energy) and emissions are managed in a coordinated manner by the operator for the short, medium and long term, in conjunction with financial planning and investment cycles. This means that e.g. adapting short-term end-of-pipe solutions to emissions may tie the operator to long term higher energy consumption, and postpone investment in potentially more environmentally beneficial solutions overall. This requires some consideration of the cross-media issues, and guidance on these and the costing and cost-benefits issues is given in the Reference Document on Economics and Cross-Media Effects [ 336, EC 2006 ]and in the BREF on Energy Efficiency *[ 333, EC 2008 ]*

### Applicability

The components described above can typically be applied to all IPPC installations. The scope (e.g. level of detail) and nature of the EMS (e.g. standardised or non-standardised) will be related to the nature, scale and complexity of the installation, and the range of environmental impacts it may have.

*[Author: add applicability issues to fit the specificities of the sector]*

### Economics

It is difficult to accurately determine the costs and economic benefits of introducing and maintaining a good EMS. A number of studies have been made but do not reflect the size or complexity of the non-ferrous metals sector. There also economical benefits that are the result of using an EMS and this varies widely from sector to sector.

In some Member States reduced supervision fees are charged if the installation has a certification.

External costs relating to verification of the system can be estimated from guidance issued by the International Accreditation Forum (http://www.iaf.nu).

The following information about the costs of implementing EMS in the non-ferrous metals sector and some of the savings made are provided below.

The costs for implementing a EMS are varying, they are strongly depending on the size of the company. But according to studies the ROI (return of investments) is within 3-5 years.

**Driving forces for implementation**

Environmental management systems can provide a number of advantages, for example:

- improved insight into the environmental aspects of the company
- improved basis for decision-making
- improved motivation of personnel
- additional opportunities for operational cost reduction and product quality improvement
- improved environmental performance
- improved company image
- reduced liability, insurance and non-compliance costs
- increased attractiveness for employees, customers and investors
- increased trust of regulators, which could lead to reduced regulatory oversight
- improved relationship with environmental groups.

**Example plants**

The features described under (b) to (f) above are elements of EN ISO 14001:2004 and the European Union Eco-Management and Audit Scheme (EMAS), whereas the features (g) and (h) are specific to EMAS. These two standardised systems are applied in a number of IPPC installations. As an example, XZY organisations within the EU non-ferrous metals industries (NACE code 27.4) were EMAS registered in July 2002, most of which operate IPPC installations TWG please provide information.

**Reference literature**

(Regulation (EC) No 761/2001 of the European parliament and of the council allowing voluntary participation by organisations in a Community Eco-Management and Audit Scheme (EMAS), OJ L 114, 24/4/2001, http://europa.eu.int/comm/environment/emas/index_en.htm)

(EN ISO 14001: 2004, http://www.iso.ch/iso/en/iso9000-14000/iso14000/iso14000index.html; http://www.tc207.org)

## 2.3 Emission measurement and use of emission data

This section is intended to ensure that the emissions reported in this document are measured in such a way that the results are representative, mutually comparable and clearly describe the relevant operating state of the plant. The methods and instruments used for sampling and analysis should be the relevant national or international methods (e.g. European Committee for Standardisation (CEN); ISO; VDI Richtlinien [ 317, Measuring Requirements 2009 ]; Netherlands Emission Regulations Ch4 (NER); UK Guidance Notes; British Standards, etc.) [ 293, European Commission 2003 ]. General principles are given below.

### 2.3.1 Measurement of captured emissions

The measurement of emissions is used to determine the substances in the clean gas or waste water so that they can be reported, used to control the process or abatement plant or used to predict environmental impacts. The techniques are generally covered in the Reference Document on the General Principle of Monitoring [ 293, European Commission 2003 ] and in the VDI Guideline for Secondary Copper [ 219, VDI (D) 2102 2007 ]

Prior to measurement, plans can be made to take account of:

- the mode of operation
- the operating state of off-gas purification or effluent treatment plants
- operating conditions in the plant (continuous, discontinuous, start-up and shut-down operations, load change) and
- the effect of thermodynamic interference factors.

Dilution of the gases or waste water is not considered acceptable. Factors should be taken into account such as variations of the process, nature and potential hazard of the emissions, time needed to obtain a measurable amount of pollutant or representative information. These factors can then form the basis for the selection of operating conditions at which the highest emissions may be recorded, the number and duration of the measurements chosen; the most appropriate method of measurement chosen and the position of the measurement locations and points determined. For waste water emissions, qualified random samples can be used or 24 hour composite samples based on flow proportional or time averaged samples taken.

For continuous operations, a minimum sample collection time or measurement time of half an hour (half hourly mean value) is usually necessary. If dust contents are low or if PCDD/PCDF are to be determined, longer measurement times and consequently, other reference times may be necessary because of the limitation of detection. Sampling or measuring should take place only during the operation of the process and dilution air should be excluded. For continuous operation when there are only slight fluctuations in the emission characteristics, three individual measurements can be performed at the highest emission level. If it is anticipated that the emission levels will be very variable during continuous operation, more measurements can be carried out; the sampling and averaging time being limited to the emissions phase.

For batch operation, the measurement time and the averaging time should be modified so that a sample or samples over the whole batch can be taken. These results can be used to calculate averages or to show where peaks occur during the cycle. Again, sampling or measurements should only be made during periods of operation and dilution air should be excluded.

#### 2.3.1.1 Sampling locations

The sampling points should meet the requirements of the relevant national guidelines. The sampling points should normally:

- be clearly marked
- if possible, have a disturbance-free flow in the measurement section
- have monitoring points that can be closed
- have the required energy supplies
- have sufficiently large working platforms, and
- ensure that the requirements for safety at work are met.

#### 2.3.1.2 Components and parameters

The most common components that are measured in the non-ferrous metals sector include dust, metals, sulphur dioxide, total carbon (also VOC, tars and hydrocarbon), PCDD/F, oxides of carbon and nitrogen oxides. Acids such as HCl and HF are determined for some processes as are chlorides and fluorides. Specific determinants include PFC and PAH for primary aluminium, PAH for carbon and graphite and some determinants that are specific to some of the reagents used for precious metals production. The components are reported in the metal-specific chapters and the methods of sampling and analysis are given in the relevant national and international guidelines on monitoring and analysis [ 317, Measuring Requirements 2009 ].

The analysis of some parameters may be covered by methods established by other bodies, for example OSPARCOM. In this particular case, several of the methods used in the sampling and measurement of emissions from the primary production of aluminium and the production of prebaked anodes are defined by OSPARCOM or are subject to assessment. The measurement and determination of PAH in particular is the subject of a review. The number of PAH to be determined and the protocol for reporting some or all of them was not certain when the original BREF document was written but the preferred reporting convention is the EPA 16 as this is compatible with the PRTR reporting requirements.

#### 2.3.1.3 Reference conditions

For emissions to air, the following off-gas parameters should also be determined to convert the emission concentrations obtained to standard conditions of 273 K, 101.3 kPa, measured oxygen content and dry gas:

- the volumetric off-gas flow (in order to calculate the concentration and emission mass flow)
- the off-gas temperature
- the water vapour content of the off-gas
- the static pressure in the off-gas duct and
- the atmospheric pressure.

The production rate can be reported so that the emissions can be reported as specific emissions per tonne of metal. The specific gas volume $Nm^3$ per tonne of metal can also be calculated.

#### 2.3.1.4 Continuous measurement

The continuous measurement of several components in gases or in waste water is possible and in several cases accurate concentrations can be reported continuously or as mean values over agreed time periods (half-hourly, daily, etc.). In these cases, an analysis of the averages and the use of percentiles can allow a flexible method of demonstrating compliance with permit conditions and the averages can be easily and automatically assessed. Member States will have their own methods of assessing compliance that, for example, allow for short-term peak emissions.

For emission sources and components that can have a significant environmental impact, continuous monitoring should be specified. Dust can have significant environmental and health effects. In the metals sectors, however, dusts contain toxic components and continuous monitoring of dust is important not only for compliance assessment but also to assess whether any failures of the abatement plants have taken place (e.g. bag burst detection). To detect bag failures, the trend of concentration can be analysed or the presence of peak emissions during reverse jet cleaning of the bags can be observed. Modern dust monitors can interface with the cleaning system to identify which section of the filter contains leaking bags so that maintenance of the filter can take place on-line.

Methods are available to continuously measure:

- dust
- $SO_2$
- $NO_X$
- CO
- fluorine and its compounds
- chlorine and its compounds
- total carbon.

Competent authorities may require continuous measurement depending on the mass flow of the pollutant. Conductivity, turbidity, pH, flowrate, temperature and some ionic species can be continuously monitored for water.

Even in cases where absolute values may not be agreed as reliable, the use of continuous monitoring can be used to give trends in emissions and as control parameters for the process or abatement plant and are therefore very important.

Some physical parameters can also be used as surrogate parameters to give an indication of the presence of certain components in the gas stream. For example, the presence of an anode effect can indicate the production of PFCs in primary aluminium production and the temperature, oxygen and dust content of the gas can give an indication of the destruction of PCDD/F. pH can also be used to indicate the effective precipitation of metals.

### 2.3.2 Environmental monitoring

*(Check whether this section is really needed. If so, put this section into an Annex to which can be crossreferred if necessary.)*

The location of the plant is always an important aspect when determining best available techniques. In several countries, production sites have mandatory measurement programmes covering the environmental impact on the surroundings of the production unit [ 226, Nordic Report 2008 ]. In other cases, measurements are carried out by local authorities or by industry as part of larger research studies financed by parties other than the production site [ 237, Austria M168 2004 ]. As discussed in Section 2.4 on diffuse emissions, studies of the environment such as air dispersion modelling, reverse air dispersion modelling, air transportation models or studies of the water flows are commonly used to help identify potential sources of components in the environment from captured or diffuse emissions and differentiate between them [ 269, Port Talbot study 2005 ]. The fourth Air Quality Daughter Directive requires environmental monitoring of air for certain substances by local authorities and if the location of the monitors is suitable then these results can be used in the assessment of emissions provided that the substances are specific to the industry concerned. A comprehensive monitoring program is also required to monitor the quality in the receiving waters in response to the EU Water Framework Directive 2000/60/EC.

The aims can be to measure certain components such as metals in the surrounding air, water or land or the deposition of dust. Biological or health effect surveys or accident warning systems can also be applicable.

### 2.3.2.1 Examples of environmental monitoring practices

#### 2.3.2.1.1 Examples from the Nordic countries

**Air monitoring**

The example below [ 226, Nordic Report 2008 ] shows a brief summary of some aspects concerning air quality in the surroundings of a zinc smelter. In Table 2.3 the annual average concentrations of some metals are shown.

| Substance | Location relative to emission point | 2003 | 2004 | 2005 | 2006 |
|---|---|---|---|---|---|
| $PM_{10}$ (µg/Nm³) | 2 km from complex | 12 | 11 | 12 | 14 |
| Zinc (ng/Nm³) | 2 km from complex | | 13.3 | | |
| Cadmium (ng/Nm³) | 2 km from complex | | 0.14 | | |
| Nickel (ng/Nm³) | 2 km from complex | | 2.2 | | |
| Arsenic (ng/Nm³) | 2 km from complex | | 0.57 | | |

**Table 2.3:** **Annual average metal concentrations in ambient air from a complex industrial area which includes a primary zinc smelter (µg/Nm³) or (ng/Nm³)**

In this case, local authorities maintain an ambient air quality monitoring system and a co-operation contract between different parties taking part in the air quality monitoring programme has been written. The system includes four measuring stations at distances of 2 to 4 km from the plant. A TEOM 1400 A is used as the $PM_{10}$ collector and analyser and is totally automatic working on a continuous basis. It is based on a filter-based direct mass measurement method. Every five years, particles for metal analysis are collected with an accessory ACCU system over a two week period.

At the measurement stations, several other parameters are also measured such as: $SO_2$ and $NO_X$. All analysers work automatically and continuously. The analysers are calibrated four times a year by an external expert. Results from monitoring stations are transferred automatically to a computer located in the office of the municipal environmental authority. The authority collects the data, reports to participants and communicates with different interested parties.

The land-sea wind effect may influence the results in spring and autumn significantly. Emissions in spring and autumn from the land and sea are deposited near to the site and the measured concentrations here are usually higher than in normal situations.

In some plants, quite a broad bio-indicator study is performed regularly to assess the effects of emissions on the surroundings. This study also includes a survey of metals in dust and a survey of airborne metal concentrations in the soil. Sample points (about 100) in the bio-indicator and metal study are located at distances of 0.1 to 30 km from the zinc smelter.

**Water monitoring**

A comprehensive monitoring program is also set up for the quality in the receiving waters in response to the EU Water Framework Directive 2000/60/EC. The monitoring is based on an authority approved and co-operative monitoring program. In one example there are 18 sample points of the sea area. Samples for water quality analyses are taken eight times per year so that samples will be taken both in summer and winter (ice covered season). The seawater monitoring program includes many different environmental parameters, e.g. quality of seawater (salinity, pH, $O_2$, temperature, colour, P-total, N-total), biological survey (phytoplankton, bottom macrofauna, macroalgaes, periphyton, fish) and metal survey (metal concentrations in fish, sediment and bottom fauna). The monitoring program (sample collection, analysis and reporting) is entirely carried out by external experts.

Trends in environmental concentrations over time show the effect that improvements in standards have achieved. Figure 2.2 shows zinc concentrations in seawater near a zinc smelter over a 30 year period. This allows the competent authority to ensure that measures taken result in the reduction of emissions.

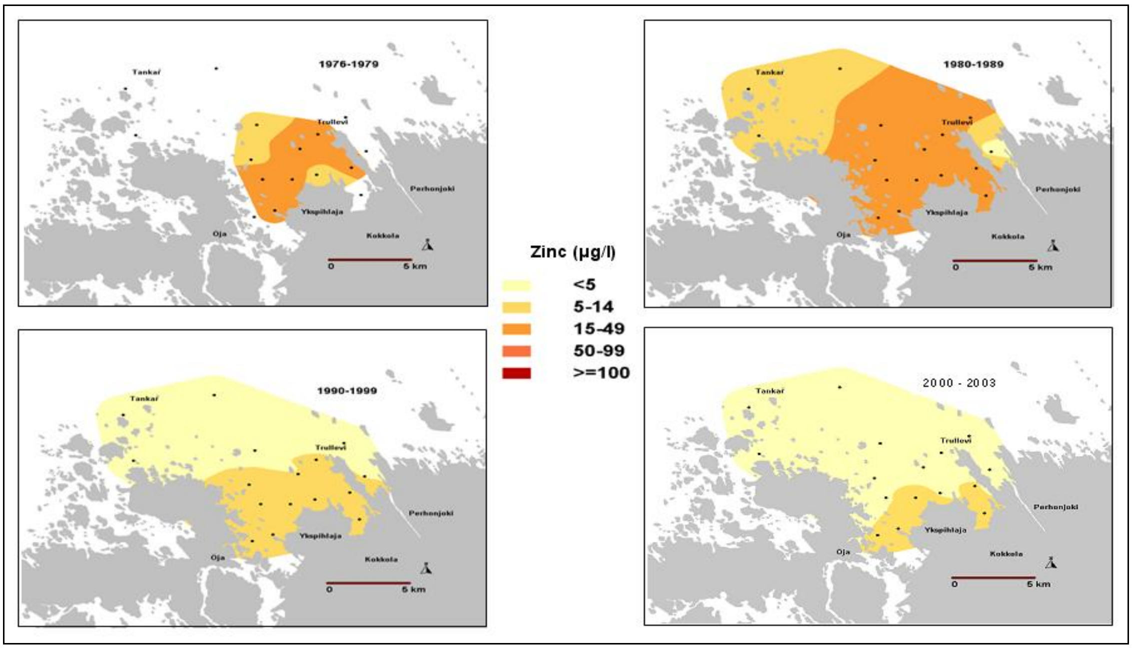


**Figure 2.2:** **Trend of zinc concentration in seawater over time near a zinc smelter**

### 2.3.2.1.2 Examples from other countries

Similar practices are used in the UK where environmental samples are taken regularly, depending on the scale of the installation and the substances emitted to establish the impact. Monitoring sites can be chosen based on the points of maximum environmental impact derived from air dispersion modelling. Samples of air, material deposited from air and from rain, soil and herbage are used to establish environmental levels and trends. Core samples of soil indicate the long-term deposition of pollutants while the analysis of grasses or crops indicate the deposition during the growing season.

Potential sources of $PM_{10}$ near a steelworks were investigated and it was possible to examine the sampled particles microscopically or to use cusum sequential trend analysis to identify possible sources [ 269, Port Talbot study 2005 ]. In this case, it was possible to show that iron deposits came from ship offloading rather than from the furnaces.

In Germany, the local authority air quality data and results from a monitoring point downwind of a smelter where the maximum ground levels of pollutants were predicted, are being used to demonstrate the effect of process improvements [ 274, Farrell Mission in DE 2008 ]. Some results derived from environmental monitoring are shown in Figure 2.3 and show the reduction in environmental levels from 1987 to 2008.

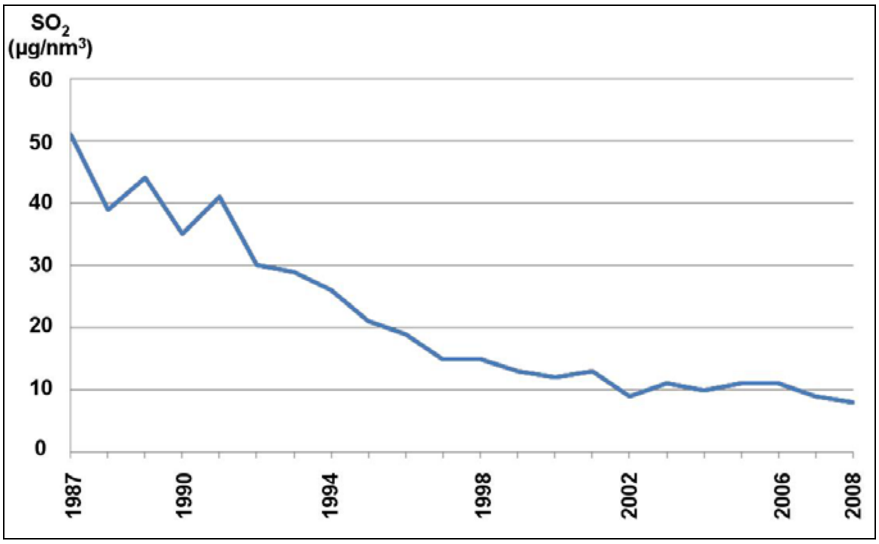


**Figure 2.3:** **Trends in the emission of $SO_2$ from a smelter (reported as kg $SO_2$ per tonne of metal produced)**

### 2.3.2.1.3 Studies in Austria

In Austria, analyses of emissions and deposition data from the town of Arnoldstein including the analysis of mosses near a smelter have been made and the results show the reduction in impact as the site has been improved and cleaner processes have been adopted. Analysis of vegetables grown in gardens between 320 and 4700 m from a secondary lead smelter have been taken as well as oil samples from cores to a depth of 10 mm [ 237, Austria M168 2004 ], [ 328, Cross-Media - Environmental Control in Selected Area 2009 ].

### 2.3.2.1.4 Studies in Flanders, Belgium

In Flanders, the air quality in the area around the industrial sites near Hoboken has been determined for several years using a network of sampling stations. This allows the trends in imissions to be studied and the results from monitoring stations have also been used to perform reverse air dispersion modelling. The environmental concentrations of some metals is shown in Table 2.4, and the trends for lead in Figure 2.4 [ 335, Luchtkwaliteit in het Vlaamse Gewest 2007 ].

| | **Municipality / district** | **Station code** | **Annual average 2007 (ng/m³)** |
|---|---|---|---|
| Pb –limit | Beerse | 00BE01 | 671 |
| Cd – target | Beerse | 00BE01 | 28.5 |
| | Beerse | 00BE07 | 14.4 |
| | Hoboken | 00HB17 | 6.8 |
| | Genk | 00GK04 | 5.3 |
| As – target | Beerse | 00BE01 | 22.6 |
| | Beerse | 00BE07 | 12.4 |
| | Hoboken | 00HB01 | 31.1 |
| | Hoboken | 00HB17 | 25.3 |
| | Hoboken | 00HB23 | 49.0 |
| | Hoboken | 00HB18 | 15.2 |
| | Hoboken | 00HB19 | 12.2 |
| | Hoboken | 00HB24 | 9.8 |
| Ni – target | Genk | 00GK02 | 34.9 |

| | | | |
|---|---|---|---|
| | Genk | 00GK03 | 32.9 |
| | Genk | 00GK04 | 81.4 |

**Table 2.4: Environmental concentrations of some metals at sampling stations in Flanders.**

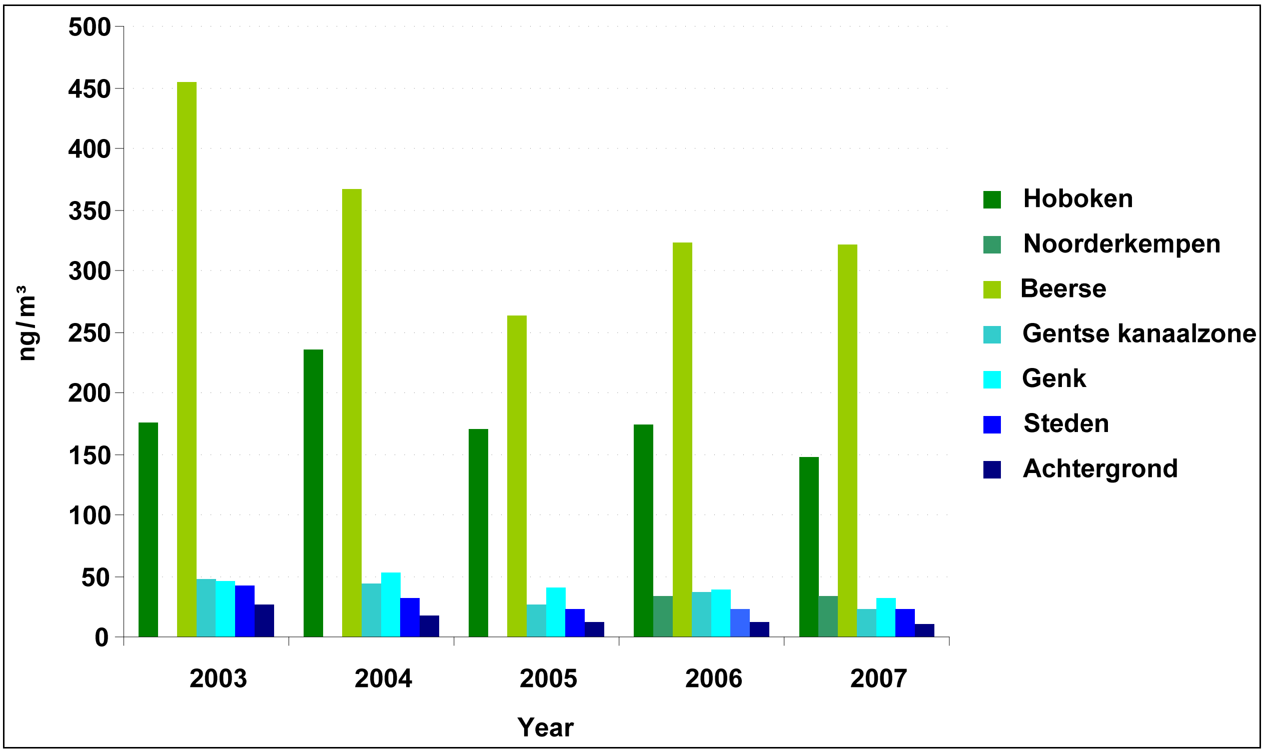


**Figure 2.4:** **The trend in lead concentrations in air from 2003 to 2007 for some sampling stations in Flanders**

### 2.3.2.2 Ecotoxicity and bioavailability

Since the original BREF was finalised, a lot of research and regulatory developments have taken place relating to assessing metals toxicity and risks to the environment. These concepts and methodologies have been assessed and endorsed by EU competent authorities in the metals risk assessments carried out under the Existing Substances Regulation 793/93/EEC and has also been approved for their use in the new EU REACH Regulation 1907/2006/EC.

The concepts and methodologies are useful when assessing various site-specific environmental conditions and the effect metal concentrations may have on the environment (i.e. on the aquatic, sediment and soil compartments). In terms of environmental monitoring, such a metal-specific risk assessment is particularly relevant as it gives details on how to make bioavailability assessment of the various metals, recognising that the toxicity of metals is dependent on a number of parameters and abiotic factors (such as hardness).

The waste water of the non-ferrous metals industries is well characterised by measuring the concentrations of its constituents. The list of metals is relatively short, compared to the organic constituents which can occur in the chemical or other industry sectors. Several research projects have looked into the link between waste water composition and its ecotoxicity towards algae. Models and methodologies for evaluating hazards, setting priorities, establishing environmental quality criteria, monitoring and assessing risks of chemicals are being developed and used in several jurisdictions. The majority of the compounds assessed are organic substances rather than inorganic metals and so the various methodologies and guidance documents provided for performing these assessments are lacking in detail on how to account for metal-specific attributes.

Questions related to the specific impact of metals on the environment and on human health have been raised. The need to establish ready and accessible metal-specific tools and data sets in order to make informed, science-based decisions have also been raised by representatives of local, regional, national and international administrations, as well as by members of non-governmental organisations, private companies and associations.

The Metals Environmental Risk Assessment Guidance (MERAG) was created by a consortium of researchers, metals associations, scientific panel reviewers and governmental reviewers (UK Government, Department for Environment Food and Rural Affairs (DEFRA)). MERAG was further adapted into an annex for the specific needs of the EU REACH regulation 1907/2007 (Technical guidance document, Annex 4 VIII 'Environmental risk assessment and risk characterisation for metals and metal compounds'). This metals annex has been reviewed and legally accepted by the European Chemical Agency (ECHA) [ 301, MERAG Guidance 2007 ].

The guidance is divided into different fact sheets that provide the risk assessors/regulators with methodologies to be used in chemicals management and environmental quality standard setting for metals and allow consideration of site-specific conditions by the assessor through the introduction of metal-specific concepts described in points 1 to 3 below:

1) Exposure assessment

The main objective of the exposure assessment is the derivation and evaluation of metal concentrations for each environmental compartment (water, air, soil, sediment) that is potentially affected by human activities.

Metal concentrations in the environment are the result of the natural background, historical contamination and the emissions associated with the use pattern and the complete life cycle of the metal (i.e. from mining to maximum separation and recycling of metals and disposal of the remaining waste). Due to the inherent variation of metal concentration in the natural environment (e.g. different natural background concentrations) and the variations of anthropogenic input, large differences in observed metal levels can be observed among different locations.

Speciation is of paramount importance; metals can occur in different valences, associated with different anions or cations, and can be associated with adsorptive agents, such as dissolved organic matter (DOM) in water, or bound to minerals in sediment or soil. Therefore, speciation depends highly on the environmental conditions and chemistry of the site. The adsorption/desorption behaviour of a metal depends strongly on prevailing environmental conditions. The exposure assessment therefore goes beyond what is achieved by a simple direct toxicity assessment.

2) Effects assessment

The main goal is long-term protection of the environmental compartment under consideration. Typical compartments that are considered for the inland environment are the aquatic (including the sediments), sewage treatment plants and terrestrial ecosystems. For each of these compartments, a predicted no-effect concentration (PNEC) should be derived. This PNEC is considered the concentration below which an unacceptable effect will most likely not occur.

MERAG provides guidance on the effect data selected for PNEC derivation to comply with the requirements (criteria) for data quality and data relevance. It takes into account the metal-specific considerations in permit setting (methodologies on data quality selection, aggregation, interpretation, and on derivation of the PNEC value are provided) [ 301, MERAG Guidance 2007 ].

The derivation of the PNEC value can take into consideration the (bio)available fraction of organisms for the specific environmental conditions of the site (toxicity models were developed to predict the bioavailability of metals for conducting risk assessment in the terrestrial, sediment and aquatic compartments). This possibility of accounting for the bioavailability of the metals is also provided for in the Directive on environmental quality standards in the field of water policy 2008/105/EC and amending Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and 2000/60/EC.

3) Risk characterisation

The guidance sets out a 'building-block' approach to allow compliance with the permit conditions, and ensures, at the same time, that the best option for managing the potential risks presented by metals/metal compounds is considered. To this end, a tiered approach is advocated since data availability will depend to a large extent on the type of metal/metal compound under investigation, allowing for further refinement of the assessment.

In 2008, the refinement tools presented in the MERAG document are only applicable for metals that have sufficient data (e.g. nickel, copper, zinc). Tools are being explored for additional metals as the science is evolving (e.g., for silver, cobalt, aluminium).

The methodologies developed under MERAG are being implemented at the field level in various EU countries. Bioavailability models are also further being developed for a wider range of environmental conditions (e.g. marine and estuarine conditions).

### 2.3.3 Reporting emission data

Any measurement report and measurement protocol drawn up should conform to the relevant national and international guidelines.

The report can contain:

- the objective
- general information on the measurements
- a description of the plant, its state and operating data
- operating conditions during the measurement
- information on the measurement planning
- sampling locations
- methods of measurement
- tabular presentation of the individual measurements including temperatures, gas flowrates or volumes
- evaluation of the results
- consideration of errors
- presentation of the quality assurance measures
- an abstract.

Current emission data in this document are normally reported as hourly or daily averages or as mass emissions per unit tonne of production. 'Bubble limits' are also given as the annual mass of a substance that is emitted (e.g. x kg zinc/yr) and may be practical in many cases. Both methods of reporting are useful in defining the performance and impact of a process. Competent authorities normally use concentration units (mg/Nm$^3$ or mg/l), mass emissions (e.g. kg/h) and/or specific emission factors (g/t of metal) in their permits or in the data reported for emissions. These forms of data can be linked provided data are available for the gas volumes of all of the process stages. This is not always the case and therefore in this document the emissions associated with the use of BAT (BAT-AELs) are normally given as daily concentration averages or mass emissions based on continuous monitoring during the operating period. The standard conditions of 273 K, 101.3 kPa, measured oxygen content and dry gas are used.

In cases where continuous monitoring is not practicable as the average over the sampling period. Concentrations of metals or other substances in water or waste water are given as a total of soluble and insoluble material. The emissions to water that have been reported or are associated with BAT are based on a qualified random sample or a 24 hour composite sample.

At the time of writing the original BREF document, there was insufficient reliable data reported to allow mass or specific emissions associated with BAT to be reported in parallel with concentrations. More information is now available.

#### 2.3.3.1 Interrelationship between concentration, mass and specific emissions (emission ratios)

Where information is available, an interrelationship can be provided to transform concentration units into specific emission factors. Emission data in both forms are very useful for the regulator and operator. However, when comparing or converting data in these forms, great care is needed to take account of diffuse (uncaptured) emissions. Diffuse emissions can form the major portion of the total emissions, depending on the process.

In Table 2.5, an example of a simple conversion of yearly averaged emissions is used to show how to convert the concentration of the pollutant of concern (mg/Nm$^3$) into the specific volumetric loading (m$^3$/t of metal) and the specific emission factor (g/t of metal). For a complex site, the total of all metals produced would normally be used to present the specific emissions.

| | |
|---|---|
| a) Measured dust concentration on an annual basis, which is normally available as a range from continuos monitoring (mg/Nm$^3$) | |
| b) Annual average dust concentration (mg/Nm$^3$) | |
| c) Volumetric off-gas flowrate on an hourly basis (Nm$^3$/h) | |
| d) Yearly operating time (h/yr) | |
| e) Annual off-gas volume (Nm$^3$/yr) | c×d=e |
| f) Annual dust emission (kg of pollutant/yr) | b×e=f (mg/yr) |
| g) Annual production capacity (t of metal/yr) | |
| h) Specific off-gas volume (Nm$^3$/t) | e÷g=h |
| i) Specific emission factor (kg/t of metal) | f÷g=i (kg/t) |
| NB: This calculation is based on the reliable knowledge of the following data:<br>• dust concentration on an annual average basis (mg/NM$^3$)<br>• volumetric off-gas flowrate on a hourly basis (Nm$^3$/h)<br>• yearly operating time (h/yr)<br>• annual production capacity (t of metal/yr) | |

**Table 2.5: Conversion of emission data**

The above interrelationships are based on the knowledge of measured values, for instance the range of annual dust concentrations and actual volumetric flowrate, which then need to be transferred into annual averages. The results of these calculations are only valid for captured emissions and are based on average values.

In the case of a new plant or a substantial change of an existing installation, the above interrelation may be based on theoretically calculated or estimated values. The data should take account of any uncertainties in measurement, for example the volume of the off-gases from any single process may vary with the composition of the concentrate, the detection limits of analytical equipment as well as the sampling methods. Reliance on the designed fan capacities can lead to errors in the estimates as variable speed fans are commonly used. This problem of volume measurement is also encountered in the estimation of uncaptured or diffuse emissions.

#### 2.3.3.2 Uses of emission data

Where information is available, the calculation of the annual dust emissions (kg/yr) and the specific emission factors of a pollutant (g/t of metal produced) allows:

- the magnitude of individual sources of emissions to air and water to be identified either within an installation or between installations;
- diffuse emissions to be reported as mass emissions per unit of time or as mass per tonne of metal produced;
- the provision of a basis for setting priorities for the future environmental management of a plant or the application of a 'bubble concept' for emissions to air or water over a complex site if this is desired.

Table 2.6 gives figures of annual dust emissions from some parts of a primary copper production process producing 170000 t/yr blister copper.

| System | Specific emission factors for dust (g/t of Cu) |
|---|---|
| Dryer | 0.2 |
| Roaster | 1.5 |
| Converter shaft filter | 0.7 |
| Pelletisation | 0.1 |
| Slag granulation | 7.2 |
| Anode caster | 36.7 |
| Hall ventilation | 19.3 |

**Table 2.6: Example of data for showing the significant mass emissions**
[ 103, Farrell, F. 1998 ]

In this particular case, the equation (b × e = f) allows the specific emission of dust to be calculated and leads to the conclusion that the anode caster and the hall ventilation are the largest single sources of dust emissions and can be given priority.

The long-term and long-range effects of emissions can be determined by using dispersion modelling and other techniques. The techniques for environmental monitoring are reported in Section 2.3.2.1.

The use of tall stacks is used to improve the dispersion of gases and this can result in environmental impacts far beyond the installation. Components such as sulphur dioxide can have very long-range, accumulative effects and in some cases, critical loads for some species can be exceeded for some pollutants. Dispersion is therefore not a substitute for low emissions.

The use of concentrations based on defined parameters and methods of measurement allows many parameters to be monitored continuously. These parameters can be linked to the abatement system that is used. Concentration measurements allow:

- easy demonstration of compliance
- demonstration of real time performance
- a high degree of abatement control and an early warning of equipment failure.

Mass or specific emissions allow different installations or techniques to be compared and are also recommended to be used. Attention should be paid to the choice of parameters in the comparison both for the pollutant as well as the production metals.

## 2.4 Diffuse emissions

Diffuse and fugitive emissions have been defined in the reference document on the General Principles of Monitoring [ 293, European Commission 2003 ] and it is concluded in that document that diffuse emissions include fugitive emissions.

*Diffuse emissions are* emissions arising from a direct contact of volatile or light dusty substances with the environment under normal operating circumstances. These can result from:

- inherent design of the equipment (e.g. filters, dryers)
- operating conditions (e.g. during transfer of material between containers)
- type of operation (e.g. maintenance activities)
- or from a gradual release to other media (e.g. to cooling water or waste water).

Diffuse emission sources can be point, linear, surface or volume sources. Multiple emissions inside a building are normally considered to result in diffuse emissions when the pollutants leave the building by natural ventilation, whereas the forced ventilation system exhaust is a channelled emission.

Examples of diffuse emissions include venting from storage facilities during loading and unloading, storage of solid matter in the open air, separation pools in oil refineries, vents, doors in coke plants, mercury emissions from electrolysis cells, processes involving solvents, etc.

*Fugitive emissions are* emissions into the environment resulting from a gradual loss of tightness of a piece of equipment designed to contain an enclosed fluid (gaseous or liquid). Typically this could be caused by a pressure difference and a resulting leak. Examples of fugitive emissions include leakages from a flange, a pump or a piece of equipment and losses from the storage facilities of gaseous or liquid products.

### 2.4.1 Sources of diffuse emissions

In metallurgical plants, diffuse emissions may arise from the following sources:

- the transport, unloading, storage and handling systems [ 294, Jansen, I. 2006 ] which is directly related to wind velocity;
- the resuspension of dusty materials from abandoned workings, storage areas or disposal points due to wind action which is related to wind velocity cubed;
- suspension of dust from roadways due to traffic movements and contamination of vehicle wheels and chassis;
- the production processes themselves.

The Emissions from Storage BREF [ 290, EC 2006 ] and Section 2.4 of this document report on the first three sources of diffuse emissions but process sources are also important [ 219, VDI (D) 2102 2007 ]

Diffuse emissions may also occur from unsealed processes and during charging, smelting and tapping operations as well as during the transfer of the molten products or intermediates from one operation to another. Of particular importance in this connection is the fact that the prevailing temperatures of the various metal, slag or matte fractions are above the volatilisation points of the low boiling accompanying metals (e.g. zinc) and oxides (e.g. SnO and PbO) so that the latter accumulate in the emitted vapours. As far as possible diffuse emissions should be captured at the source via secondary hoods and the extracted off-gas should be routed to the gas-cleaning system.

Ventilation air with dust leaving through openings in walls and roofs of buildings is also a source of diffuse emissions from a plant. When considering prevention measures, particular consideration should be given to worker conditions. Minimising diffuse emissions from a building by, for example, closing windows or otherwise containing them in the building is not a suitable approach because of considerations that need to be given to the exposure of the workers in the building. The collection of diffuse emissions in a building should therefore be focused on preventing at source (e.g. by measures such as smoother feeding into the smelter or improving the slag tapping hood where feasible and appropriate) in order to control the dust emissions in the building and thereby controlling the exposure of workers. Workplace measurements and monitoring blood and urine levels in workers can also show trends in the success of improved capture of diffuse emissions [ 228, IZA plant data 2008 ].

### 2.4.2 Measurement of diffuse emissions

It is generally recognised that diffuse emissions pose a particular challenge due to their very nature. Measurement methodologies [ 323, VDI 4285 part 1 and 2 2008 ], [ 324, VDI 2008 ]have been used in order to determine:

- The global effect of the diffuse emissions from a specific plant. Measuring the imissions near a plant can give useful information, although the variations in wind directions can make the results difficult to interpret. When enough measurement devices are in place near a plant, an estimate can be made of the global amount of emitted substances that can be uniquely linked with the plant under consideration (metals, acid mist, etc., but, e.g. Not dust). The accuracy of such an exercise, however, is no better than 50 %, making this method only suited for evaluations over longer time periods. Also the accuracy of this method at lower levels is very questionable.

- The relevant sources of diffuse emissions. Diffuse emissions arise from various sources, and the quantification of diffuse emissions depends on the type of emissions source.

Several methods that have been used to estimate diffuse emissions have been reported [ 229, Umicore etc 2007 ]. The methods are:

- For diffuse emissions from buildings, measurements to determine the flowrate and concentration through vents and windows [ 160, Steudtner 1998 ]. The method that is used to measure the volume and composition of diffuse dust emissions has proved to be relatively reliable [ 158, Petersen, K. 1999 ]. The flow conditions of the sources of diffuse emissions are not stable and so sampling emissions from roof vents is not accurate. Accuracy can be improved if the cross-section of the measurement plane of roof-line vents is subdivided into sectors of identical surface area (grid measurement). During the measurements, sampling probes are installed at selected locations. The sampling equipment employed must be designed for infinitely variable suction control. By selecting different sampling probe diameters, the sample flowrate can be adapted to the prevailing off-gas flow velocity. The dust content of the sample gas streams is collected on a filter medium and determined by gravimetric methods [ 293, European Commission 2003 ].

- Continuously monitoring the dust concentration in the workplace using fixed or personal samplers can identify the main sources of diffuse emissions. The results can then give information on critical steps in the processes if the results are correlated with the process operations that are taking place during sampling [ 229, Umicore etc 2007 ].

- Using emissions characteristics (emission factors) as a basis for estimating diffuse dust emissions occurring during storage, handling and transportation of bulk materials (input materials, scrap, etc.). The use of emission factors in this context can only give a rough guide to the magnitude of the emission.

- Using reverse dispersion modelling (RDM) [ 322, CEN 15445 2008 ], to predict the relevant dust sources. Generally the results obtained have a relative value only within the particular installation and for the components measured but some greater success has been reported in Belgium [ 298, Mensink RDM paper 2005 2005 ]. The application of this method also becomes difficult in situations where the amount of dust generated at the plant is small compared to the background dust. This method can be both costly and time consuming. RDM is described in the CEN methodology EN 15445-2008.

- Release of tracers (marker gases) at a known rate from points in an installation and measured downwind along with the pollutants. The results can be used to estimate pollutant emissions based on assumptions of diffusion and absorption.

Some installations are using these measurement methodologies to estimate diffuse emissions at their sites. These methodologies have been developed on a trial and error basis with local expertise, knowledge of local conditions, experience, specific configuration of the plant, etc. They are not at a stage where they can yield accurate and reliable actual figures, but may give indicative emission levels or the trends of the emission over a certain period of time.

There are no measurement methodologies applicable for general use by all sites, and no measurement methodology is the same from one site to another. There are significant effects from other sources in the vicinity of a site such as other operations, traffic and other sources that make extrapolation very difficult. The results obtained are therefore relative or benchmark values that can indicate the reductions achieved by measures taken to reduce diffuse emissions.

When estimating the proportions between diffuse emissions and point source emissions, comparisons such as 70 % vs. 30 % have been made but these are very site-specific and time related.

The assessment of the impact of diffuse emissions and their reduction over time should be compared with the relative proportion of diffuse and point source emissions from the particular site. Comparison of these results with EQS, OEL or PNEC values which are based on sound science is used to assess the share or impact of diffuse emissions in surrounding environment.

The sampling locations must meet the occupational health and safety standards, be readily accessible and adequately sized.

The measurement of diffuse emissions from area sources is more complex and requires more elaborate techniques because:

- the emissions source can be a large area and only be roughly defined
- the emissions characteristics are governed by the meteorological conditions and subject to major fluctuations
- the uncertainties associated with the measured data can be substantial.

### 2.4.3 Prevention of diffuse emissions – off-gas collection techniques

The process steps involved in the production of non-ferrous metals involve the potential production of dust, fumes and other gases from material storage, handling and processing. The techniques for the prevention of diffuse emissions from the storage and handling stages are covered earlier in Section 2.6. Section[rr1] 2.4.3 deals with process gases. The techniques involved follow the hierarchy of prevention, minimisation and the collection of fumes. Assessment of potential sources of diffuse emissions should also take account of the resuspension of dusty materials from abandoned workings, storage areas or disposal points due to wind action and vehicle movements. Diffuse emissions are also caused by inadequate or poorly maintained gas collection systems and this is discussed here.

Furnace sealing (or the use of sealed furnaces) combined with process control is the technique that should be applied wherever possible to prevent or contain emissions from process plants. Section 2.8 covering furnaces indicates where furnace sealing is possible and where other collection techniques may be used to provide integral gas collection [ 246, French Report on SDHL process 2008 ].

Computerised fluid dynamics (CFD) studies and tracers have been used to model the flow of furnace gases and also the movement of fused electrolytes [ 233, Farrell Nordic Mission 2008 ] so that diffuse emissions can be prevented or minimised. The use of these techniques has resulted in optimised gas collection systems. Modification to furnace or electrolyte charging systems to give small, even additions of raw materials have also been developed in parallel and also contribute to the prevention of diffuse emissions [ 233, Farrell Nordic Mission 2008 ].

Other techniques are available to collect the diffuse emissions that are not preventable or contained [ 73, Theodore, L. et al. 1992 ], [ 77, Soud, H.N. 1995 ], [ 74, Startin, A. 1998 ], [ 76, Soud, H.N 1993 ]. Gases and fumes that escape from the processes are released into the working area and then escape into the surrounding environment. They therefore affect operator health and safety and contribute to the environmental impact of the process. Process gas collection techniques are used to prevent and minimise these diffuse emissions.

Diffuse emissions are very important but are hard to measure and quantify. Methods of estimating ventilation volumes or deposition rates can be used to estimate them. One reliable method has been used over a number of years at one site [ 160, Steudtner 1998 ]. The method that is used to measure the volume and composition of diffuse dust emissions has proved to be reliable [ 158, Petersen, K. 1999 ] and the results of the monitoring exercise are reproduced below in Table 2.7. The results show that the magnitude of diffuse emissions can be much more significant than collected and abated emissions. The lower the controlled emissions, the more significant the diffuse emissions. Diffuse emissions can be more than two to three times the quantity of controlled emissions [ 219, VDI (D) 2102 2007 ].

| | **Dust emission (kg/yr)** | |
|---|---|---|
| | **Before additional secondary gas collection (1992)** | **After additional secondary gas collection (1996)(1)** |
| Anode production in t/yr | 220000 | 325000 |
| Diffuse emissions: | | |
| total smelter | 66490 | 32200 |
| smelter roof line | 56160 | 17020 |
| Controlled emissions (primary smelter): | | |
| smelter/acid plant | 7990 | 7600 |
| secondary hoods stack | 2547 | 2116 |
| (1) Emissions after an investment of EUR 10 million to give an improved diffuse gas capture and treatment system. Additional energy = 13.6 GWh/yr | | |

**Table 2.7: Comparison of abated and diffuse dust loads at a primary copper smelter [ 158, Petersen, K. 1999 ]**

Light detection and ranging techniques (LIDAR) may also be used to measure some diffuse gaseous components such as $SO_2$ and VOCs.

### 2.4.4 Applied processes and techniques (all these examples are for process related diffuse emissions (no transport, storage, handling, resuspension etc. as in 2.4.1 mentioned). The logic to present and include the different sources of diffuse emissions

**(see 2.4.1) should be improved. Compare structure with the iron and steel BREF. )**

Dust, fumes and gases are collected by using sealed furnace systems, by total or partial enclosure of launders, furnace tapping systems, transfer points and other handling systems or by hooding [ 73, Theodore, L. et al. 1992 ]. Hot gases from launders can be collected and transferred as combustion air so that the heat content is also recovered. Sealed furnaces can be charged from sealed lance or burner systems, through hollow electrodes, through hoods or tuyères or by docking systems that seal onto the furnace during charging. Hoods are designed to be as close as possible to the source emissions while leaving room for process operations. Moveable hoods are used in some applications and some processes use hoods to collect primary and secondary fumes. Separate tertiary collection systems designed to collect all remaining emissions are also used; they are often called 'house in house' or 'dog house' systems.

Controlled emissions have known sources and can be captured and treated, diffuse emissions can evolve almost anywhere on a plant site including from poorly designed or inefficient gas collection systems. The main sources of diffuse emissions are material storage and handling, dust sticking to vehicles or streets and open or poorly enclosed process units or working areas [ 290, EC 2006 ]. In the recent years, some companies have reduced their diffuse emissions efficiently by adopting measures that are applicable to their installation but not necessarily applicable to all installations.

The measures reported are:

- Increasing the burden of the furnace or cell to provide a better seal and to improve the collection of off-gas;
- renewal or optimisation of off-gas collection and filter units;
- 'house in house' or 'dog house' collection systems (see Figure 2.5);
- reduction of furnace downtime by improved refractory lining (thereby reduction of startup and shutdown times which cause higher emissions for a limited time);
- closing the roofs of the process buildings and modernisation of the filters;
- closing of delivery, material storage and refining areas, and installation of off-gas collection systems;
- improving material handling (e.g. by wetting bulk materials before and during loading) and reduction of transport frequencies (e.g. by use of bigger wheel loaders);
- installation of obligatory vehicle washing (for internal and external vehicles);
- optimised cycle of road cleaning;
- reinforcement of plant areas, driveways and optimised cleaning;
- closing and decontamination of old storage or disposal areas.

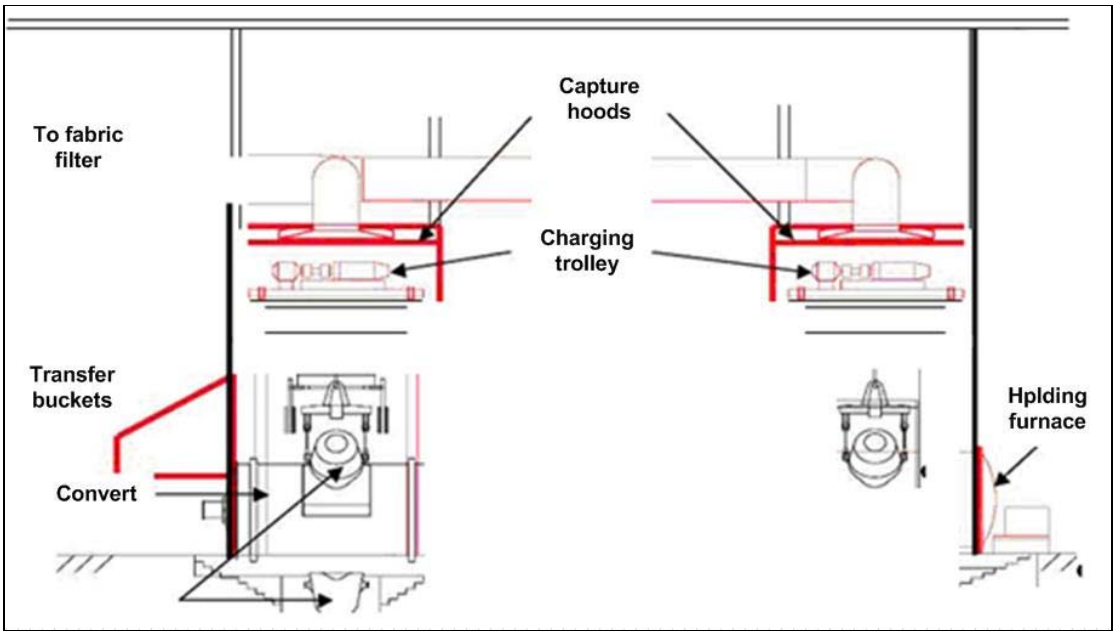


**Figure 2.5: House in house collection system**

#### 2.4.4.1 Use of energy in gas collection systems

Gas collection requires the movement of significant volumes of air. This can consume vast amounts of electrical power and modern systems focus the design on capture systems to increase the rate of capture and to minimise the volume of air that is moved [ 121, Rentz, O. et al. 1999 ]. The design of the collection or hood system is very important as this factor can maintain capture efficiency without excessive power consumption in the remainder of the system. Sealed systems such as sealed furnaces can allow a very high capture efficiency to be attained and have an advantage over semi-sealed furnaces. Batch processes such as converters have widely varying gas flowrates and are also difficult to seal and often secondary hoods are needed [ 243, French comments on MnFe alloys 2008 ].

Ducts and fans are used to convey the collected gases to abatement or treatment processes. The effectiveness of collection depends on the efficiency of the hoods, the integrity of the ducts and on the use of a good pressure/flow control system. Variable speed fans are used to provide extraction rates that are suitable for changing conditions such as gas volume, with minimum energy consumption. It is also possible to use an intelligent system to operate the fans automatically when process stages that produce fumes are operated. The house in house concept shown in Figure 2.5 uses this principle to prevent excessive energy consumption. The systems can also be designed to take account of the characteristics of the plant that it is associated with, e.g. the abatement plant or sulphuric acid plant. Good design and maintenance of the systems is practised.

#### 2.4.4.2 Design criteria

Collector systems and extraction rates are designed on the basis of good information about the characteristics of the material to be collected (size, concentration, etc.), the shape of the dust cloud at the extremes of operation and the effects of volume, temperature and pressure changes on the system. Computational fluid dynamic studies can be used to achieve optimum design and extraction efficiencies [ 226, Nordic Report 2008 ].

Correct measurement or estimation of the gas volume, temperature and pressure are made to ensure that sufficient rates of extraction are maintained during peak gas flows. Some of the characteristics of the gas and dust are also critical to good design to avoid problems of abrasion, deposition, corrosion or condensation and these are measured. Another significant factor is the provision of access to furnace filling or tapping areas while maintaining good rates of collection, operator experience is used at the design stage to provide this.

## 2.4.5 Techniques to consider in the determination of BAT

The sections of this document entitled 'Techniques to consider in the determination of BAT' set out techniques considered generally to have the potential for achieving a high level of environmental protection in the industries within the scope of the document. The background to the way the techniques are described is given in Section 2.1.2 and Table 2.2.

### 2.4.5.1 Some examples of techniques to consider Wording should be more specific.

*Maybe the process related techniques to consider should be relocated to the metal specific chapter. Also include the house in house technique (figure 2.5) and relocate to copper.*

**Description**

The techniques to consider are based on the application of the principles of techniques reported above in Section 2.4.4. These techniques rely on the professional design and maintenance of the collection systems as well as the on-line monitoring of emissions in the clean gas duct. The following examples are used to illustrate good practise, it is not an exhaustive list and other examples may also be applicable:

a. The use of sealed furnaces can contain gases and prevent diffuse emissions. Examples are sealed smelting furnaces, sealed electric arc furnaces and the sealed point feeder cell for primary aluminium production. Furnace sealing still relies on sufficient gas extraction rates to prevent pressurisation of the furnace. The point feeder cell, illustrated in Figure 2.6 is usually connected to a well-sized extraction system that provides a sufficient rate of extraction to prevent the escape of gases during the opening of cell covers for short periods, e.g. anode changes.

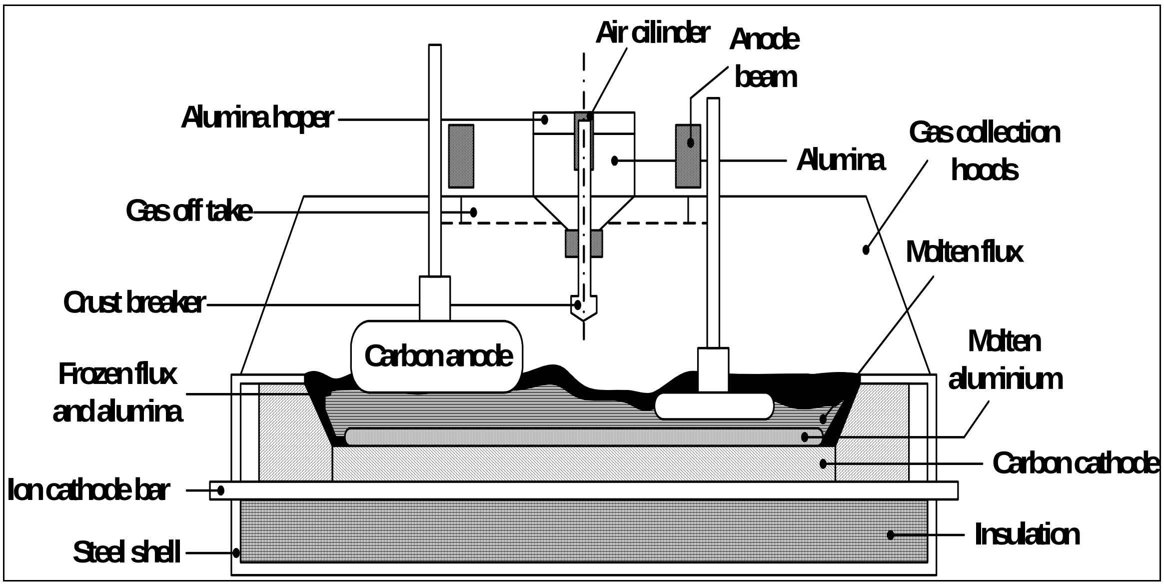


Figure 2.6: Point feeder prebaked anode cell

b. The use of sealed charging systems for the furnaces to prevent diffuse emissions during furnace opening. Examples are the use of charging skips that seal against a furnace feed door and the use of through-hood charging systems. These techniques may be applicable to all new and existing processes particularly for non-continuous processes.

c. An important established practice to achieve good extraction is the use of automatic controls for dampers so that it is possible to target the extraction effort to the source of the fumes without using too much energy. The controls enable the extraction point to be changed automatically during different stages of the process. For example, the charging and tapping of furnaces do not usually occur at the same time and so the charging and tapping points can be designed to be close together so that only one extraction point is needed. The extraction point is also designed to allow good access to the furnace and give a good rate of extraction. The hooding is constructed robustly and is maintained adequately.

An example of this is an adaptation of a short rotary furnace (see Figure 2.7). The feed door and tapping holes are at the same end of the furnace and the fumes collection hood allows full access for a slag ladle and feed conveyor. It is also robust enough to withstand minor impacts during use.

*This figure is included more than one time. Rewrite the BREF to mention it only one time.*

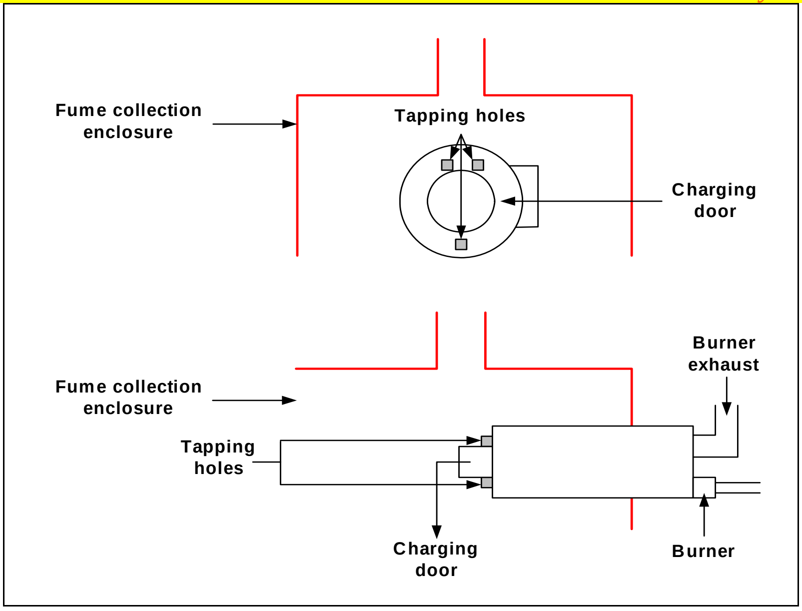


**Figure 2.7:** **Coincident charging and tapping system**

*Coincident to what?*

This principle is easily applied to a short rotary furnace but the principle of targeting the extraction effort to a changing source of fumes is also achieved by automatically controlling dampers to extract the main source of fumes during the operating cycle, e.g. charging, tapping. The short rotary furnace and the TBRC may also be totally enclosed.

The 'house in house' or 'dog house' concept shown in Figure 2.5 is used in other applications as a tertiary collection system. An intelligent system is used to operate the fans automatically when process stages that produce fumes are operated. The 'house in house' concept uses this principle to prevent excessive energy consumption.

These techniques may be applicable to all new and existing processes particularly for non-continuous processes.

d. If sealed furnaces are not available for example when retrofitting an existing open furnace, maximum sealing to contain furnace gases can be used.

An example of this is the use of a 'fourth hole' in the roof of an electric arc furnace to extract the process gases as efficiently as possible and is shown in Figure 2.8.

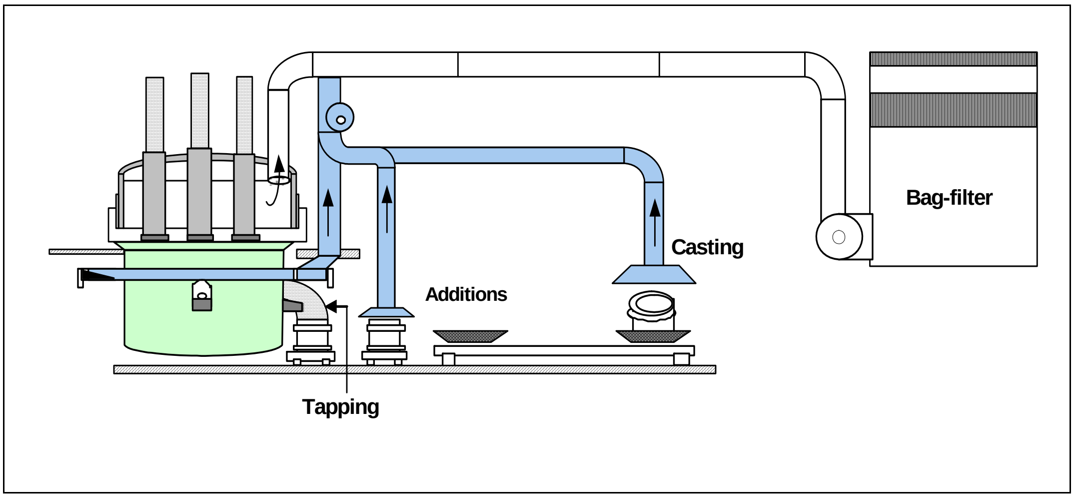


**Figure 2.8: Fourth hole fumes collection**

e. Improvements have been made to fume capture by applying computational fluid dynamic (CFD) modelling to the furnace gases to assist in developing optimum fume collection. The deployment of a guided cover curtain to achieve maximum performance has resulted from this work that assessed smoke patterns. Significant progress was also made by modifying the charging pattern to an electric reduction furnace by feeding small quantities of charge material on a regular basis rather than full batch charging. The main effect was the reduction in surging that caused diffuse emissions and the prevention of over cooling the furnace and the results on PCDD/F reduction were significant [ 233, Farrell Nordic Mission 2008 ].

f. Maintenance of the collector hood, the ducts, the filter system and the fan is vital to ensure that collection or extraction rates remain at the designed level. It is also important to use a system of dampers and alternative extraction points to direct suction to the points where fumes are being emitted. An example of this is when the furnace is tilted to tap off slag or metal and the fourth hole extraction point is not then connected to the ducting. Dampers should be used to direct suction to the tapping point and automatic change-over of dampers is preferable.

g. Physical damage from collision or abrasion, deposition in ductwork and deposition on fan blades are some of the problems that can be encountered. Regular inspection and preventative maintenance should be used to ensure that these problems do not occur. This technique is applicable to all new and existing processes.

h. The collection of gases from a batch converter can be difficult as ladle transfers interfere with the collection hoods. Some installations collect all of the fume from the roof line at the expense of a high energy cost. Another installation uses a system of up to three hoods in addition to the main hood. These hoods can be connected either to the sulphuric acid plant (hood 1) or to the secondary cleaning system (hoods 2 & 3). During filling and pouring operations, the individual hoods are motor driven to the positions that ensure optimal collection efficiency. The secondary hood gas collection system is shown in Figure 2.9.

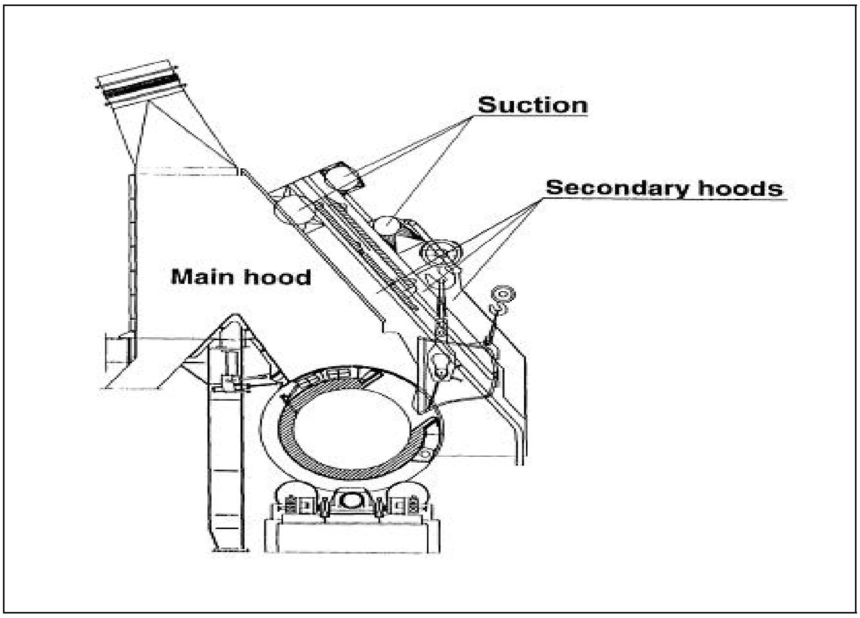


**Figure 2.9:** **Secondary hooding system for a converter**
[ 198, Velten 1999 ], [ 233, Farrell Nordic Mission 2008 ]

Gases that are not collected by the secondary hoods can be collected in a tertiary collection system that encloses the whole operating area such as "house in house" or "dog house" concept shown in Figure 2.5.

i. The following example shows how tapping fumes from a blast furnace can be collected by a secondary fume collection system. The dedusting equipment is composed of various hoods located above the tap-hole of a blast furnace, the main metal runner and the device where the liquid metal is poured into the torpedo ladle. The collected fumes are cleaned in a separate fabric filter. The tap-hole fume collection system (viewed from the top of the blast furnace) is shown in Figure 2.10.

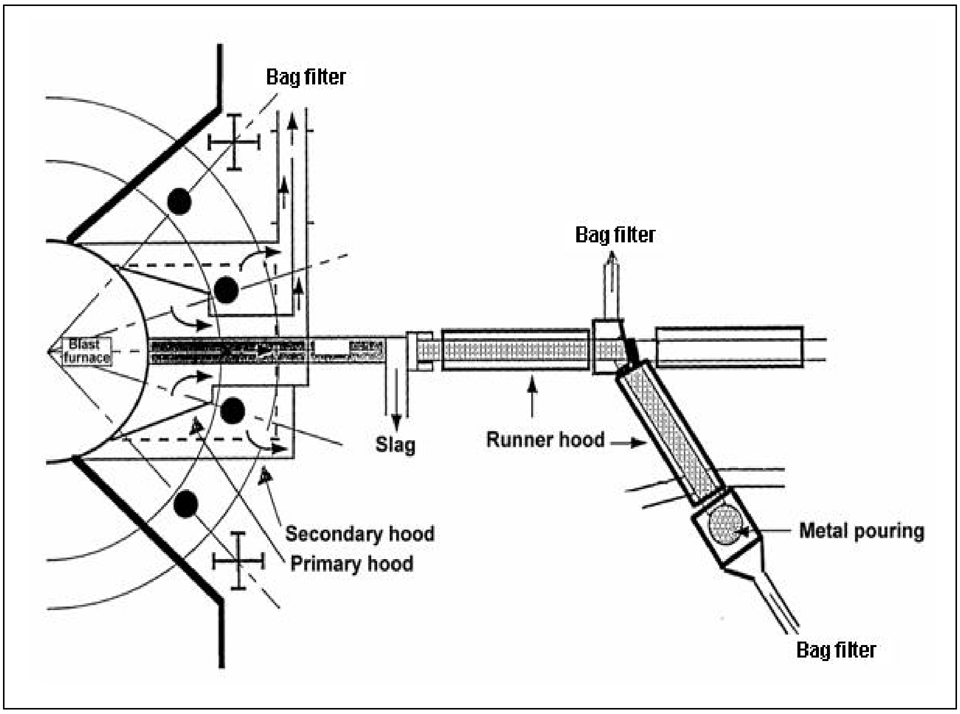


**Figure 2.10:** **Tap hole fume collection**
[ 192, SFPO 1999 ]

**Achieved environmental benefits**
Efficient capture of the diffuse emissions of metals, dust, sulphur dioxide and other compounds. Most dusts are returned to the processing stages or are sold to recover valuable metals.

**Cross-media effects**
Energy use is increased in most cases.

**Operational data**
This is included where available in the descriptions of examples a) to g) given above.

**Applicability**
This technique is generally applicable to most existing plants.

**Economics**
Information on economics has not been provided but the examples are operating economically.

**Driving force for implementation**
The driving force for these techniques is the reduction reduction of diffuse emissions that can account for up to 80 % of the total emissions from this sector.

**Example plants**
Plants in DE, AT, FR, BE and PL.

**Reference literature**
[ 196, Finkeldei, L. 1999 ], [ 233, Farrell Nordic Mission 2008 ], [ 274, Farrell Mission in DE 2008 ].

### 2.4.5.2 Secondary fume collection

*The heading must be changed. All of the examples in section 2.4.5.1 are examples of secondary fume collection from point feeder, charging, tapping, converter, tapping except the fourth hole extraction which can be regarded as primary emissions from the EAF. The structure of this chapter should be improved.*

**Description**
As reported above, diffuse emissions can be highly significant, therefore if diffuse emissions cannot be prevented or minimised to an acceptable level, secondary fume collection systems can be used.

Some furnaces can be equipped with secondary hoods in order to prevent diffuse emissions during charging or tapping as described in Section 2.4.5.1 above. Emissions can not be [prevented by hoods they can only be collected close to the emission source. The fan suction is provided directly at the source of the fumes to optimise the reduction of diffuse emissions. It is possible to use an intelligent system to operate the fans automatically when process stages that produce fumes are operated. The 'house in house' concept shown in Figure 2.5 uses this principle to prevent excessive energy consumption. Variable speed fans are also used.

Alternatively, the air could be extracted at the roof ventilator, but a large volume of air would have to be handled which might not be cleaned effectively in a fabric filter. Other disadvantages are high energy consumption, high investment and more waste (used filter media). Secondary fume collection systems are designed for specific cases. Energy use can be minimised by automatically controlling the point of extraction using dampers and fan controls so that the systems are deployed when and where they are needed, for example during charging or during roll out of a converter.

In the process shown in Figure 2.11, the airflow rate is controlled via a closed-cycle control system by reducing dampers. Ventilator fans with speed controls are used in order to minimise the energy consumption. 580000 $Nm^3/h$ of secondary gases are captured and cleaned in fabric filters. 13.6 GWh/yr of electrical energy are consumed and 700 kg of dust is collected per hour.

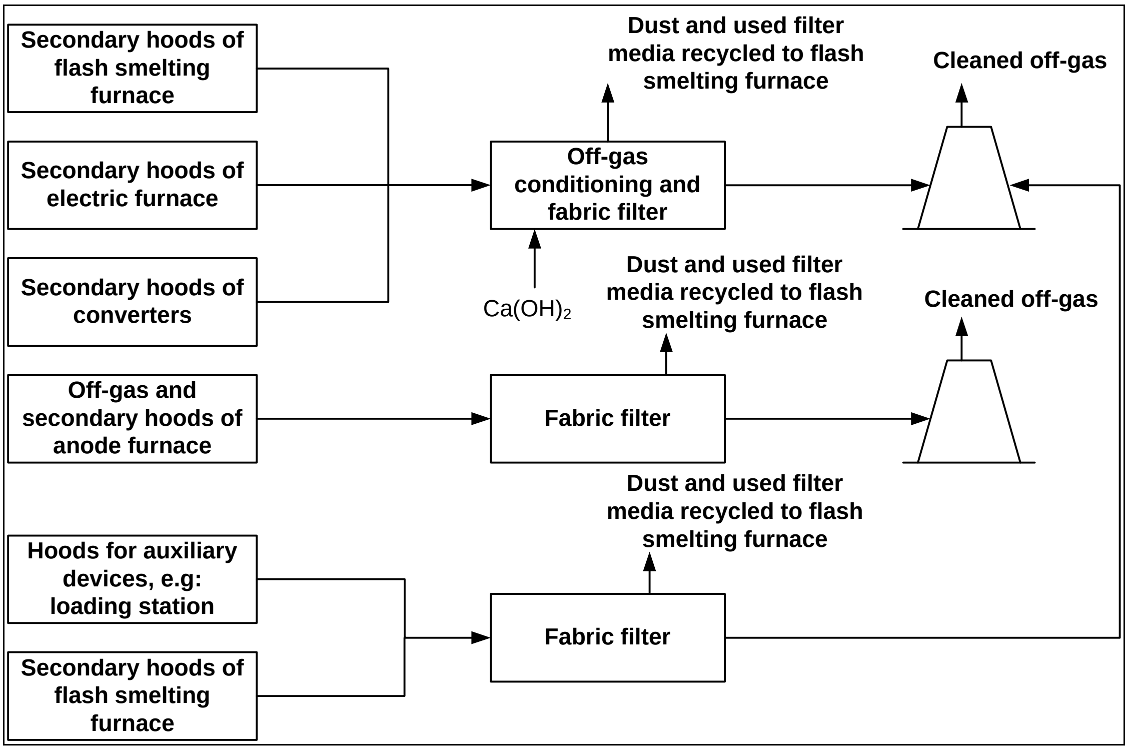


**Figure 2.11:** **Outline of a secondary fume collection system for a primary copper process**
**[ 121, Rentz, O. et al. 1999 ]**

### Achieved environmental benefits

Reduction of diffuse emissions of metals dust, sulphur dioxide and other compounds.
*Has there ever be a investigation to determine a collection efficieny??*

### Cross-media effects

High energy consumption and higher waste production (used filter media).

### Operational data

Included in the description above.

### Applicability

Reported in the description above.

### Economics

Economic information has not been provided

### Driving force for implementation

The driving force for this technique is the reduction of diffuse emissions that account for up to 80 % of the total emissions from this sector.

### Example plants

DE.

### Reference literature

[ 160, Steudtner 1998 ], [ 121, Rentz, O. et al. 1999 ].

## 2.5 Process control techniques and optimising process feedstock (the logic of the structure of this chapter should be changed. Present the information in a few blocks.

*A. General processes and Techniques (include 2.1)*
*First block:*

- *A1: Energy management (steam, waste heat etc.)*
- *A2: Material management*
  - *Diffuse emissions*
    - *Storage, handling of input materials*
    - *Processes related diffuse emissions in specific chapters*
    - *Management of products, residues, waste (internal, external, disposal)*
- *A3: Water and Waste water management*

*Second block*

- *B: General techniques to consider in the determination of BAT*
  - *B1.Environment management sytems (include 2.2 if necessary, 2.20.1)*
  - *B2Energy management and process control and optimisation (include 2.9.2.1, 2.9.2.9)*
  - *B3Material management*
    - *Techniques to improve the use of secondary materials?*
    - *Techniques to reduce diffuse emissions from storage, handling, preparation of raw materials*
    - *Techniques reduce emissions to water from raw materials*
    - *Special facilities in NFM?*
    - *Management of products, residues, waste (internal, external, disposal)*
  - *B4Monitoring*
    - *Captured emissions*
    - *Diffuse emissions*
    - *Ambient air, environmental monitoring (shorten this, relocate to an Annex)*
    - *Waste water*
  - *B5Noise (if relevant)*

*Third Block*

- *C General BAT Cocnlusions*
  - *C1 EMS 2.20.1*
  - *C2 Energy management 2.20.3; 2.20.9*
  - *C3 Matarial management 2.20.10*
  - *C4 Internal management of products, residues and wastes*
  - *C5 Diffuse emissions prevention from storage (2.20.2) and fume collection (2.20.4)*
  - *C6 Water and waste water management 2.20.8*
  - *C7 Monitoring 2.20.11*
  - *C8 Noise*

*Relocation of relevant information from Chapter 2 to specific sections for:*

- *Dust*
- *Sulphur*
- *NOx*
- *Mercury*
- *Dioxins*

### 2.5.1 Process control techniques

The principles of best available techniques include the concepts of how a process is designed, operated, controlled, manned and maintained (see Section 2.2). These factors allow good performance to be achieved in terms of emissions prevention and minimisation, process efficiency and cost savings. Good process control is used to achieve these gains and also to maintain safe conditions [ 291, Competitive Report 2001 ].

### 2.5.2 Techniques to consider in the determination of BAT

The sections of this document entitled 'Techniques to consider in the determination of BAT' set out techniques considered generally to have potential for achieving a high level of environmental protection in the industries within the scope of the document. The background to the way the techniques are described is given in Section 2.1.2 and Table 2.2.

**Description**
Process operation and control has developed in this sector and is applied to a variety of processes. The techniques are described below:

1. Sampling and analysis of raw materials is commonly used to control plant conditions and to assay the quantity of metal present. Good mixing of different feed materials should be achieved to get optimum process performance, higher conversion efficiency, reduced emissions to all environmental media, reduced energy use, increased quality and reduced level of reject products. Small-scale pot furnaces are used to identify the correct raw material mixtures. Fluctuations of moisture content in the feed of a furnace can cause process gas volumes that are too large for the designed aspiration capacity, resulting in diffuse emissions.

2. Feed weighing and metering systems are used extensively. Loss in weight silos, belt weighers and scale weighers are used extensively for this purpose.

3. Microprocessors are used to control material feed rate, critical process and combustion conditions and the additions of gases. Several parameters listed below are measured to allow processes to be controlled and alarms are provided for critical parameters:

    - on-line monitoring of temperature, furnace pressure (or depression) and gas volume or flow;
    - gas components ($O_2$, $SO_2$, CO);
    - on-line monitoring of vibration is used to detect blockages and possible equipment failure;
    - on-line monitoring of the current and voltage of electrolytic processes;
    - on-line monitoring of emissions to control critical process parameters;
    - on-line monitoring of acid strength and metal concentrations;
    - on-line monitoring of parameters for hydrometallurgical processes (e.g. pH, redox potential, temperature);
    - sampling and analysis of intermediate and end solutions of hydrometallurgical processes.

4. Monitoring and control of the temperature of melting furnaces to prevent the production of metal and metal oxide fumes by overheating.

5. Monitoring and control of the temperature of electrolytic cells to identify hot spots that indicate short circuiting in the cell.

6. The oxygen coefficient of a furnace can be automatically controlled by a mathematical model that predicts the changes in the composition of the feed and furnace temperatures; the model is based on more than 50 process variables. In the primary aluminium industry, mathematical models are also used in conjunction with monitoring cell operating conditions to prevent anode effects, an 80 % reduction in

polyfluorocarbon (PFC) emissions has been achieved since 1990 [ 299, TWG KOM Report 2007 ].

7. Process gases are collected using sealed or semi-sealed furnace systems. Interactive variable speed fans are used to ensure that optimum gas collection rates are maintained and can minimise energy costs.

8. Solvent vapours are collected and recovered as far as possible using sealed reactors or local vapour collection in combination with chillers or condensers. Further removal and incineration of solvent vapours is practised to prevent the emissions of VOCs and odours.

9. Operators, engineers and others should be continuously trained and assessed in the use of operating instructions, the use of the modern control techniques described and the significance of alarms and the actions to be taken when they go off.

10. Levels of supervision are optimised to take advantage of the above and to maintain operator responsibility.

11. Environmental management and quality systems are used.

12. Hazard and operability studies are carried out at the design stages for all process changes.

13. Robust maintenance systems are used. There is growing use of dedicated maintenance staff forming part of the operator teams who supplement the dedicated maintenance teams.

14. Process design aspects which are described in various sections of this document; these design aspects are used commonly in this sector. Full process design is approached with care using professional engineers who have experience and knowledge of the process and of the environmental impact and requirements.

15. Slag, metal and matte are analysed on the basis of samples taken at intervals so that the use of fluxes and other raw materials can be optimised, the metallurgical process conditions can be determined and the metal content of the materials agreed upon.

16. For some processes special regulations such as the Seveso or Waste Incineration Directives may have to be taken into account.

**Achieved environmental benefits**
The prevention of emissions of metals, dust and other compounds.

**Cross-media effects**
None have been reported.

**Operational data**
No operational data has been reported but more information is available in the metal-specific chapters.

**Applicability**
These techniques are generally applicable to most plants.

**Economics**
No economical data has been provided but the processes are operating economically.

**Driving force for implementation**

Reduction of emissions saving raw materials.

**Example plants**

Plants in DE, AT, FR, BE, PL, NL.

**Reference literature**

[ 299, TWG KOM Report 2007 ] [ 196, Finkeldei, L. 1999 ].

# 2.6 Receipt, storage and handling of raw materials and residues

The main raw materials used in the production of non-ferrous metals are ores and concentrates, secondary raw materials, fuels (oil, gases and solid fuel) and process gases (such as oxygen, chlorine and inert gases). Other materials such as fluxes, additives and process chemicals (e.g. for abatement systems) are also used. This variety of materials possesses many handling and storage problems and the specific technique used depends on the physical and chemical properties of the material (see also the Emissions from Storage BREF [ 290, EC 2006 ]). In general, the storage of dusty material in the open space should be avoided. Conveying systems should be equipped with enclosure. Fabric filters need to be examined and maintained regularly [ 307, Austria BE277 2006 ]. The following applied processes and techniques are used to prevent emissions to the environment.

## 2.6.1 Applied processes and techniques

### 2.6.1.1 Ores and concentrates

Ores and concentrates may be delivered to the site by road, rail or ship. Dust prevention, dust collection and abatement systems are used extensively at the discharge points.

Process control is becoming more important to improve conversion efficiency, reduce energy consumption and reduce emissions and is frequently based on effective sampling, analysis and recording of raw materials to establish optimum process operating conditions. This influences the choice of techniques for storage and handling.

The unloading, storage and distribution of solid material is carried out by similar techniques to those used for solid fuels. Generally, more stringent containment methods are adopted for these materials as they are generally more reactive, have a smaller particle size and are more easily suspended in air or washed into water. Automatic quick sealing devices are commonly used. Fluxing and slagging agents are also received on site and are handled in a similar manner to ores and concentrates.

Ores or concentrates (if they form dust) and other dusty materials are usually stored in enclosed buildings. Closed, covered stockpiles and silos are also used. Open stockpiles are used for large, lumpy material but are usually formed on a hard impervious surface, such as concrete, to prevent material losses, land contamination and contamination of the ore. Some large materials are not stored on a hard surface as damage can frequently occur and cause hidden problems. Bays are often used to segregate different grades of ore.

Ores and concentrates are normally used by large installations and therefore silos are not frequently used for primary storage but can be used for intermediate storage and the preparation of ore/flux blends. 'Loss in weight' dosing systems and belt weighers, etc. are used to meter ores and fluxes to achieve effective optimum blends and improved process control.

Water sprays are frequently used to suppress dust but some operators require dry feed to the processes and are reticent about using water sprays. Alternative methods, such as using atomising sprays to give fine water mists, are used for dust suppression without over wetting the material. Some concentrates naturally contain sufficient water to prevent dust formation.

Sealing agents (such as molasses, lime or polyvinyl acetate) can be used to prevent dust formation in windy conditions. Sealing can prevent oxidation of surface layers and subsequent leaching of material to ground or surface waters.

Unloading minerals may be a potential source of significant dust emissions. The main problem occurs when a rail car or other tipping vehicle discharges by gravity. The rate of discharge is not controlled and results in a high volume of displaced air and dust, which can overwhelm dust extraction systems. Enclosed delivery halls using automatic door closure are used.

Polycarbonate screens which seal against the tipping car are used. In this case, displaced air is passed to a sprung section and surge container to absorb the energy of the discharge; the increase in air volume is damped, allowing the extraction system to cope.

Material can be reclaimed by an underfeed conveyor, grab crane or a front-end loader, and totally enclosed conveyors are used to transport dusty material. Transfer by pneumatic, dense phase systems are also used. For dusty materials extraction, filter systems may be used to deal with dust from static off-loading points and conveyor transfer points. In the case of using open conveyors, dust can be produced if the belt is running too fast (i.e. more than 3.5 m/s). When a front-end loader is used, dust can be generated during the whole transporting distance.

Solids may adhere to wheels and other parts of vehicles and will contaminate roadways both on and off site, the use of wheel and under body washes (or other cleaning techniques if freezing temperatures are encountered) to decontaminate vehicles are frequently employed. The use of front-end loaders that are bigger than necessary can make this problem more serious.

Road sweepers or other specialised equipment using a combination of water jets and vacuum collection are commonly used to remove deposited dust including that from old storage areas to keep internal roads clean and prevent resuspension of the dusts.

Depending on the local topography, precautions against flooding and the consequent emissions of toxic materials need to be taken.

#### 2.6.1.2 Secondary raw materials

This industry is particularly active in recovering metal from a variety of sources and consequently uses a wide range of secondary raw materials. Scrap metal, skimmings or dross and flue or filter dust are used as sources of non-ferrous metals and these materials contain a number of metals or metal compounds. An integrated approach within an installation or between a group of companies in close proximity can encourage the use of secondary raw materials [ 277, Finland Paper on Industrial ecology 2004 ]. Secondary raw materials are also used in some primary processes.

The source of the secondary raw material may give information of the potential emissions due to the presence of acids, oils, organic contaminants (that can produce PCDD/F during melting processes), anions and components such as ammonia from the reaction of skimmings or dross with moisture. This directly influences the potential emissions to air, water and land and any of the components of these materials can be emitted. Materials are checked (e.g. by inspection and sorting) for unforeseen impurities and contamination and this can be cost effective in maintaining a cleaner product and reducing emissions.

The physical state of the material also affects the storage and handling methods. These materials can be dusty, oily and range in size from fine dusts to entire components. These factors affect the delivery, handling and storage methods used. The techniques used for primary raw materials are used together with those below.

Secondary raw materials can be delivered to site as loose material, in tote bags or in drums. The physical state of the material dictates the delivery method and the storage method used. The source of the material also has a significant impact and there are several methods available for grading material. Quality control and analysis of the feed material is practised in most cases.

Large components and material such as swarf or grindings are stored on concrete areas that may be in the open, covered or inside buildings. Some large materials are not stored on a hard surface as damage to the surface can occur. The material is usually stored in segregated piles to keep different grades and alloy compositions separate.

Dusty materials and skimmings or dross are also stored in segregated piles, which may be in the open, covered, or inside buildings. These materials can be pyrophoric or may react with moisture to form ammonia or other gases such as arsine or stibine, depending on the composition. The storage method therefore takes these factors into account. Cold dusty material can be coated with material such as molasses to form a dry crumb, which is not dust-forming. The coating material does not affect pyrometallurgical processes.

Secondary raw materials may be contaminated with a variety of other materials such as oils, acids and organic matter which could be washed into drainage systems. The potential contamination of rain and other water by such contaminants is taken into account in the design of storage methods and the treatment of water run-off from these areas. Bunded areas, sealed floors and oil interceptors are used to prevent emissions to water.

Materials are handled by a variety of methods depending on storage. Grabs, conveyors and shovels are used. Secondary materials frequently need to be blended prior to processing or pretreatment and intermediate storage is used.

#### 2.6.1.3 Fuels

The fuel may be used directly as a heat source, as a reducing agent or both. This should be identified for each installation. Fuels may be delivered to site by pipeline, road, rail or ship. The methods used for delivery are outside of the scope of this document but the use of road transport for frequent deliveries can give rise to noise and congestion.

The delivery and storage of fuel is usually controlled by the operator to prevent spillage and leaks, the techniques used include the following:

**Liquid fuels**

- Road and rail tankers are most commonly used for delivery. The site storage systems feature the use of vented or floating roof storage tanks, which are sited in sealed areas or bunds with sufficient capacity to contain the contents of the largest storage tank (or 10 % of the total volume of individual tanks if it is greater). Efficient oil interceptors are used to prevent the discharge of oil in site run-off water.

- Venting of gases from the storage tank back into the delivery tank is frequently practised unless floating roof storage tanks are used. Automatic resealing of connecting hoses is used when liquids and liquefied gases are delivered. Delivery connections are sited inside the bund.

- Regular checks of the tank contents to identify leaks and safe volume for receipt is common practice. Alarms are used. Occasionally the use of inert atmospheres will be encountered.

- Pipelines may also be used for liquid fuel delivery and may incorporate intermediate tank storage. Fuel distribution from the site storage tanks to the process is usually by overhead pipeline, by service trenches or less commonly by buried pipeline. Barriers are used for damage protection of overhead pipelines. The use of underground pipes hinders the prompt identification of fuel leaks that can cause contamination of the ground and subsurface water.

- If there is a risk of groundwater contamination, the storage area should be impermeable and resistant to the material stored.

### Gaseous fuels

- Pipelines are the most common delivery system for gaseous fuels. Although liquid petroleum gases LPG can be classified as a liquid, the techniques for gases are used.

- Some pyrometallurgical processes (i.e. the carbothermic production of ferro-alloys in closed submerged electric arc furnaces) produce a carbon monoxide rich off-gas as a by-product. The amount of CO varies largely depending on the metal and the production process. The off-gas can contain CO from lower amounts (low CV gas) up to 90 % (high CV gas). The gas is cleaned in a cascade wet scrubber and then distributed throughout the site as a secondary fuel or sold to neighbouring mills. Excess gas may be used for the production of electricity or flared off.

- The delivery of gases is often associated with pressure reduction equipment or occasionally compression equipment. In all cases the use of pressure and volume monitoring is frequently practised to identify leaks and gas monitors are sometimes used to monitor the workplace and in the vicinity of storage tanks.

- Distribution by overhead pipeline or pipelines in service trenches is common and damage protection methods are adopted.

### Solid fuels

- Road, rail or ship deliveries are used for solid fuel transport. Storage in silos, closed stockpiles, open stockpiles and in buildings are used depending on the type of fuel (e.g. coke, coal) and its tendency to form dust.

- Open stockpiles are not used frequently but those that exist are designed to give an even, sloping face to the wind and can have retaining walls to reduce the effect of wind and contain the material. Material can be reclaimed using an underfed conveyor, a grab crane or a front-end loader.

- Conveyor systems are designed to minimise the number of direction changes and the drop height at these changes to reduced spillage and dust formation. Closed, covered or open conveyors are used depending on the potential for dust formation; extraction and dust filtration is used if needed. In the case of open conveyors, dust can be produced if the belt is running too quickly (i.e. more than 3.5 m/s). Belt scrapers are used to clean the return section of the belt to prevent spillage.

- The moisture content of the fuel can be controlled to prevent the release of dust. Dust explosions are possible with dry and fine material. A contract specification for the fuel and the acceptable fines content can help to reduce the impact [ 243, French comments on MnFe alloys 2008 ].

- Some open stockpiles are treated with water sprays or sealing agents (such as polyvinyl acetate or molasses) to prevent dust formation in windy conditions, such as sealing agents which can also prevent surface oxidation of the fuel. Solid matter can be washed into drainage systems and efficient settlement is often used to prevent emissions to water from open stockpiles.

- Solid fuel can be distributed on site by truck, conveyor or by pneumatic 'dense phase' systems. Day storage or surge storage, usually in silos or hoppers, is used frequently. These systems usually incorporate dust extraction and filtration equipment.

#### 2.6.1.4 Process chemicals and gases

Acids and alkalis and other chemical reagents are often used in the main process and in abatement equipment, and may be produced during the process. They may be used to leach metals, precipitate compounds or can be used for off-gas or effluent treatment processes. Chemical compounds may be produced as part of the main process.

The supplier generally specifies the appropriate storage of these materials. Many of these reagents can react together and the storage and handling methods usually take this into account by segregating reactive materials. Liquids are usually stored in drums or tanks in open or enclosed bunded areas and acid or chemical-resistant coatings are used. Solids are generally stored in drums or bags (big bags) internally with isolated drainage systems; silos are used for some materials such as lime. Pneumatic transport systems are used.

Gases are used for a variety of purposes in the production of non-ferrous metals. The industry can use large quantities of process gases and the consumption of particular gases influences the method used for transport and distribution.

Oxygen is used to improve combustion, provide oxidation and improve conversion processes and natural gas; butane or propane are used to reduce metal oxides. Carbon dioxide, nitrogen and argon are used to provide inert atmospheres and to degas molten metal. Chlorine is used in the chlorination step of electrolytic magnesium production to degas molten metal and to remove unwanted metallic components (e.g. magnesium) from aluminium and in the Boliden-Norzinc process. Carbon monoxide and hydrogen are used in the main processes. Hydrogen and sulphur dioxide are used to reduce oxides and salts. Chlorine and oxygen are used in leaching processes and chlorine is also used in the Boliden-Norzink process. Specific applications are discussed under individual metal production processes in Chapters 3 to 12.

The operator can produce gases on site although contract gas production is encountered and these installations also supply other sites. Several sites use oxygen to improve combustion and nitrogen for spark suppression of pyrophoric materials. The same cryogenic or pressure swing process produces both gases and the low grade nitrogen produced can be suitable for some inerting operations. In a similar way, combustion gases which have a low oxygen content, are used to prevent autoignition.

Gases can be transported by tanker and pipeline. Chlorine is usually stored as a liquid in drums or tanks and is distributed by evaporation and suction line, therefore gas leakage is prevented. Inventory and pressure control and monitoring can provide leakage detection for all gases.

Flow balancing and pressure decanting are used for the mixing of gases (e.g. argon/chlorine mixtures). For small volumes, premixed gases can be supplied.

Distribution of gases within the site is normally achieved by pipelines, which are carried overhead using good damage protection systems. Health and safety regulations govern the use and distribution of chlorine.

#### 2.6.1.5 Residues

A variety of residues are produced by the processes in this sector. Many form the basis of raw materials for other parts of the industry. Section 2.6.1.2 above describing secondary raw materials covers most of the techniques that are used. Later chapters describe in more detail the specific residues from the processes and the techniques for handling and storage.

### 2.6.2 Current emissions and consumption levels

Consumption of raw materials is dependent on the metal being produced and this information is included in Chapters 3 to 12.

There are potential emissions of VOCs to air and of oils to water or land during loading, storage, unloading and transfer of liquids and gases. There are potential emissions of VOCs to air from tank breathing and pipeline leaks.

There are potential emissions of dust and metals to air and land from the loading and unloading operations, the transfer and storage of solid material and the resuspension of dust from the storage areas and conveyors. Suspended solids, metals, oil and various anions such as sulphate (depending on the ore and its treatment) can be emitted to water.

### 2.6.3 Techniques to consider in the determination of BAT

The sections of this document entitled 'Techniques to consider in the determination of BAT' set out techniques considered generally to have potential for achieving a high level of environmental protection in the industries within the scope of the document. The background to the way the techniques are described is given in Section 2.1.2 and Table 2.2. (See also the Emissions from Storage BREF [ 290, EC 2006 ]).

#### 2.6.3.1 Examples of some techniques

**Description**
The applied techniques discussed above in Section 2.6.1 are all capable of preventing emissions to all environmental media to a certain extent. The techniques that are used depend to a large extent on the type of material that is being used. For example large, heavy items are treated by a completely different range of techniques than fine, dusty material. These issues are specific to individual sites and materials. There are, however, several techniques that are considered more effective in preventing emissions from raw material handling. These techniques are shown below:

- Liquid storage systems should be contained in impervious bunds that have a capacity capable of containing at least the volume of the largest storage tank within the bund.
- Storage areas should be designed so that leaks from the tanks and from delivery systems are intercepted and contained in the bund.
- Materials of construction of the tanks should be resistant to the materials stored. In some cases, double walled tanks are appropriate.
- Leak detection systems should be used where appropriate.
- Tank contents should be displayed and associated alarms that indicate leaks should be used. Planned deliveries and automatic control systems to prevent the overfilling of storage tanks should also be used.
- Storage of sulphuric acid and other reactive materials should be stored in double walled tanks or tanks placed in chemically-resistant bunds of the same capacity. If there is a risk of groundwater contamination, the storage area should be impermeable and resistant to the material stored.
- Delivery points should be contained within the bund to collect spilled material. Back venting of displaced gases to the delivery vehicle should be practised to reduce the emission of VOCs. Automatic resealing of delivery connections should be used to prevent spillage.
- Incompatible materials should be segregated (e.g. oxidising agents and organic materials) and inert gases used for storage tanks or areas, if needed.
- Oil and solid interceptors should be used for the drainage from open storage areas. The storage of material that can release oil should be on concreted areas that have curbs or

other containment devices. Effluent treatment methods for the chemical species that are stored should be used.
- Transfer conveyors and pipelines should be placed in safe, open areas above ground so that leaks can be detected quickly and damage from vehicles and other equipment can be prevented.
- If buried pipelines are used for non-hazardous materials, their course should be documented and marked and safe excavation systems adopted.
- Well-designed, robust pressure vessels for gases (including LPG) should be used with the pressure monitoring of the tanks and delivery pipework to indicate rupture and leakage. Gas monitors should be used in confined areas and close to storage tanks.
- Sealed delivery, storage and reclamation systems should be used for dusty materials. Silos can be used for day storage. Completely enclosed buildings can be used for the storage of dusty materials and may not require special filter devices.
- Sealing agents such as molasses and poly vinyl acetate (PVA) should be used where appropriate and compatible to reduce the tendency for material to form dust.
- Enclosed conveyors should be used and have well-designed, robust extraction and filtration equipment to prevent the emissions of dust from delivery points, silo vents, pneumatic transfer systems and conveyor transfer points.
- Non-dusty, non-soluble material should be stored on sealed surfaces with drainage and drain collection.
- Swarf, turnings and other oily material should be stored under cover to prevent washing away by rainwater.
- Rationalised transport systems should be used to minimise the generation and transport of dust within a site. Rainwater that washes dust away should be collected and treated before discharge.
- Wheel and body washes or other cleaning systems should be used to clean vehicles used to deliver or handle dusty material. Local conditions will influence the method, e.g. ice formation. Planned campaigns for road sweeping should be used.
- Inventory control and inspection systems should be used to prevent spillages and identify leaks.
- Material sampling and assay systems should be integrated into the material handling and storage system where possible to identify raw material quality and plan the processing method. These systems should be designed and operated to the same high standards as the handling and storage systems.
- Storage areas for reducing agents such as coal, coke or woodchips should be surveyed to detect fires caused by self-ignition.
- Good design and construction practices should be used and adequate maintenance practiced.

**Achieved environmental benefits**

The environmental benefits are the prevention of diffuse emissions of metals, dust and other compounds.

**Cross-media effects**

None are reported.

**Operational data**

None are available.

**Applicability**

These techniques are generally applicable to most plants.

**Economics**

None was provided but the processes are operating economically.

**Driving force for implementation**

The reduction of emissions and saving raw materials.

**Example plants**
Plants in DE, AT, FR, BE, PL and NL.

**Reference literature**
[ 196, Finkeldei, L. 1999 ], [ 290, EC 2006 ].

## 2.7 Pretreatment, preparation and transfer of raw materials

*Some of this pretreatment steps are very specific, e.g. treatment of Al dross and swarf. They should be included in the specific sections.*

### 2.7.1 Applied processes and techniques

Ores, concentrates and secondary raw materials are sometimes in a form that cannot be used directly in the main process. Drying/thawing may be needed for control or safety reasons. The material size may need to be increased or decreased to promote reactions or reduce oxidation. Reducing agents such as coal or coke and fluxes or other slag-forming materials may need to be added to control the metallurgical process. Fluxes are added to optimise the recovery of the target metal and to separate impurities.

Coatings may need to be removed to avoid process abatement problems and improve melting rates. All of these techniques are used to produce a more controllable and reliable feed for the main process and are also used in precious metals recovery to assay the raw material so that toll recovery charges can be calculated.

#### 2.7.1.1 Thawing

Thawing is performed to allow frozen material to be handled. This occurs, for instance, when ores or concentrates or solid fossil fuels such as coal are discharged from a train or ship in the wintertime. Thawing can be achieved by using steam jets in order to just melt the ice and to be able to unload the raw material.

#### 2.7.1.2 Drying

Drying processes are used to produce a raw material that is suitable for the main production process. Rotary, steam coil and other indirect dryers are used and the economics, availability, reliability and energy use applicable to an installation should be assessed for any particular instance.

The presence of water is often avoided for several reasons:

- It is dangerous when large volumes of steam are produced rapidly in a very hot furnace which could result in an explosion.
- Water can produce a variable heat demand in a concentrate burner, which upsets the process control and can inhibit autothermal operation.
- Separate drying at low temperatures reduces the energy requirements. This is due to the energy required to superheat the steam within a smelter and the significant increase in the overall gas volume, which increases the fan duty.
- Corrosion of plant and pipework, etc. can be caused.
- Water vapour may react with carbon to form $H_2$ and CO.
- Large volumes of steam can cause diffuse emissions as the process gas offtake capacity can be insufficient to handle them.

Drying is usually achieved by the application of direct heat from a burner or by steam jets, or indirectly using steam or hot air in heat exchanger coils. The heat generated from pyrometallurgical processes, e.g. anode furnaces, is also often used for this purpose as well as the CO-rich off-gas that can be burned to dry the raw material. Rotary kilns and fluidised bed dryers are used. The dried material is usually very dusty and extraction and abatement systems are used to collect dusty gases. Collected dusts are returned to the process. Dried ores and concentrates can also be pyrophoric and the design of the abatement system usually takes this into account. Nitrogen blanketing (sometimes as a by-product from oxygen production) or the low residual oxygen in combustion gases can be used to suppress ignition. Dryer off-gases may contain $SO_2$ and treatment of the gases may be considered.

### 2.7.1.3 Crushing, size reduction and screening

Crushing, size reduction and screening is practised to reduce the size of products, residues or raw material so that it is suitable for sale or further processing. Many types of crusher are used including cone crushers and ball crushers. Wet or dry materials are crushed and a blending stage can be included. The specific equipment used will depend on the raw materials to be treated. Dry crushing is potentially a major source of dust emissions and extraction and abatement systems are used and the collected dusts are returned to the process. Damp materials can be crushed where dust formation can cause problems and where wet pelletising stages follow.

Granulation is used to produce small particles of slag, which are suitable as shot blasting material, road fill or a material that can be reprocessed to recover the metal content. Molten slag is cast into a water bath or poured through a stream of water. Granulation is also used to produce metal shot. Granulation processes have the potential to form fine dust and aerosols, which should be controlled.

Electronic components are a source of several non-ferrous metals and these may be ground in shredders or mills to liberate the circuit boards and other material from the metallic components so that separation can take place.

### 2.7.1.4 Battery breaking

Battery breaking is used to recover lead, nickel, cadmium and other materials from batteries. For lead/acid batteries, hammer mills are used to break the battery cases to liberate lead (as grids) and lead compounds (as paste) and allow the recovery of the plastic case material (mainly polypropylene). The electrolyte is also removed and treated or used. Two-stage crushing can be used to control the particle size and prevent the lead oxide from being impacted into the plastic during a single stage mill. Plastic material is separated and washed to improve the quality and to produce plastic that is suitable for recycling. The acid content of the batteries can contaminate land and water if it is not collected and handled properly. Sealed acid resistant drainage systems can be used with dedicated collection and storage tanks. The milling stages can produce an acid mist, and this can be collected in wet scrubbers or mist filters.

Nickel/cadmium batteries are pyrolised to remove any plastic coating and to open the batteries. Pyrolysis is carried out at low temperatures and the gases are treated in an afterburner and then a fabric filter. Cadmium and nickel are recovered from the electrodes and steel from the casing material.

### 2.7.1.5 Blending

Blending is performed to mix ores or concentrates of varying quality and to combine fluxes or reducing agents with the ore to produce a stable feed to the main process. Blending can be achieved in proprietary blending equipment, in the grinding stage or during conveying, drying and storage stages. Accurate blends are produced using bedding plants, loss in weight dosing systems, belt weighers or by volume from the loading equipment. Blending can be a very dusty operation and high levels of containment, extraction and dedusting are used. Collected dusts are returned to the process. Wet mixing is also used to avoid the production of dusts; slurry is produced that is then dewatered and used in a pelletising process. Coating and binding agents may also be used for this purpose. Depending on the process, it may be necessary to pelletise the blended material before further processing such as sintering.

### 2.7.1.6 Briquetting, pelletising and other agglomeration methods

Many techniques are used to treat concentrates, flue dusts and other secondary material and they include the baling of wire or small scrap, compressing briquettes of material as mentioned before and extruding or rolling pastes to produce even-sized balls of material. Coating and binding agents are used for this purpose to reduce dust development in subsequent process steps.

Briquettes and pellets which contain a mixture of fine ore or concentrate, recycled dust and additional material such a reducing agents are often produced to ensure efficient smelting conditions. After adding binders or water, the mixture is fed into a press to produce a pillow shaped briquette or into a rotary pelletising drum, pelletising disc or mixing machine to produce pellets. The binding material should be of such properties that the briquettes have sufficient green strength to enable them to be handled easily and to remain unbroken when they are charged to the furnace. Various types of binders can be used, such as black liquor (from the paper pulping industry), molasses and lime, sodium silicate, steel slag or cement and they also reduce dust formation. Pitch can be added to improve the green strength. Coarse fractions of filter dust from the furnace baghouse filter and filter dust from crushing and screening operations can be mixed with the other materials to be briquetted.

### 2.7.1.7 Sintering and calcination

These processes are used to increase the size of the raw material or the chemical composition so that it is suitable for further processing. Agglomeration and sintering allow a more even gas flow through a furnace bed and reduce dust formation, gas volume and diffuse emissions [ 106, Raffinot, P. 1993 ].

Sintering and calcining are also used for this purpose and additionally are used to adjust the chemical form of the mix or to convert any sulphur present, e.g. the calcination of dolomite into dolime in the production of magnesium. The main binding mechanism in ore sintering is achieved by bringing the ore up to a temperature where the gangue minerals start to melt, whereby individual particles are fused together in a matrix of molten slag. In some cases, the formation of new crystals across former grain boundaries, will play some role in the sintering process. The sinter is usually crushed and classified and the fine materials are returned to the sintering process, and sometimes the returned material is 2 to 4 times larger than the sinter produced. The feed particles are then sent to the smelter.

The sintering and roasting of sulphide ores are often carried out together at high temperatures and in this case the gases produced are high in sulphur dioxide. The oxidation of sulphur provides the heat necessary for the process. Generally, the ore is blended with return sinter and fluxing agents and may be pelletised before sintering. In the case of oxides such as secondary raw materials, coke is also added.

Sinter plants use a moving grate, continuous grate or a steel belt to carry the material through heating and cooling zones, some plants use steel pallets to contain the feed. The gases are drawn upwards or downwards through the bed (up-draught or down-draught sintering). A sintering machine that uses a combination of up-draught and down-draught stages is also used and is capable of minimising gas volumes and diffuse emissions and recovers heat efficiently. Sometimes a layer of sintered material is used between the grate and the blend is used to protect the steel grate.

The sintering of sulphide ores is exothermic, other materials use natural gas as a fuel. The hot gases are usually recycled to preheat the bed or the combustion air. The sinter is cooled by air draught on the bed or in a water quench. The sinter is then sieved and sometimes crushed to produce a final feed material of constant size. The fine materials are returned to the sintering process.

Calcining is performed in rotary, fluidised bed or multiple hearth furnaces, and there is normally no addition of carbon during the process. Calcination of sulphide concentrates performs the roasting stage and is discussed in Chapters 3 to 12 for metal production.

#### 2.7.1.8 Fuming processes

These processes are used to fume volatile metals such as lead or zinc, from a substrate. The processes use high temperatures and a source of carbon to produce an inert slag by fuming or volatilising metals from the material. This allows the metals to be recovered usually as an oxide for further processing. Waelz kilns, Herreshoff and slag fuming furnaces are used. Fuming is also achieved during batch-converting processes when volatile metals are removed during the process.

#### 2.7.1.9 De-coating and de-oiling

De-coating and de-oiling operations are usually performed on secondary raw materials to reduce the organic content of the feed to some main processes. Washing and pyrolysis processes are used. Centrifuging can recover oil and reduce the load on the thermal system. Major variations in organic content can cause inefficient combustion in some furnaces and produce high volumes of combustion gases that contain residual organic compounds. The presence of coatings can also reduce the melting rate significantly [ 122, ETSU 1994 ], [ 118, Laheye, R. et al. 1998 ]. These events can cause significant emissions of smoke, PCDD/F and metal dusts to air unless the gas collection and combustion systems are sufficiently robust. Sparks or burning particles can be produced that can cause significant damage to abatement equipment. In-furnace de-coating of contaminated scrap is also less efficient in most cases than de-coating shredded material in a separate kiln due the production of more dross [ 122, ETSU 1994 ] but some furnaces are especially designed to receive organic contaminants.

The removal of oil and some coatings is achieved in a specially designed furnace such as a swarf dryer. In most cases, a rotary furnace is used at a low temperature to volatilise oil and water. Direct and indirect heating of the material is used. An afterburner operated at a high temperature (more than 850 °C) is used to destroy the organic products produced in the furnace, and the gases are usually filtered in a fabric filter.

Mechanical stripping is also used frequently to remove insulation from cables and coatings from other materials. Some processes use cryogenic techniques to make the coating brittle and therefore easier to remove. Washing with solvents (sometimes chlorinated) or with detergents can also be used. Solvent vapour systems with integral condensers are the most common. These processes are also used to degrease production items. Treatment systems to prevent water contamination are used in these cases.

#### 2.7.1.10 Incineration and pyrolysis

Incineration and pyrolysis processes are normally used to treat photographic film, sweepings, catalysts and other materials to concentrate the precious metals content or to recover nickel. They are also used to pretreat catalysts to remove the organic content before further treatment. These processes are usually carried out at low temperatures to prevent the carryover of the metals. The gases produced from the incinerator are then treated in an afterburner and fabric filter. The potential formation of PCDD/F should be considered for these processes.

Simple box kilns and rotary furnaces are used for the incineration or pyrolysis stage. Raw materials are fed into the box kilns in trays. The metal-rich ashes are collected or quenched before they are processed further.

### 2.7.1.11 Leaching and washing procedures

Leaching or washing procedures are used to concentrate metal from ores or concentrates in a liquid phase. Washing is used to remove impurities such as alkali and alkaline earth compounds from some concentrates and secondary raw materials before further processing. Washing is also used to reduce the content of cadmium, chloride and sulphate, etc. in residues or to recover them as by-products.

Examples of leaching and washing procedures are given below:

- Waelz oxide can be washed to produce material that is suitable for use in a primary process;
- cadmium in filter dust can be removed before the dust is recycled to a smelter;
- secondary lead materials are leached to remove chlorides, alkalis and zinc before re-smelting.

Leaching is also used to remove metals from complex matrices or to concentrate the precious metals that are used to coat catalysts. Ores such as quartz are washed and screened before use. Open or closed circuit washing processes are used and a bleed of liquor is used in a closed circuit system. Waste water is treated before discharge.

### 2.7.1.12 Separation techniques

These processes are used to remove impurities from raw materials prior to their use. The separation techniques for ores and concentrates (such as flotation) are generally used at the mine when the material is concentrated or beneficiated, but these techniques are also used at several production sites to treat slag to remove metal-rich fractions such as the removal of material that contains copper from slag.

Separation techniques are more frequently used for secondary raw materials and the most common is magnetic separation to remove items of iron. Manual and mechanical separation techniques are used to pretreat waste streams such as the removal of batteries, mercury contacts, etc. from electronic equipment according to the WEEE Directive or the separation of the car catalyst from the steel casing. The separation makes it possible to recover more metals in dedicated processes. Heavy media and density separation (swim/sink) is used by the scrap processing industry but may be encountered in the non-ferrous metals industry for example in the processing of battery scrap to remove plastic material. In this case the density and size difference of the various fractions is used to separate metal, metal oxides and plastic components using a water carrier. Air classification is also used to separate metals from less dense materials such as the plastic and fibres from electronic scrap. Flotation is also used to enrich leach residues and is used in the copper sector to recover copper from furnace slag. The use of water pulses, called jigging, is used for solids separation [ 243, French comments on MnFe alloys 2008 ].

Magnetic separation is used to remove pieces of iron to reduce the contamination of alloys. Generally, overband magnets are used above conveyors. Sloping hearths in a reverberatory furnace are used to melt zinc, lead and aluminium to leave large, higher melting point impurities (e.g. iron) on the hearth for further processing.

Moving electromagnetic fields (eddy current separation) are used to separate aluminium from other material. A variation on this technique uses this moving electromagnetic field to pump molten aluminium or other metals without direct contact between the metal and mechanical components.

Other separation techniques involve the use of colour, UV, IR, X-ray, laser and other detection systems in combination with mechanical or pneumatic sorters. These are used, for example, to separate nickel/cadmium batteries from other battery types and the techniques are being developed for other applications.

#### 2.7.1.13 Transfer and charging systems

These systems are used to convey the raw materials between pretreatment stages and then into the main process. Techniques similar to those used for raw materials are used and similar problems of dust production, containment and extraction exists. Pneumatic, dense air and air slide systems are also used and can even out variations in feed quality. Collected material is re-used.

Pretreated materials may be drier than raw materials and more stringent methods are used to prevent dust emissions. Water spray systems are generally not used but high standards of housekeeping are needed. Conveyors for the transport of dust-forming materials are generally enclosed and, in these cases, efficient extraction and abatement systems are employed at exposed, sensitive areas such as conveyor change points. An alternative is the use of fine water sprays or mists. Bottom scrapers are used on conveyors to prevent the carryover of material on the return section of the belt. Dense phase, pneumatic conveying systems are also used frequently.

Some materials arrive in drums, big bags or other packaging. If the material is dusty, the emptying of these containers should be done in dust-capturing systems, e.g. sealed devices under aspiration, under sprinkling, or in enclosed buildings. In some cases, mixing these materials with water or with wet raw materials is appropriate depending on the material as long as no reactions can occur. In other cases, separately handling them in closed systems is preferable.

### 2.7.2 Current emission and consumption levels

The potential emissions to all environmental media are similar to those from raw material handling. In addition, there are emissions to air of smoke, acid gases, fumes and dust from thermal processes and dust from mechanical processes and emissions of metals to water from granulating and filtering systems. The emissions from these processes are usually collected.

### 2.7.3 Techniques to consider in the determination of BAT

The sections of this document entitled 'Techniques to consider in the determination of BAT' set out techniques considered generally to have potential for achieving a high level of environmental protection in the industries within the scope of the document. The background to the way the techniques are described is given in Section 2.1.2 and Table 2.2.

#### 2.7.3.1 Examples of some techniques to consider

**Description**
The techniques that are used depend, to a large, extent on the type of material that is being used, for example large, heavy items are treated by a completely different range of techniques than fine, dusty material. These issues are specific to individual sites and materials. The preprocessing and transfer operations however often deal with materials that are dry or are likely to produce process emissions to any of the environmental media. More detailed design of the process equipment used at this stage is therefore needed and the processes need to be monitored and controlled effectively. The nature of the material (e.g. dust-forming, pyrophoric)

should be taken into account in the assessment of potential sources of diffuse emissions. Extraction and abatement systems in particular need to be carefully designed, constructed and maintained. The review of applied techniques in this section includes the issues that will be encountered in the various process options. The emissions of VOCs and PCDD/F in thermal processes also should be assessed as contamination of the raw materials is a significant potential source of these emissions and pretreatment is a technique to consider to reduce them. The techniques listed above for raw material handling (see Section 2.6.1) should also be referred to.

The following techniques, however, are considered to be the most important:

- The use of pretreatment and transfer processes with well designed robust extraction and abatement equipment to prevent the emissions of dust and other material. The design of this equipment should take account of the nature of the emissions, the maximum rate of emissions and all of the potential sources.
- The use of enclosed conveying systems for dusty materials such as pneumatic, dense air and air slide systems. These systems should be provided with extraction and abatement equipment where dust emissions are possible.
- Processes that 'flow' directly into the subsequent process if possible to minimise handling and conserve heat energy.
- The use of wet grinding, blending and pelletising systems if other techniques for the control of dust are not possible or appropriate.
- Thermal cleaning and pyrolysis systems (e.g. swarf drying and de-coating) that use robust afterburning equipment to destroy combustion products, e.g. VOCs and PCDD/F. The gases should be held at a temperature greater than 850 °C (1100 °C if there is more than 1 % halogenated organic material), in the presence of at least 6 % oxygen for a minimum of two seconds. Lower residence times may also result in the complete destruction of VOCs and PCDD/F but this should be demonstrated on a local level. Gases should be cooled rapidly through the temperature window of PCDD/F reformation.
- Manual and mechanical separation techniques to pretreat waste streams such as the removal of batteries, mercury contacts, etc. out of electronic equipment according to the WEEE Directive or the separation of the car catalyst from the steel casing.
- Reducing the impact of VOCs. Washing processes to remove oil or other contaminants should use benign solvents. Efficient solvent and vapour recovery systems should be used with these techniques.
- The use of steel belt, up-draught or fully enclosed down-draught sintering processes. Steel belt sintering has several advantages for certain metal groups and can minimise gas volumes, reduce diffuse emissions and recover heat. Off-gas extraction systems should prevent diffuse emissions.
- The use of rotary kilns with wet ash quenching for the processes involving the volume reduction of material such as photographic film. Smaller installations may use a moving grate furnace. In both cases, the combustion gases should be cleaned to remove dust and acid gases if they are present.
- If required to minimise the generation of smoke and fumes and to improve the melting rates, separation processes should be designed to produce clean materials that are suitable for recovery processes.
- The collection and treatment of liquid effluents before discharge from the process to remove non-ferrous metals and other components.
- The use of good design and construction practices and adequate maintenance.

**Achieved environmental benefits**
The prevention of emissions of metals, dust and other compounds.

**Cross-media effects**
An increase in the use of energy.

## Operational data

A summary of the pretreatment methods is given in Table 2.8.

| Pretreatment method | Materials | Metal group | Comment |
|---|---|---|---|
| Drying | Concentrates and fluxes | All | Dry feed to a smelter can have benefits in energy efficiency and reduced gas volumes |
| Crushing | Slag | All | Mechanical or water-based |
| | Batteries | | 1 or 2 stage mechanical. Potential acid emissions to all media |
| Blending | Concentrates and fluxes | All | Use of conveying, briquetting and blending stages |
| Agglomeration | Concentrates and fluxes<br>Residues | All (Rarely Cu and Ni) | Coating and pelletising |
| Sintering | Concentrates and fluxes | Pb, Zn and ferro-alloys | $SO_2$ and dust emissions |
| Fuming | Filter dusts and slags | Pb and Zn | Filter dusts from a variety of processes contain Pb and Zn |
| De-coating, de-oiling | Cable and swarf<br>Centrifuging can recover oil and reduce the load on the thermal system | Cu, Al, Ti, etc. | VOC and PCDD/F emissions from thermal systems. Mechanical and cryogenic systems are available |
| Incineration | Film and catalysts | Precious metals | VOC and PCDD/F emissions |
| Leaching | Raw material and residues | Pb, Zn and PMs | |
| Separation | Plastic material, electronic components and metals | Pb, Cd, PM and Al | Air or liquid-based systems |
| De-greasing | Products using solvent or aqueous based systems | Cu, etc. | Potential for chlorinated hydrocarbons |
| Pyrolysis | Packaging waste | Al | Potential for PCDD/F emissions |

**Table 2.8: Summary of pretreatment methods**

## Applicability

These techniques are generally applicable to most plants.

## Economics

None was provided but the processes are operating economically.

## Driving force for implementation

Emissions are reduced of and raw materials saved.

## Example plants

Plants in DE, AT, FR, BE, PL and NL.

## Reference literature

[ 196, Finkeldei, L. 1999 ].

## 2.8 Metal production processes

*From my point of view this whole section could be relocated to the Annex of this document and only parts of it should be used in specific metal sections to improve the understanding or to complete. These descriptions of all furnaces are confusing and to a large extent not consistent regarding furnace names and producible metals. Furthermore only a few plays a key role, some are used only rarely and not in Europe.*

There are several processes or combinations of processes used to produce and melt metals. Pyrometallurgical and hydrometallurgical processes are both described in this section. The order in which they appear is not significant and does not signify a ranking. The techniques described in the metal-specific Chapters 3 to 12 give more details of the pyrometallurgical or hydrometallurgical process, the metals that they are used for and the specific advantages and disadvantages in those applications.

Furnaces are used for a variety of purposes in this industry such as roasting or calcining raw materials, melting and refining metals and for smelting ores and concentrates.

The same type of furnace or process may be used for a variety of purposes and it is therefore intended to give an overview of the various applications [ 21, European Commission, DG XI 1991 ], [ 25, OSPARCOM 1996 ], [ 34, UNECE 1995 ].

An important aspect in the choice of process is the relationship with the collection of fumes and gases; sealed, semi-closed and open processes are encountered. The design of the fume collection system is strongly influenced by geometry, which in some instances can make fume collection difficult. Computerised fluid dynamics (CFD) studies and tracers have been used to model the flow of furnace gases and also the movement of fused electrolytes [ 233, Farrell Nordic Mission 2008 ] so that diffuse emissions can be prevented or minimised. The use of these techniques has resulted in optimised gas collection systems (see Section 2.4.3).

The use of transfer systems that require collection hoods to be moved from a furnace is an illustration of this factor. The other important factor in the applicability of a particular process type is the type and variability of the raw material used; some processes allow a range of materials to be used but others need a defined type of material. Modification to furnace or electrolyte-charging systems to give small, even additions of raw materials have also been developed in parallel and also contribute to the prevention of diffuse emissions [ 233, Farrell Nordic Mission 2008 ]. These issues are considered further in the individual metal-production Chapters 3 to 12. In a similar manner, the operation and maintenance of these systems is also critical. The types of furnaces likely to be encountered are summarised in Table 2.9.

| Metal | Type of furnace likely to be encountered | Comment |
|---|---|---|
| Copper | Flash smelting furnaces<br>Bath smelting furnaces<br>Electric furnaces<br>Rotary furnaces or converters<br>Blast and shaft furnaces<br>Induction furnaces<br>Reverberatory furnaces (also hearth and chamber furnaces) | A variety of applications depending on the raw material and process stage. |
| Aluminium | Molten electrolyte cells<br>Reverberatory (and closed-well) furnaces<br>Rotary, tilting rotary and shaft furnaces<br>Induction furnaces | Molten electrolyte cells only for primary production. |
| Lead | Imperial smelting furnace (ISF)<br>Doerschel (rotating/rocking) furnace<br>Flash furnace (Kivcet)<br>Bath furnace (QSL, Ausmelt/ISA smelt)<br>Short rotary or tilting rotary furnaces<br>Heated kettle<br>Sinter machine<br>Blast furnace<br>Electric furnace *(Is there an example for electric furnaces used for lead production[rr2]??)*<br>*TBRC (Kaldo) This furnace is introduced as a BAT, so why is it not included here?* | A shaking ladle is used to produce tine from lead/tin alloys. |
| Zinc | ISF and New Jersey distillation<br>Fluidised bed roaster, sinter machine<br>Induction and crucible furnace<br>Slag fuming furnaces and Waelz kiln | Temperature control of melting is vital. |
| Precious metals | Electric furnace<br>Blast furnace<br>TBRC (Kaldo)<br>Crucible furnace<br>Rotary and static incinerator<br>Cupel and BBOC<br>Vacuum distillation | A variety of applications depending on the raw material and process stage. |
| Mercury | Rotary kiln or tube furnace<br>Herreshoff furnace | |
| Refractory metals | Pusher furnace<br>Band furnace<br>Batch furnace<br>Rotary furnace<br>Electron beam furnace<br>Vacuum induction furnace<br>Herreshoff furnace | Pusher, band, batch and rotary furnaces are used for powder production. Electron beam furnace is used for ingot smelting herreshoff furnace is only used for Mo concentrate roasting. |
| Ferro-alloys | Blast furnace<br>Electric and submerged arc furnace, electric furnace<br>Reaction crucibles<br>Metallothermic reactors | The electric arc furnace is used as an open, semi-closed and closed furnace. The induction furnace is also used for remelting. |
| Alkali metals | Molten electrolyte cells<br>Electric furnaces, induction furnaces | Induction furnaces are mostly used for remelting. |
| Nickel and cobalt | Flash smelting furnaces<br>Bath smelting furnaces<br>Electric furnaces, reverberatory furnaces<br>Converters<br>Fluidised bed roaster<br>Rotary kilns & furnaces<br>Induction furnaces | A variety of applications depending on the raw material and process stage. |

| Metal | Type of furnace likely to be encountered | Comment |
|---|---|---|
| Carbon and graphite | Pit furnaces, vacuum furnaces<br>Electric furnaces | |

**Table 2.9: Typical furnace applications**

## 2.8.1 Furnaces for roasting and calcining

### 2.8.1.1 Rotary kilns

Rotary kilns use the same arrangement as a rotary furnace but operate without melting the charge as shown in Figure 2.12.

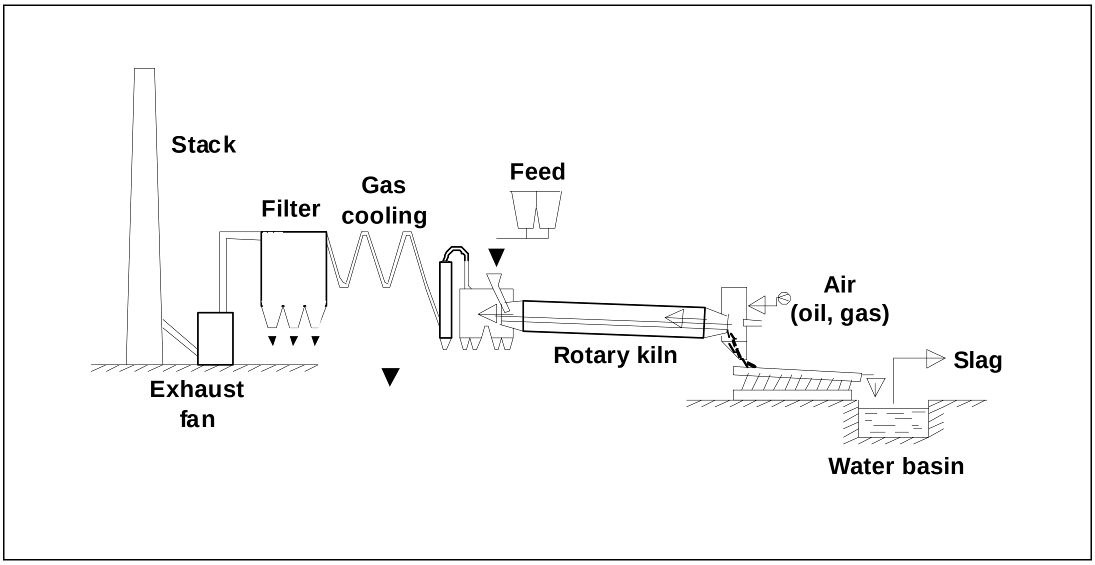


**Figure 2.12: Rotary kiln**
[ 121, Rentz, O. et al. 1999 ]

These kilns are used for a variety of fuming and calcining processes. Principal examples are the production of zinc oxide by fuming in a Waelz kiln; the production of calcine for the ferro nickel process; the calcination of aluminium hydroxide and the calcination of magnesium hydroxide to a light burnt magnesium oxide for electrolytic magnesium production. Other applications are the pretreatment of a variety of raw materials at high temperatures, the incineration of photographic film and paper and the drying of concentrates and blends of material at lower temperatures.

### 2.8.1.2 Fluidised bed reactors

These furnaces are especially suitable when good temperature control is required for example for the roasting of copper, nickel, cobalt and/or zinc sulphidic concentrates and dead roasting of zinc concentrates and partial roasting of copper concentrates as well as for $Al_2O_3$ calcining.

Combustion air is blown through tuyères in a grid at the bottom of the furnace and through the fluid bed of material being roasted on the grid. The concentrate is fed on to the top of the bed. The oxygen reacts with the sulphides in the bed to produce oxides (called the calcine). $SO_2$ gas is formed at about 900 to 1000 °C by the oxidation of sulphide to form oxide.

Part of the calcine is removed mechanically from the furnace but some is carried over in the gas stream and is removed in a waste heat boiler, cyclones or an ESP system. The roasting removes some minor impurities like chlorine, fluorine, selenium and mercury into the gas phase.

The heat evolved in the roasting is recovered as steam by cooling coils in the bed and in the waste heat boiler. Utilisation of the steam may vary somewhat depending on the need at the plant site, but part of it is always used for heating in the process.

### 2.8.1.3 Multiple hearth or Herreshoff furnace

The multiple hearth or Herreshoff furnace consists of a tower that contains 8 to 16 annular-shaped refractory brick hearths arranged vertically and enclosed in a cylindrical, refractory-lined steel shell. Material is usually fed to the outside of the top hearth of the furnace and is moved to the centre of this hearth by rabble arms where it falls to the centre of the second hearth. The material flow on the second hearth is from the centre out where it falls to the outside of the third hearth. This zigzag flow is repeated until the roasted material is discharged. The rabble arms are attached to a central, vertical rotating tube which is air cooled. Gas or oil burners are provided at various points in the furnace depending on the combustion characteristics of the material. The cooling air that is used to cool the central tube normally is used as preheated combustion air for the furnace.

The furnace is shown in Figure 2.13.

This furnace is used to roast sulphide ores, to produce metal directly in the case of mercury or an oxide such as molybdenum oxide. Vaporised rhenium that is liberated in the roasting process of molybdenite can be recovered from the roaster off-gas by using a wet scrubbing system together with a subsequent rhenium recovery plant.

The multiple hearth furnace is also used to regenerate activated carbon. It is also reported to be used to treat steelmaking dust, leaching residues and coating sludges to recover zinc as an alternative to the Waelz process [ 227, IZA Report 2008 ]. It is reported to be used to produce steel and other metals from the residues in conjunction with a reduction furnace [ 257, Paul Wurth 2008 ].

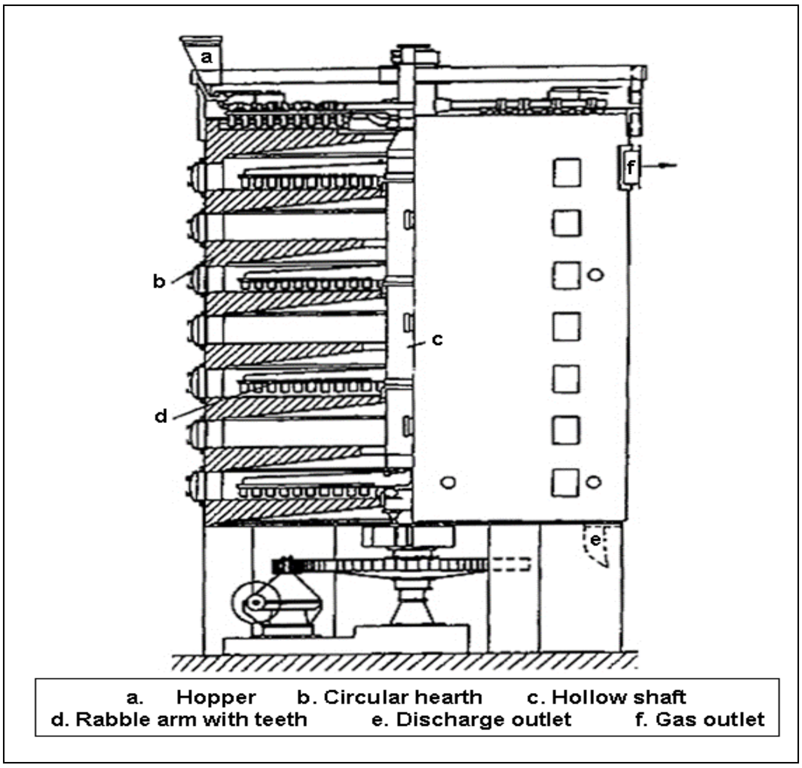


Figure 2.13: The Herreshoff or multiple hearth furnace

### 2.8.1.4 Sintering furnaces

The raw materials for the sintering plant are concentrates, ore fines, flue dusts and other secondary material. In the sintering plant the material is first agglomerated to the required extent and may be pelletised. The agglomerated material is fed to the sintering furnace in a layer or in carriers, heated gases are passed up (up-draught) or down (down-draught) through the bed or travelling grate sinter machine.

In the steel belt sintering machine, a multi-compartment oven is used through which the green agglomerate is carried on a perforated steel conveyor belt. The agglomerate is dried in the drying compartment by circulating gas from the last cooling compartment. In the preheating compartment the temperature of the agglomerate is increased so that the material is calcined and the carbon in the bed is ignited. Heating gas is taken from the second cooling compartment. In the sintering compartment the sintering temperature is achieved. Heating gas, in addition to the energy from the burning of carbon and oxidation of iron, is taken from the first cooling compartment.

The front-end compartments are down-draught, cooling air to the three cooling compartments is blown through the bed. In case additional energy is required to control the temperature profile in the compartments, CO gas from the smelting process or natural gas is burned in the preheating and sintering compartments. Part of the product sinter or pellets is used as the bottom layer on the steel belt to protect it from too high temperatures. The exhaust gases are cleaned in cascade scrubbers and/or fabric filters. Dusts are recycled back to the agglomeration. The furnace is shown in Figure 2.14.

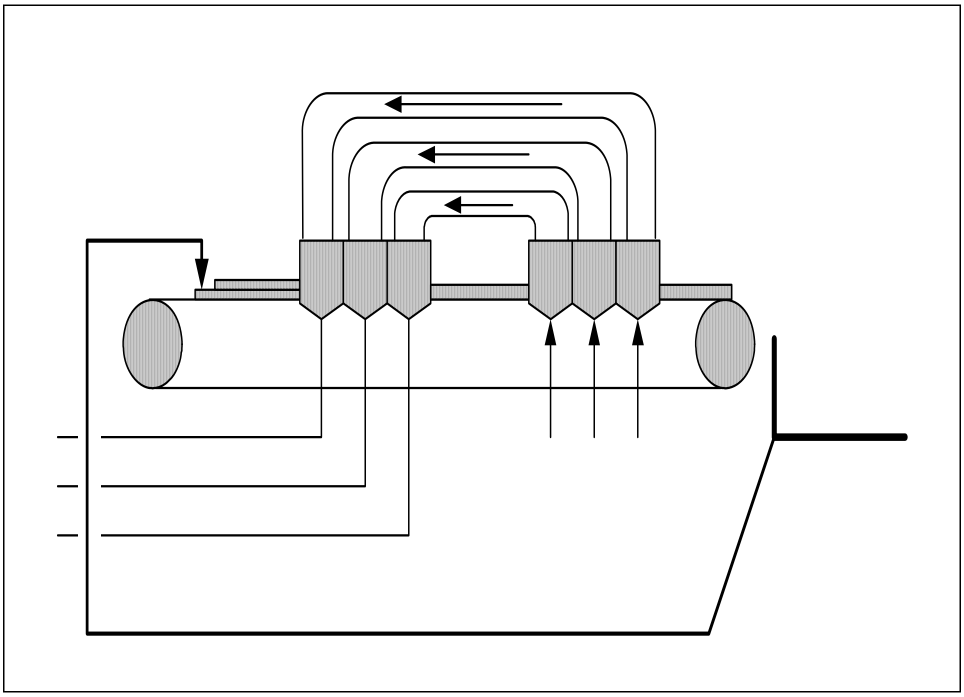


**Figure 2.14: Steel belt sintering furnace**

*This figure is not very helpful without explaining texts or legend.*

Sintering furnaces are applied to the sintering of a variety of ores, dusts and sludges. The steel belt sintering furnace is used for chromite pellets, manganese ore and niobium concentrate but may have other applications.

## 2.8.2 Smelting furnaces

Smelting involves the use or producion of a lot of heat and much of this heat is recovered from the off-gases in waste heat boilers. Heat within a furnace, however, should be controlled to allow effective smelting and, at the same time to protect the furnace. Cooling systems are used to protect the furnaces and to extend the life of the refractories. Waterfalls can be used to cool the outer shell or dedicated cooling elements can be used to cool the linings. Long campaigns are enjoyed when well designed furnace cooling is employed.

Cooling is also beneficial at the throat of a furnace to prevent the buildup of slag and other materials that prevent effective sealing of off-gas collection hoods. Developments have provided reliable and safe cooling systems in these sensitive areas.

### 2.8.2.1 Reverberatory, hearth or closed-well furnaces

The reverberatory furnace is also known as the hearth or closed-well furnace. It is used for smelting concentrates and secondary material. Two general types exist, a simple bath furnace for the smelting of calcine or concentrates and a reverberatory hearth furnace for melting or refining. Furnaces can sometimes be tilted to pour or blow metal. Tuyères can be used for the injection of treatment gases or for the addition of fine material.

The furnace is constructed in a number of configurations depending on the particular metal and application. Variations include the provision of sloping hearths and side-wells for specific melting purposes; tuyères and lances for the addition of gases.

Slag is usually removed by tapping.

When sulphide ores are smelted in a reverberatory furnace, the sulphur dioxide concentrations are normally low due to the high volume of combustion gases and the low rate of sulphur elimination in the furnace. The furnace is shown in Figure 2.15.

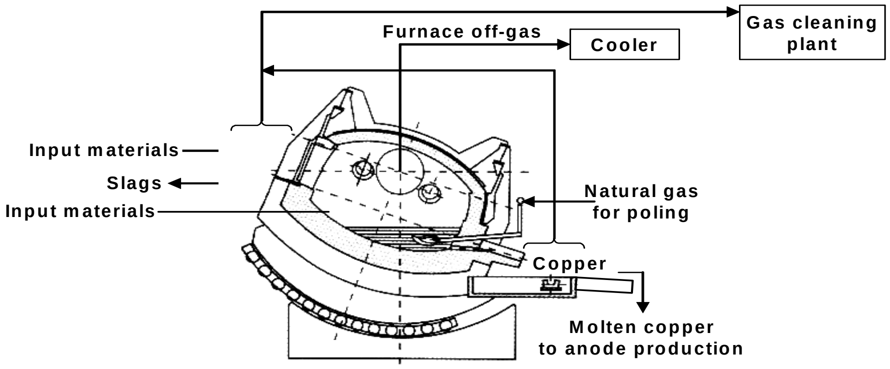


**Figure 2.15: An example of a tilting reverberatory hearth furnace used for secondary materials [ 121, Rentz, O. et al. 1999 ], [ 219, VDI (D) 1999 ]**

These furnaces are used for smelting a variety of primary and secondary raw materials and for fire-refining. The use of a reverberatory (closed-well) furnace for melting and recovering aluminium is described below in Section 2.8.4.7.

### 2.8.2.2 Blast furnaces (and the Imperial Smelting Furnace)

These are shaft furnaces and use a heated air blast from tuyères in the lower part of the furnace to burn coke that is mixed with the furnace charge of metal oxide or secondary material and fluxing agents. Materials are often briquetted before charging. The combustion of a portion of the coke raises the furnace temperature and the remainder produces CO, which, along with hydrogen produced by the water gas reaction, reduces the metal oxides to metal. The reaction produces a gas that is rich in carbon monoxide. This can be collected, cleaned and burnt to preheat the blast air or may be burnt off in a separate afterburner or in an oxygen-rich part of the furnace. In some instances, raw materials such as zinc oxide dusts are fed via the tuyères.

The metal collects on a hearth or crucible at the bottom of the furnace and may be tapped continuously or on a batch basis. When tapped batch-wise, the slag floats on top of the metal and the metal is tapped from a separate tap-hole. Fume extraction and abatement is used during the tapping process.

The furnace shell is normally water cooled either over its entire height or in the lower part. The blast furnace can also be called a water jacket furnace. There are two variations of the blast furnace depending on the feeding method and the operating temperature used to melt the metal. Furnaces can be:

- hot top where the charge material is fed via a bell or a conveyor via a transfer lock;
- cold top where the furnace is charged from a hopper and the feedstock provides the top seal itself.

The furnaces are shown in Figure 2.16 and Figure 2.17.

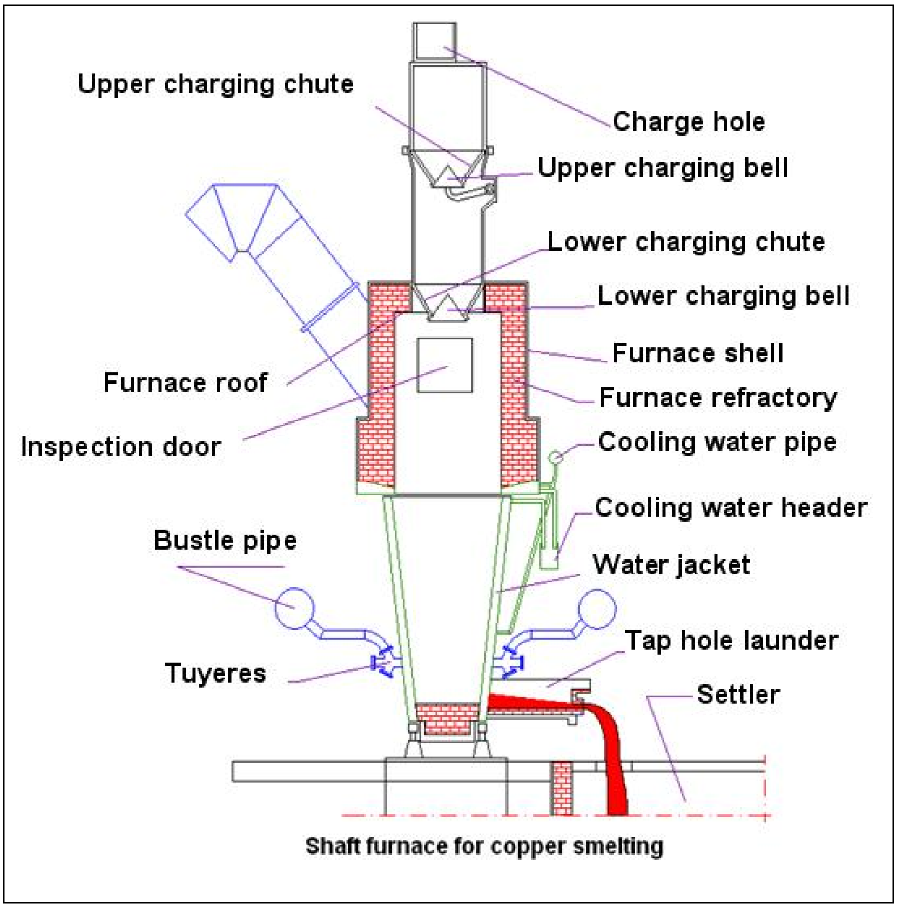


**Figure 2.16: Blast furnace for primary copper smelting**

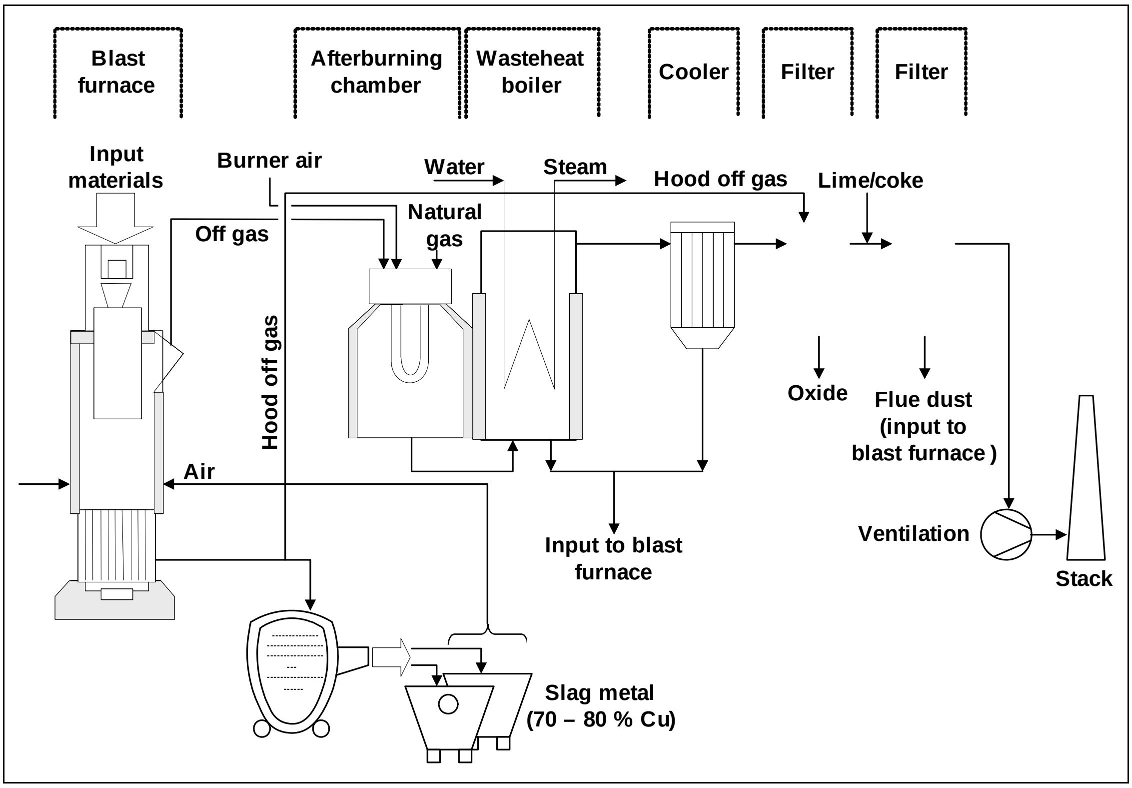


**Figure 2.17: Blast furnace for secondary copper production**
[ 121, Rentz, O. et al. 1999 ], [ 219, VDI (D) 1999 ]

Blast furnaces are used to smelt and recover a variety of metals including precious metals, copper and lead from primary and secondary raw materials as well as high carbon ferro-manganese. Developments allow the charging of fine materials into the furnace via the tuyères and this can avoid briquetting and reduce the handling of dusty material.

One specific application of the blast furnace is the Imperial Smelting Furnace that is used for mixed lead and zinc concentrates. This furnace uses a molten lead splash condenser after the blast furnace section to collect zinc vapour released in the gases while lead collects on the hearth. The zinc and cadmium collected in the condenser is purified in a fractional distillation system (New Jersey distillation column).

### 2.8.2.3 Electric reduction furnaces

The process in an electric reduction furnace is normally to reduce an element in an oxide state into metallic form. The process normally involves adding the oxide and a reducing agent, often carbon, to the furnace. Metallic components can also be added. To bring the reactants up to the reaction temperature as well as to support the endothermic reactions, electrical energy is added. This electrical energy is converted to heat energy in a concentrated reaction zone near the electrode in the furnace. The furnaces are shown in Figure 2.18, Figure 2.19 and Figure 2.20.

Some furnaces will use a slag layer to develop the necessary energy. Others are based on resistance in the burden itself or in a coke bed. Some processes seem to clearly keep a plasma arc from the electrode tip to the coke bed or crater. Such electric reduction furnaces are sometimes called submerged arc furnaces. The reason is that the submerged arc is an important part of the conversion from electrical energy to heat energy in the reaction zone of the process. The electrical supply is normally based on a three-phase electrical power supply. The electrical power supply will be transformed from high voltage to low voltage. A DC (direct current) electricalal supply can also be used and, in this case, the arc strikes between the electrodes and the carbon furnace lining or the electrodes and the raw materials in the lower part of the furnace.

The electric reduction furnace can be divided into the following main components shown below:

- equipment for adding raw materials such as ores, concentrates and reducing agents or a mix of raw material to the furnace;
- equipment to supply electrical energy to the furnace consisting of an electrical grid, transformers, bus bars and electrodes;
- the furnace body or shaft consisting of a shell, the lining and the furnace hood that protects the equipment from the heat;
- equipment for tapping the metal and slag from the furnace. Often the metal should be sized afterwards in a crushing process;
- the off-gas system (off-gas ducts connected to cleaning facilities such as cyclones, scrubbers or filters) here with an energy recovery unit as well as the filter for the gas-cleaning .

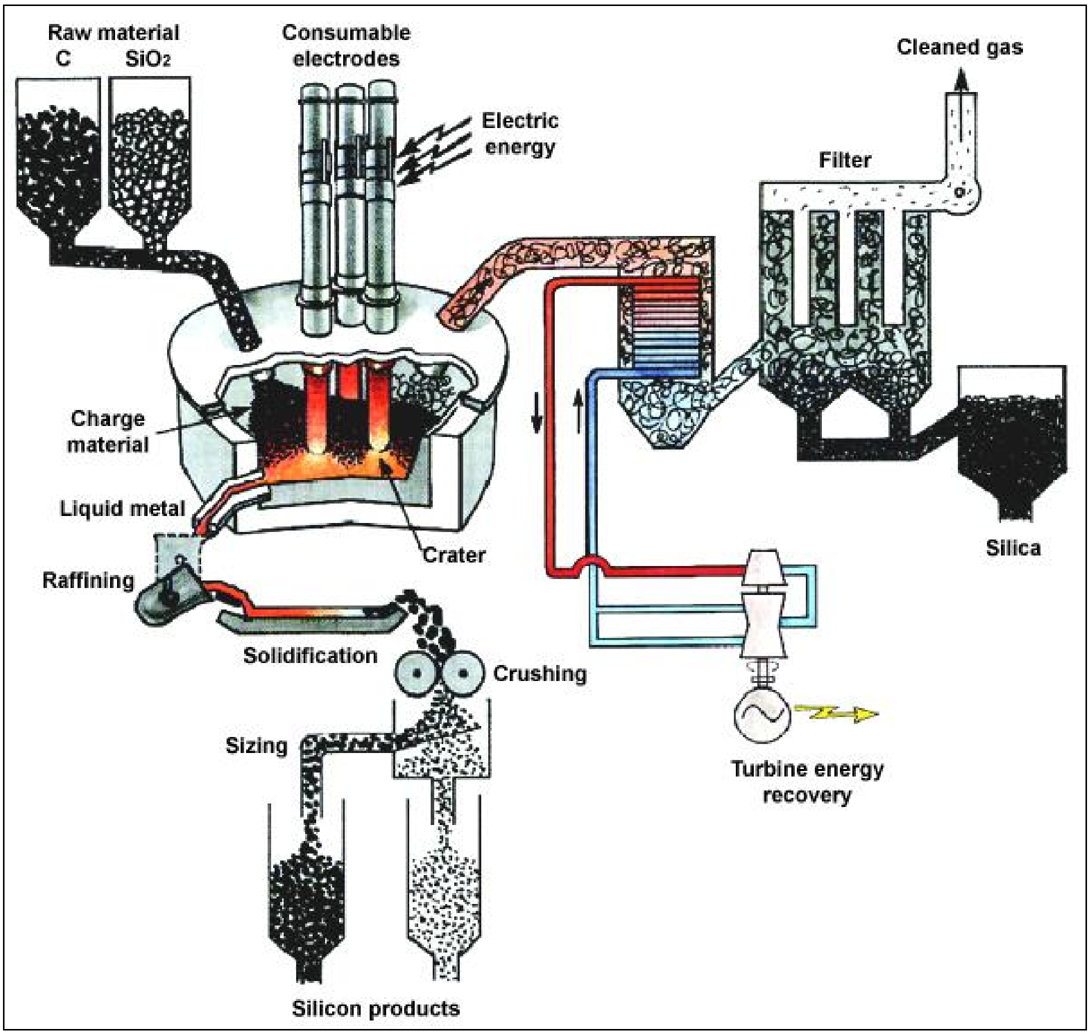


Figure 2.18: **Electric reduction furnace process and auxiliary equipment**

The raw material may be charged to the furnace in different ways. For smaller furnaces, the raw material can be charged by using a charging car. The charging car may sometimes also be used for the necessary stoking in order to break down crust formation in the upper part of the furnace charge. Large electric arc furnaces are normally charged by charging tubes where the charge flows from the tubes to the furnace charge level.

The electrical supply system will transform the electrical energy that normally is at high voltage down to low voltage/high current level that is required for the process. The furnace transformers are normally situated symetrically around the furnace in order to obtain electrical symmetry and short electrical connection lines to avoid unnecessary losses. On smaller, older furnaces a single three-phase transformer is sometimes used. The operation of single-phase transformers has some advantages on the furnace control. The electrodes are connected to the electrical supply system through the bus bar. The electrodes can be prebaked or of the Søderberg type. They are made from graphite or carbon material and are consumed in the process and they have to be replaced continuously.

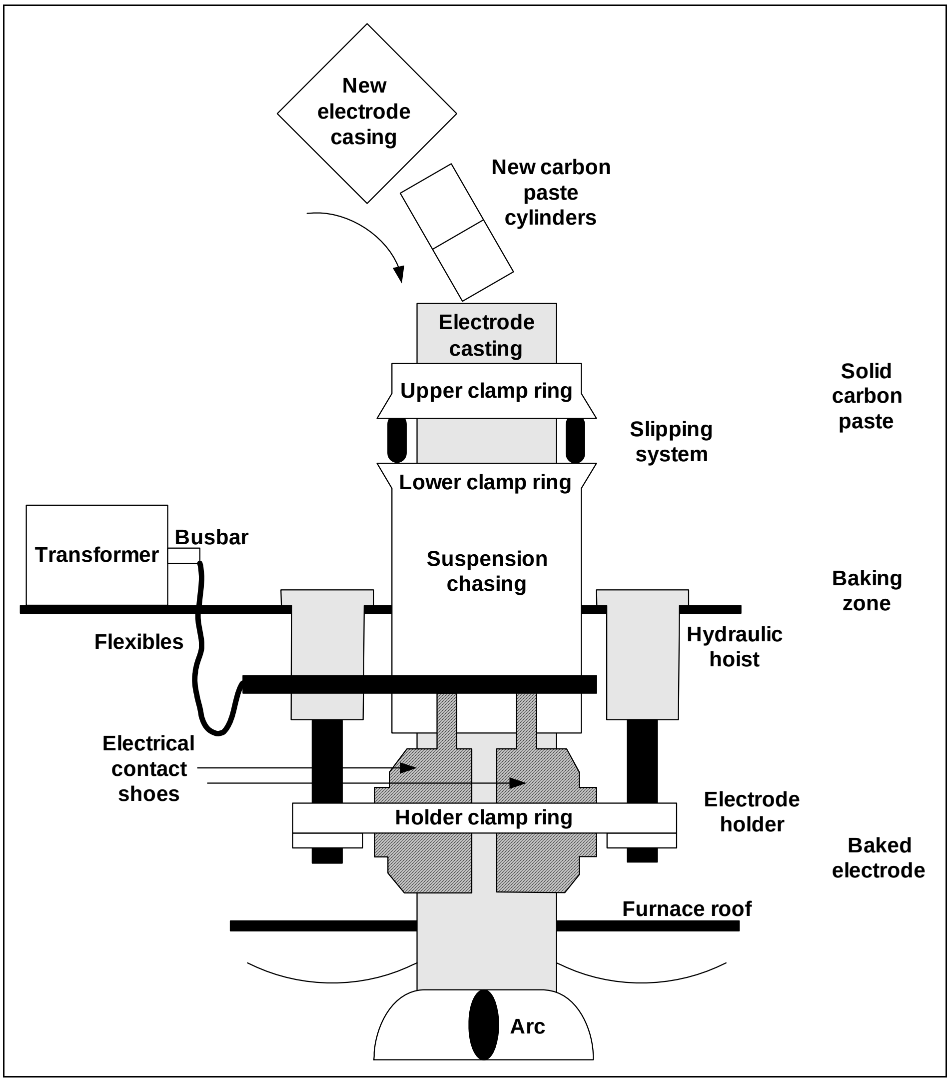


**Figure 2.19: Søderberg electrode system in an electric arc furnace**

The Søderberg system that is shown in Figure 2.19 is based on an outer steel electrode casing which acts as a mould for the carbon paste. The carbon paste is baked to a solid electrode inside the steel casing when the electrode is heated, passing the upper contact clamp area. The solid carbon electrode will be consumed in the furnace partly by thermal reaction and partly by oxidation. Significant concentrations of carbon monoxide can be produced. Some installations use hollow electrodes which allow material to be fed into the furnace through the electrode.

The raw material provides part of the resistance in the electrical circuit and promotes the formation of the electric arc, which produces the high temperatures needed. The depth of insertion of the electrodes regulates the resistance. Direct current arc furnaces exist and use anode pins or conducting hearths. The electric arc furnaces can be operated batch-wise or continuously.

The furnaces can be open, semi-closed or totally closed using feed chutes and sealing valves for charging. In the latter case, all of the furnace gases are extracted efficiently, cleaned and can be used as a source of fuel using the high concentrations of CO or to preheat feed materials using the heat content [ 112, Outokumpu Oy (SF) 1998 ]. The hoods and occasionally the furnace body can be water-cooled to control the process and prevent damage.

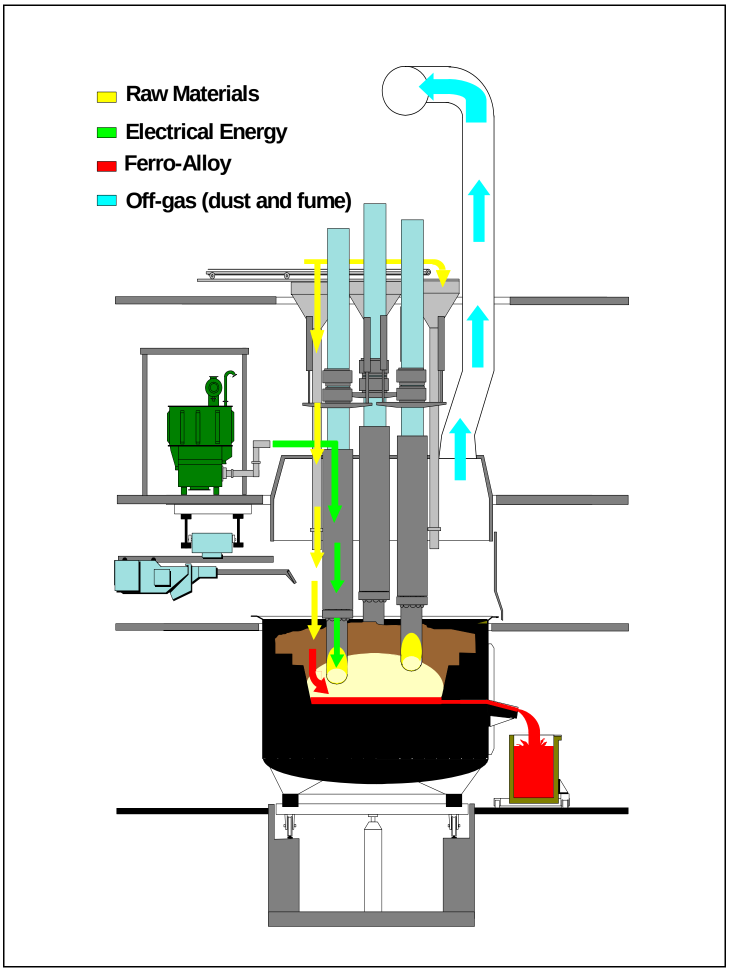


**Figure 2.20:** **Rotary electric reduction furnace**

Molten or solid raw materials are fed in a number of ways using launders, feed pipes or through a hollow electrode. Closed or semi-closed conditions are easy to maintain. In smelting processes, the roasted ore concentrates are transferred on to the liquid melt either through the top of the furnace or sideways by individual chargers and the electrodes are immersed in the molten slag layer.

These furnaces are used for smelting a range of ferro-alloys and can be used to preheat or pre-reduce material to exploit the CO content. They are also used for melting and refining refractory metals and high temperature alloys and, in these cases, they are operated under vacuum.

### 2.8.2.4 Electric (resistance) furnaces

This type of furnace uses a similar arrangement to the electric reduction furnace. Depending on the size of the furnace, three to six Søderberg or prebaked electrodes are immersed into the liquid layer. The melting temperature is maintained by means of electric resistance heating. The furnace is usually operated continuously. The furnace is shown in Figure 2.21.

Molten or solid raw materials are fed in a number of ways using launders, feed pipes or through a hollow electrode. Sealed or semi-sealed conditions are easy to maintain. In smelting processes the roasted ore concentrates are transferred on to the liquid melt either through the top of the furnace or sideways by individual chargers and the electrodes are immersed in the molten slag layer.

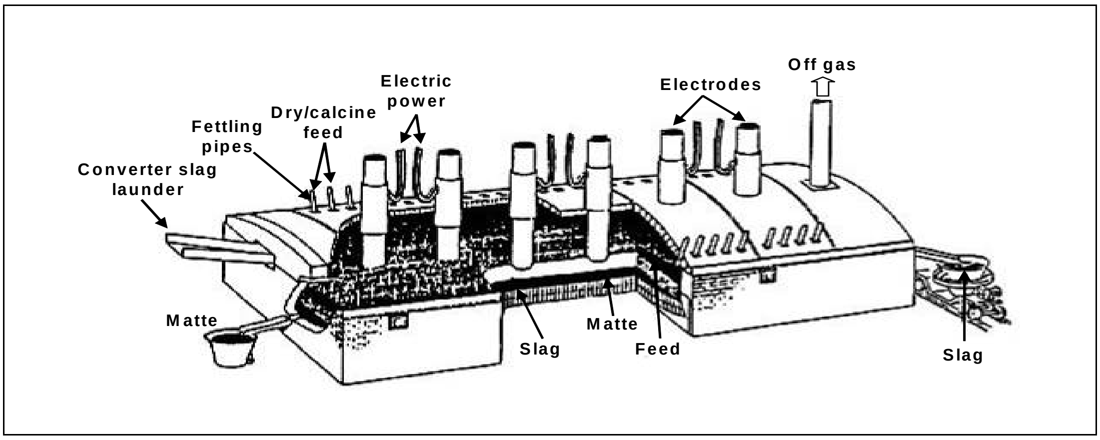


**Figure 2.21: Electric furnace for concentrate or calcine smelting**

Electric furnaces can be operated in a number of ways using coke and slagging agents depending on the application. The carbon electrodes are consumed as oxides and are reduced but the gas volumes produced during operation are kept to a minimum as there are no gases produced by the combustion of a fuel. These furnaces are usually sealed and the gases are easily collected and treated to remove and, if possible to re-use dust, CO and sulphur dioxide.

These furnaces are used in the production of a number of metals from primary and secondary raw materials including precious metals, lead and copper and can be used for slag cleaning [ 121, Rentz, O. et al. 1999 ]. Some slags from primary smelting, e.g. copper, are usually cleaned in circular furnaces. They are also used for the recovery of precious metals, particularly silver.

In principle, electric furnaces process the same types of secondary raw materials. Reducing agents used in electric furnaces likewise include coke but also other materials. The heat required for smelting is generated exclusively by electrical energy which is introduced by electrodes immersed in the molten slag which acts as electrical resistance. The burden is prepared with a composition to suit the specific smelting programme and is fed to the furnace via an enclosed charging system. The molten products are drawn off into buckets or ladles via different tap-holes. Reduction smelting results in the volatilisation of mainly zinc, tin and lead which are discharged as oxides with the off-gas and collected in the dust collection system which consists of a dust pot, process gas cooler and a filter.

### 2.8.2.5 Refractory-lined pits and crucibles

Refractory lined pits and crucibles are simple pits formed in $Al_2O_3$ or other refractory material and refractory-lined steel cylinders that are arranged to form crucibles. They are commonly used for metallothermic reactions. Refractory lined pits and crucibles are often used in the production of special ferro-alloys such as ferro-vanadium and ferro-molybdenum as well as for refractory metals. Fume collection can be a problem with this type of furnace and well designed and operated gas extraction is needed.

### 2.8.2.6 Ausmelt/ISA Smelt furnaces and the the KRS furnace

(What about Sirosmelt)

The Ausmelt/ISA Smelt furnaces and the the KRS furnace are cylindrical bath furnaces that use a steel lance for the injection of natural gas, oil or coal, and oxygen or air into the melt. The lance is submerged into the molten bath and relies on the formation of a coating of slag to prevent rapid deterioration. The furnace is shown in Figure 2.22.

Other raw materials are fed into the furnace by a sealed conveyor where they react at a high rate and are melted. The submerged combustion lance stirs the bath and produces a slag along with the desired metal or matte. The separation of the molten phases requires a separate settling furnace from where the phases are tapped separately. The furnace can be used on a batch basis when conditions in the furnace, such as the gas blown through the lance, are changed at the end of a batch. Examples of a batch operation are:

- the smelting of copper/lead secondary material to a copper lead matte in a first stage followed by conversion of the matte to blister copper by blowing with oxygen;
- the treatment of zinc leach residues.

Continuous operation is possible using two furnaces in series, e.g. as suggested for the ISA lead production process.

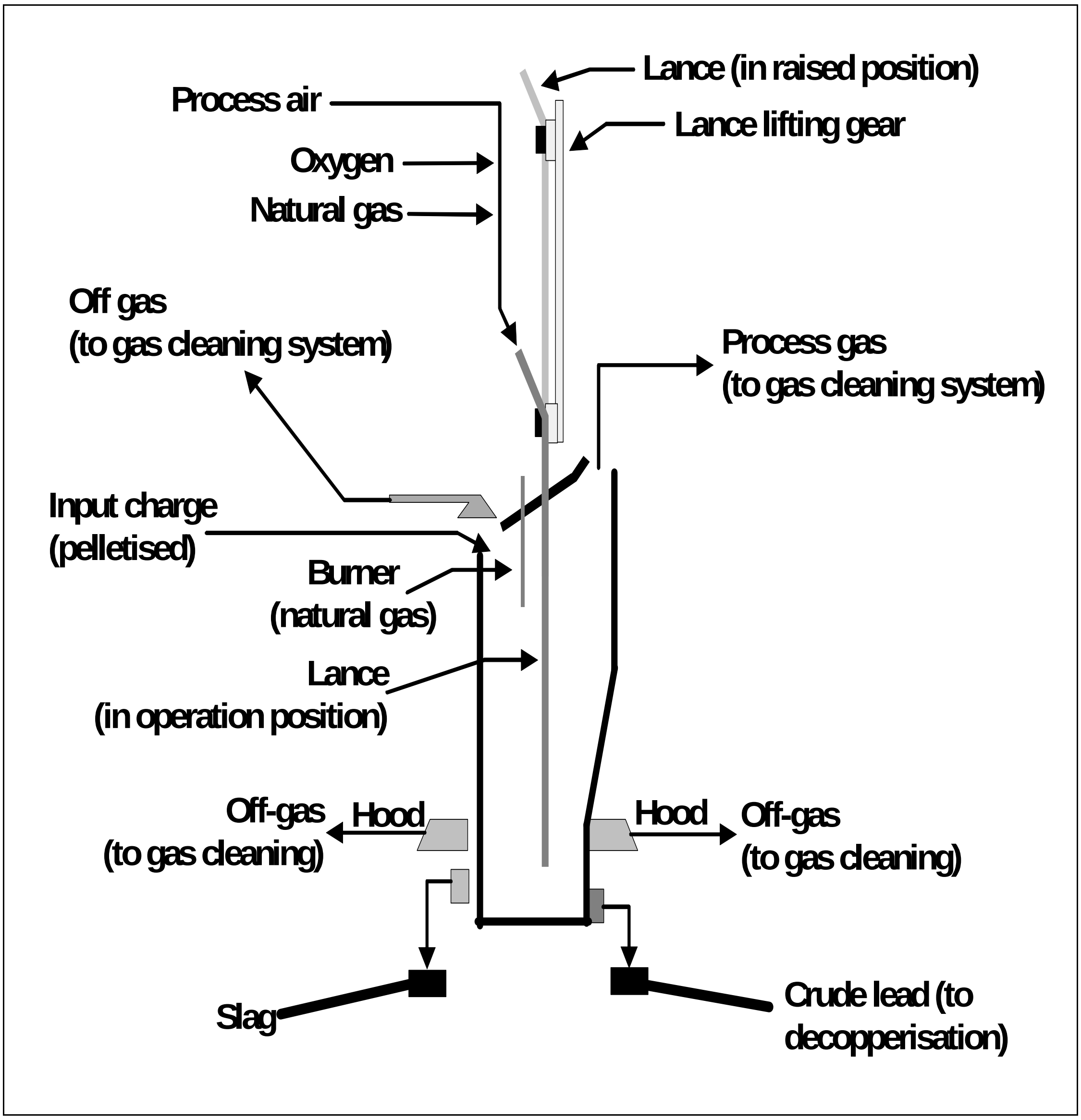


**Figure 2.22: The Ausmelt (Sirosmelt)/ISA Smelt process**

[ 121, Rentz, O. et al. 1999 ]

The furnace uses a robust hood and an extraction system to collect and treat fumes from the furnace system and tapping operations. When sulphide concentrates are smelted, the gases are passed to a sulphur removal system.

There are a number of applications for this type of furnace including the production of copper matte from concentrates ~~(ISA Smelt)~~ and converting, production of copper from secondary raw materials (KRS), the production of lead from primary and secondary materials ~~(ISA Smelt)~~, the treatment of spent pot lining and the fuming of zinc ~~(Ausmelt)~~ [ 37, Ausmelt Ltd. 1995 ].

The Ausmelt/ISA Smelt furnace ~~is also used for the production of copper and lead from mixed feed. This furnace~~ is used as a continuous direct smelting furnace as well as for batch and stepwise operations. When smelting copper concentrate to matte, the process uses moist feed that is fed continuously with fluxes into the furnace.

Unlike the blast and electric furnace technologies, the KRS currently uses an intermittent two-stage process consisting of a smelting and a conversion step. There are several furnaces operating this way. In the KRS process for example, the first step produces a metallic phase (black copper) and a slag phase which is drawn off via the slag tap-hole and granulated with water. The iron silicate sand produced is marketed as a building material. The black copper remains in the furnace. In a second, conversion step, the black copper is converted to a metal and a converter slag under oxidising conditions by adding alloy scrap. The converter slag is transferred via a launder to the tin-lead alloy furnace (rotary furnace) for further processing. The KRS converter metal flows to a rotating-and-tilting furnace designed for temperature-holding service from where it is poured into ladles and transferred to the anode furnace for pyrometallurgical refining. Final refining is accomplished in the copper electrolysis unit. The quality of the refined copper (cathode copper) measures up to that of copper won from primary raw materials [ 234, UBA Copper, lead, zinc and aluminium 2007 ].

### 2.8.2.7 Top blown rotary converter (TBRC) and tilting rotating oxy-fuel furnace (TROFF)

*What about the name KALDO???*

The TBRC and TROFF are rotating and tilting furnaces that uses lances for heating and blowing purposes. The furnaces are small and are housed in an enclosure to contain secondary emissions, which are treated. Rotation of the furnace promotes good mixing of the charge and complete reaction of the components but can lead to abrasion of the refractory lining. The furnace is shown in Figure 2.23.

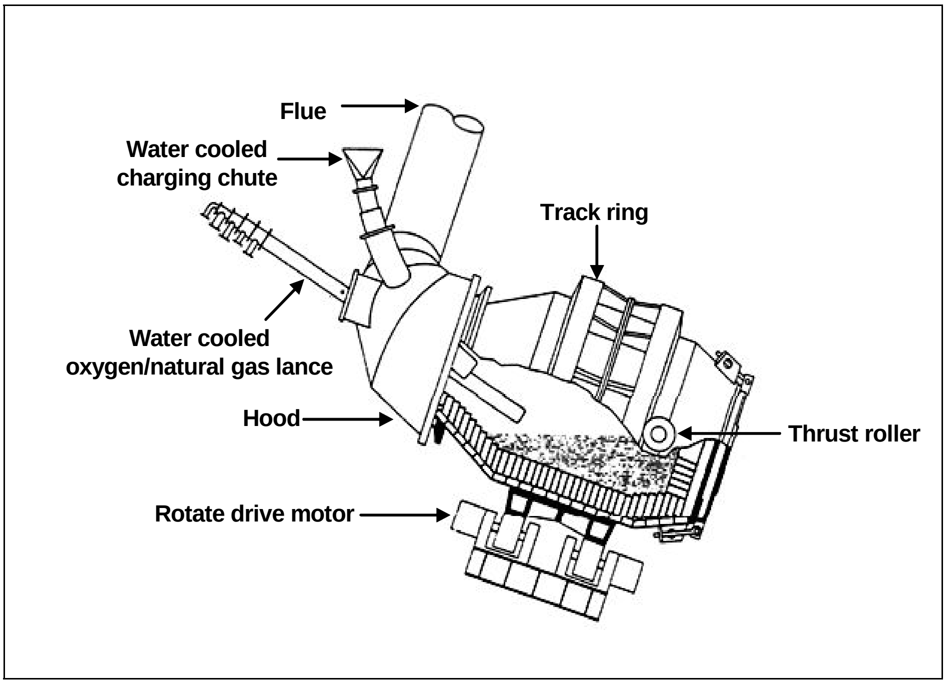


Figure 2.23: TBRC and TROFF

Oxygen and fuel are added via the lances, which blow onto the surface of the melt. The use of oxygen results in the production of low off-gas volumes and high sulphur dioxide when sulphides are smelted. The process is normally carried on a batch basis and it is common to use a number of these furnaces for smelting, converting and slag cleaning. It is used to produce primary and secondary copper and lead, ferro-nickel and for the recovery of precious metals.

Other commercial designs of tilting rotary furnaces are also used for smelting and examples are the mini-smelter and the tilting rotating oxy-fuel furnace (TROFF).

### 2.8.2.8 The Noranda, El Teniente, Baiyin and Vanyukov processes

The Noranda reactor uses a cylindrical refractory-lined furnace for smelting. Pelletised concentrate and additives are charged on to the bath of molten slag at the top end of the furnace. Burners fired by natural gas or oil situated at both ends produce the heat necessary for processing. Oxygen-enriched air is blown into the molten bath through tuyères, causing sulphur and iron to oxidise. The furnaces are shown in Figure 2.24and Figure 2.25.

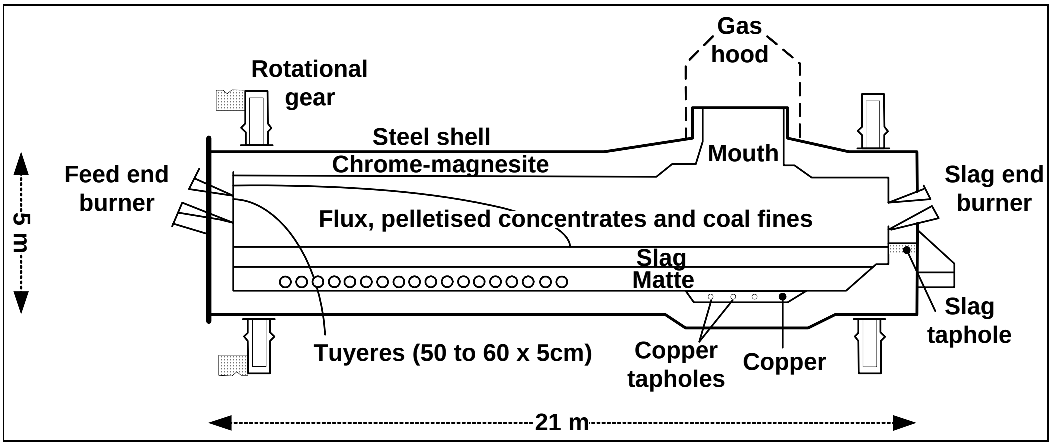


Figure 2.24: The Noranda reactor

During continuous smelting in the furnace, the melt segregates into two liquid phases: slag and matte. Due to their various densities, they settle to form two layers. Matte is tapped periodically from the bottom of the furnace and the slag flows out continuously opposite the charging end. The furnace is sealed and extracted and the launders are provided with extraction.

This process is used to smelt copper concentrates and can produce blister copper when using concentrates with low impurity levels or high-grade matte. The normal operating practice is to produce a copper-rich matte to undergo further conversion.

The El Teniente, Baiyin and Vanyukov processes are similar to the Noranda process. In the El Teniente process, wet concentrates are added to the furnace using a Gar gun and dry concentrates are added via the tuyères. Initially matte is seeded into the furnace to help the process and to produce white metal. The Baiyin process uses a rectangular furnace that is divided into smelting and settling zones. In the Vanyukov process, the oxygen-enriched air is blown into the slag layer rather than the matte layer.

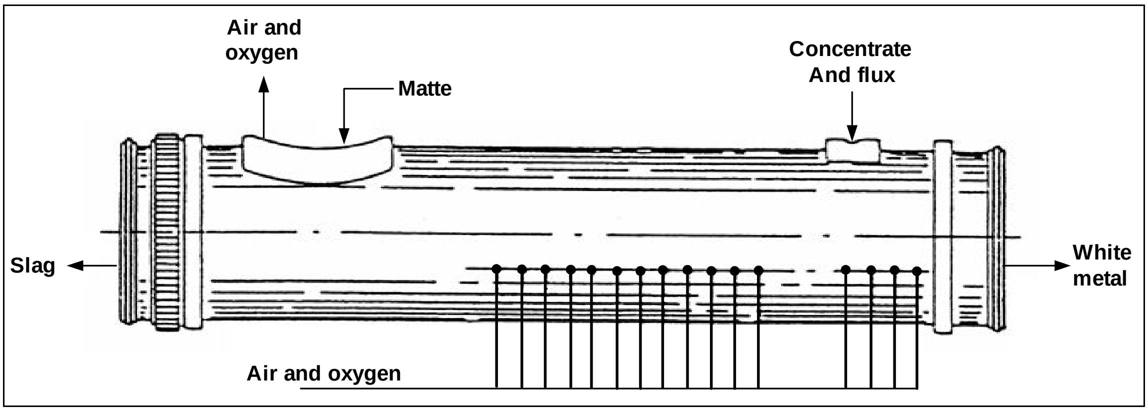


**Figure 2.25: El Teniente reactor**

### 2.8.2.9 Mitsubishi process

The Mitsubishi process employs three interconnected furnaces; a bath smelting furnace, an electric slag cleaning furnace and a converting furnace. Gravity flow is used between the furnaces and avoids the transfer by ladle. All of the furnaces are sealed and extracted, heat from the process gases is recovered and treated to remove dust and sulphur dioxide. The furnace is shown in Figure 2.26.

The dried concentrates, air, oxygen and additives are charged into the bath furnace by means of lances and subsequently melted to form matte (60 to 65 % copper content) and slag. This mixture flows continuously through a channel into the electric hearth furnace that serves as a settling furnace to separate the slag. Matte is continuously discharged from the settling furnace through a siphon into the converting furnace.

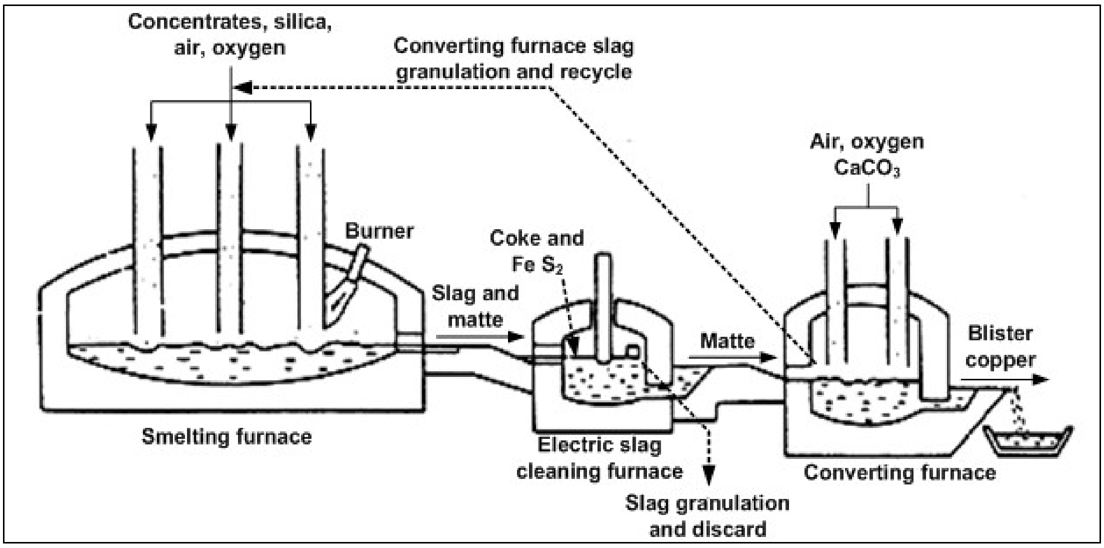


Figure 2.26: The Mitsubishi process

In the converter air, oxygen and additives are blown onto the liquid bath via water-cooled lances to produce blister copper. The converter slags are recycled to the smelting furnace, which can also be fed with anode scrap. It is possible that the converter stage could be used with other smelting furnaces. This process produces blister copper continuously.

### 2.8.2.10 QSL furnace

The QSL furnace is a horizontal cylinder divided into an oxidation zone and a reduction zone. The furnace is lined with chrome-magnesite bricks to cope with a temperature of 1250 °C. Tuyères at the furnace bottom supply oxygen to the oxidation zone and a mixture of air and coal dust to the slag reduction zone. Primary and secondary raw materials are used and can be moist and sized from large lumps to fine material. They are fed into the top of the furnace mixed with coal to provide heat and reducing conditions and fluxes to yield a slag with a low melting point which can later be used as a construction material subject to quality control. The furnace is shown in Figure 2.27.

The oxidation zone produces lead bullion, sulphur dioxide and a lead-rich slag. This flows into the reduction zone so that a further quantity of lead bullion is produced, and this flows in the reverse direction to the lead tap-hole. Slag is tapped from the reduction end and then granulated. Lead bullion is tapped from the oxidation end and then refined. Hoods and complete enclosures extract gases from the outlets and launders. The exhaust gases contain 10 to 13 % $SO_2$ and are used for heat recovery and then dedusted in an ESP before passing to a sulphuric acid plant. Other process gases are cleaned in fabric filters.

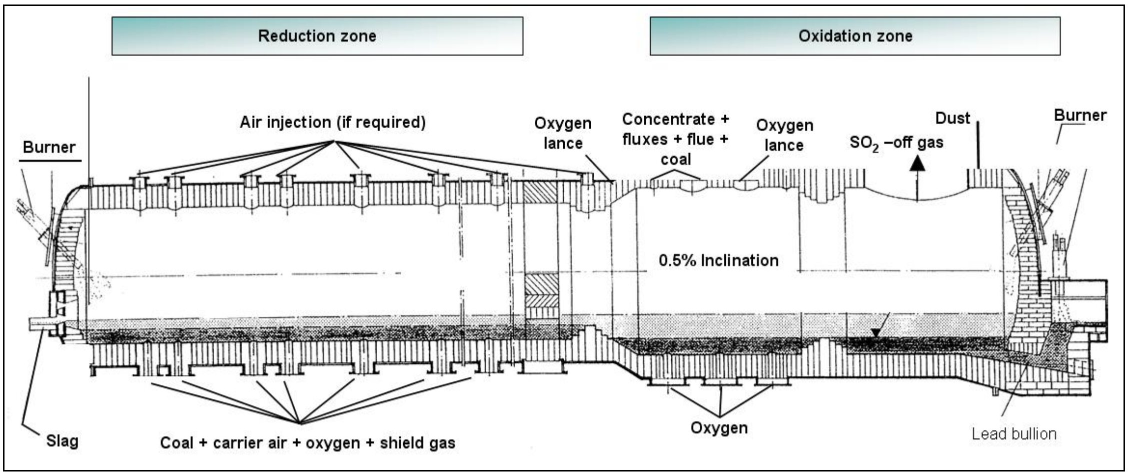


**Figure 2.27: QSL process**

[ 99, Hähre, S. 1998 ]

The QSL process was designed to produce lead from concentrates and some secondary materials in a single bath furnace and to maximise energy recovery.

### 2.8.2.11 Cyclone smelting furnaces

Cyclone smelting furnaces include the flame cyclone reactor (FCR) and the Contop reactor. With these high-intensity flash-smelting processes, the copper concentrates and flux are smelted with oxygen in cyclone-type combustion chambers. In the Contop process, the cyclone is disposed vertically and the reacted mixture falls into a settling chamber below the cyclone. In the FCR process, the combustion takes place in a vertical reaction shaft and the separation of the matte and slag occurs in a further horizontal reactor. Slag and white metal or copper-rich matte are separated in the forehearth and tapped off. The white metal or matte is processed in a standard converter. The furnace is shown in Figure 2.28.

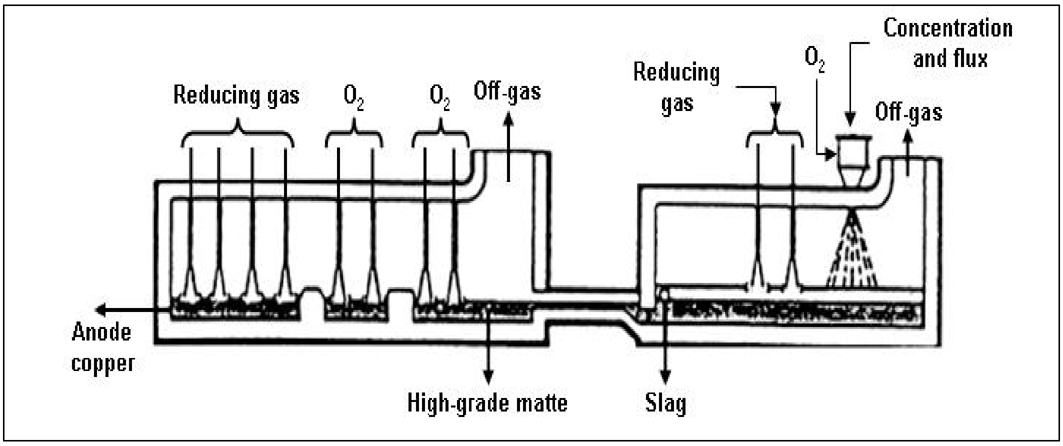


**Figure 2.28: Contop process**

These processes are mainly used to smelt copper concentrates.

### 2.8.2.12 Outotec flash furnace

The Outotec flash furnace is used for smelting of dried concentrates by utilising the energy content of the concentrates for the production of the heat needed for the smelting of concentrate and flux. The concentrate feed mixture is fed continuously with oxygen-enriched air through a concentrate burner into the vertical reaction shaft of a sealed furnace where the reactions between oxygen and concentrate takes place rapidly in suspension. The heat of reaction melts the particles. The fused particles produce matte and slag. Sulphur dioxide is formed at the same time. In older installations, process air preheating to about 200 to 800 °C was used to achieve autogenous operation, but the majority of installations achieve autogenous operation by using oxygen enrichment to about 30 to 90 % oxygen in process air. The degree of oxygen enrichment is determined by the concentrate quality and the heat balance requirements. The continuous off-gas flow leaves the furnace through the uptake shaft for heat recovery and dust removal. It has a high, constant sulphur dioxide concentration and sulphur is recovered from the gas mainly by conversion to sulphuric acid after dust is removed. In some installations, oxygen is added to the uptake shaft for afterburning dusts and sulphatising air is fed into the boiler. It is possible to recycle weak acid into the uptake shaft under certain conditions, to decompose it so that the $SO_2$ generated can be recovered in the acid plant.

The molten slag and matte particles are settled out of the gas in a horizontal settler part of the furnace forming a molten bath where the phases separate without an external settler. The matte is tapped out of the furnace to ladles or led via a launder to a granulation stage depending on the method of conversion used. The slag is tapped continuously or semi-continuously out of the furnace and can be further processed in a slag furnace or in a slag flotation circuit for copper recovery. In some installations the low copper content in slag allows the slag produced in the primary smelter to be discarded or used directly.

The Outotec flash furnace is shown in Figure 2.29.

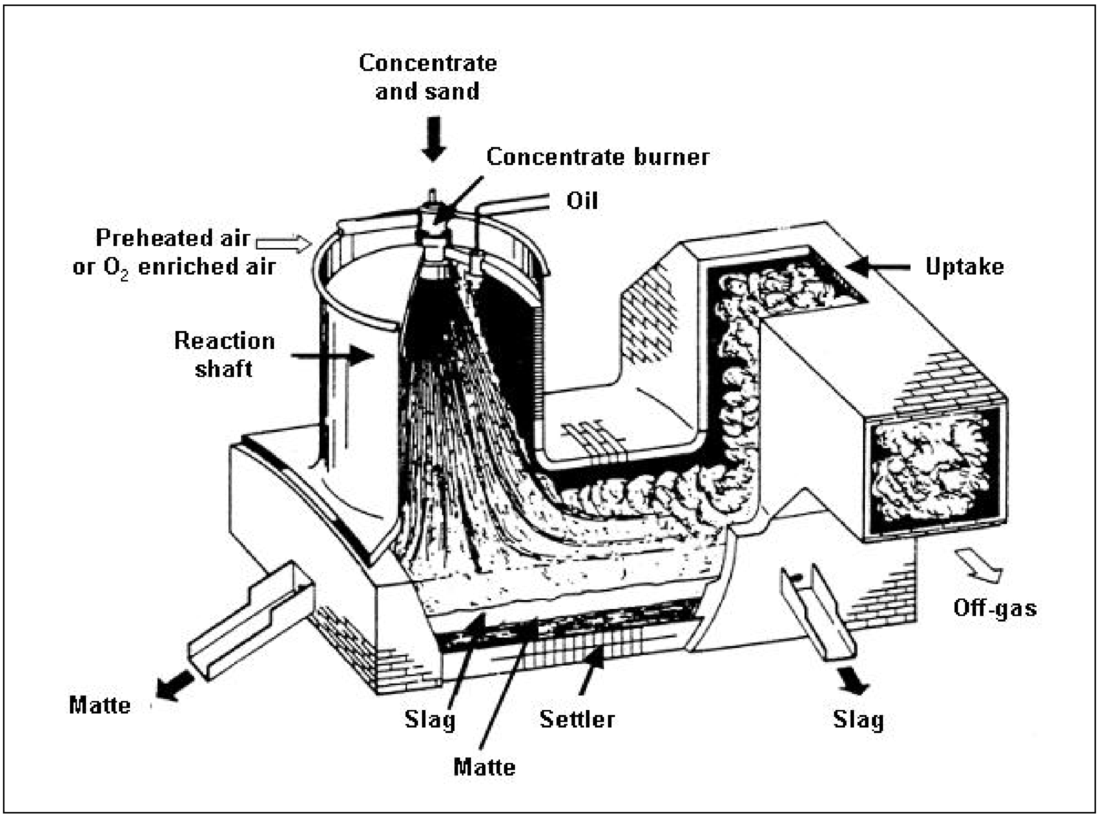


**Figure 2.29: The Outotec flash furnace**

The flash furnace is established for the production of copper and nickel matte. The furnace produces a high-grade matte and so the main part of the sulphur in the concentrate is released in the smelter gases and enables the conversion process (e.g. the discontinuous Peirce-Smith converter) to eliminate the remaining sulphur more easily.

This process is also used to produce blister copper directly from suitable concentrates which are low in iron avoiding the need for a conventional converter that would produce additional sulphur dioxide. In this direct to blister process, the furnace slag contains a high copper concentration and so slag cleaning to remove this copper is an essential part of the process.

The furnace has been used on a demonstration scale for the production of lead bullion, for pyrite smelting and for fuming jarosite waste.

The same type of furnace is also used in the flash converting process for the conversion of ground, granulated matte into blister copper. The process has similar features to the flash smelting process, i.e. autogenous operation with oxygen-enriched air and a continuous flow of off-gas with a high sulphur dioxide content.

### 2.8.2.13 INCO furnace

The INCO is a flash furnace similar to the Outotec flash furnace but uses pure oxygen to operate autogenously. Copper ore concentrate blended with slagging agents are blown horizontally into the furnace from both ends and the off-gases are collected at the centre of the furnace.

The INCO furnace is shown in Figure 2.30.

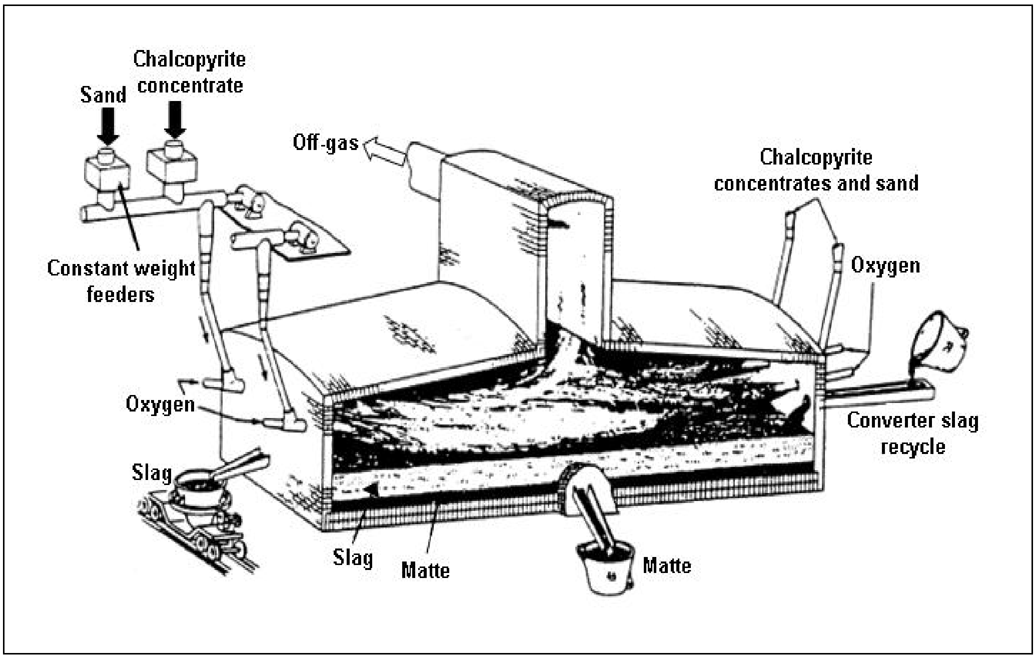


**Figure 2.30: The INCO Furnace**

The concentrates are roasted and melted in suspension in the furnace and fall into the settler in the same manner as the Outotec flash furnace. The heat produced by roasting is sufficient for an autothermal smelting process. The slag, which has a medium copper content, flows out continuously at one end of the furnace and the matte is tapped periodically at the centre of one sidewall. The waste gas contains up to 75 % $SO_2$.

### 2.8.2.14 Kivcet (KSS) furnace

The Kivcet is a flash furnace similar to the Outotec flash furnace. Dry and blended charge components and oxygen are fed continuously through burners at the top into an oxidation shaft. At the same time, coke breeze is added. The furnace is shown in Figure 2.31.

The charge is ignited as it enters the reaction shaft, temperatures of up to 1400 °C are reached and complete desulphurisation takes place immediately. The coke breeze is only heated as it falls down the shaft. The coke floats on the slag bath and reduces PbO. Partly reduced slag and bullion flow under a submerged partition wall into the reduction section of the furnace, which is electrically heated and where additional coke or coal is added for final reduction.

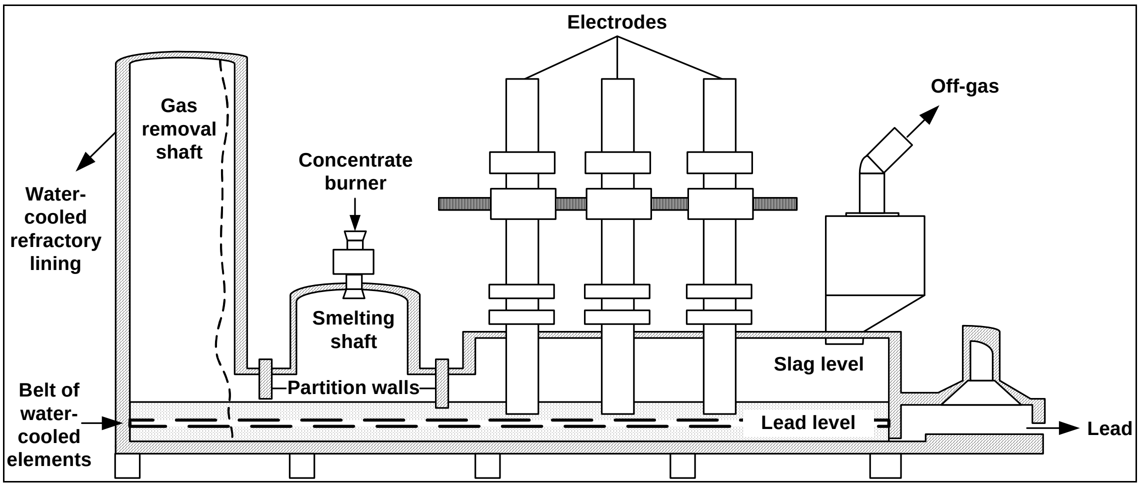


**Figure 2.31: The Kivcet Furnace**

Lead bullion is sent for refining, the slag may be sent to a Waelz kiln, and the flue dust from the oxidation is directly sent back to the furnace. The process is also used for copper production. The flue dust from the reduction stage is treated in an ISF.

## 2.8.3 Converters

### 2.8.3.1 The Peirce-Smith Converter

Peirce Smith Converters (PSC) are run batch-wise and use tuyères to blow air or oxygen into the matte to react the matte in two-stages to produce blister copper or high-grade nickel matte and slag. They are also used for the production of ferro-nickel and some metal oxides. Automatic slag quality control can also be used [ 329, Magnus and Olsson 2007 ]. This is by far the most common converting vessel and is used to produce copper and high-grade nickel matte and for refining ferro-nickel. The furnace is shown in Figure 2.32.

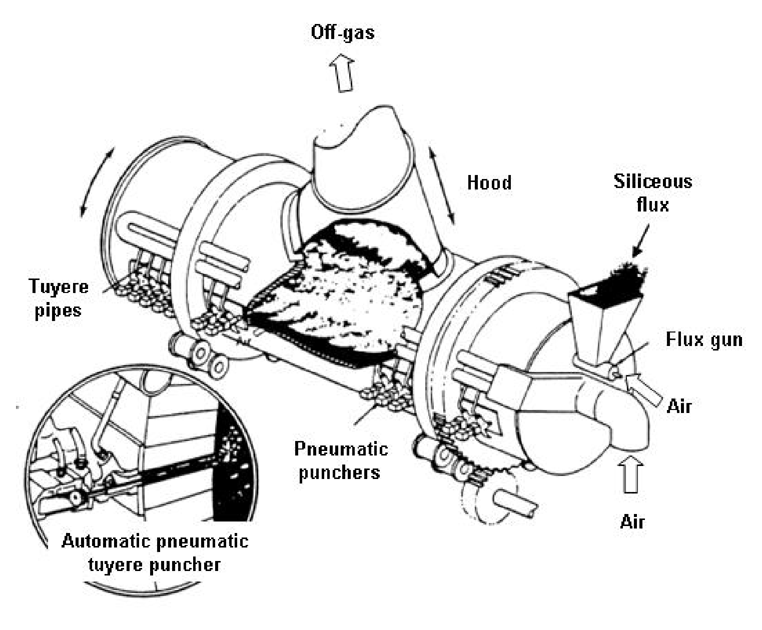


Figure 2.32: The Peirce-Smith converter

The converter can also be used for three different types of converter duties and as an anode furnace:

**a) Matte converter**

Large volumes of hot gases are produced during the blowing periods and are collected by means of hoods over the converter opening. The space between the converter housing and the hood allows the access of bypass air, which causes dilution of the $SO_2$-rich effluent gases. The $SO_2$ concentration varies depending on the process cycle. During initial blowing, $SO_2$ concentrations can be considerably higher than 10 %, however, during the subsequent blowing period, and when the converter is turned away from the hood, $SO_2$ concentrations are much lower and often nil. The varying $SO_2$ concentration does not provide a satisfactory feed to the acid plant, which requires a relatively steady flow. This is overcome in multi-converter plants by converter scheduling to attain a relatively steady flow. The gases can also be mixed with the much stronger smelter gases. The use of oxygen for enriching the blast air will also increase the $SO_2$ content; however, the enrichment is limited due to the rapid increasing refractory wear. Water-cooled hoods are now being used in some plants.

The converter is charged via ladles with liquid matte and the slags produced during the conversion of the matte and the blister copper produced are subsequently poured into ladles from the converter. During these tapping processes, diffuse emissions are released. The use of additional fume extraction facilities (e.g. secondary hoods and air curtains) and the control of converter positioning to prevent blowing during the converter roll out, can reduce these emissions. Through-hood and tuyere charging systems are also used so that it is not always necessary to tilt the converter away from the hood during the charging of metal scrap and fluxes.

**b) Scrap converter**

In secondary copper melting (Peirce-Smith) converters are distinguished into scrap converters and matte converters - both operated batch-wise. Scrap converters use coke and iron-rich materials as fuel and reducing agents respectively. In matte converters, the matte-borne sulphur is used as the energy source. Input materials for scrap converters include alloy scrap, suitable Cu-Fe scrap as well as (mostly liquid) black copper. The matte converter processes liquid copper-lead matte and copper-rich return slags in some cases, together with black copper - with the addition of solid copper scrap. Matte converter off-gas contains high $SO_2$ concentrations and is sent to a contact process unit for sulphuric acid production. This is why matte converters for secondary copper recovery are predominantly installed in primary copper production sites as these are equipped with sulphuric acid production units.

**c) Alloy converter**
The direct to blister flash furnace process produces a slag that is treated in an electric furnace to produce a lead/iron/copper alloy. This alloy is converted using a batch process in which the oxidised iron and lead pass into the slag phase and blister copper is produced.

**d) Anode furnace**
The PSC is also used as an anode furnace where the blister or black copper produced by the converter are refined. These furnaces use tuyères for further air blowing followed by the addition of a reducing agent (usually natural gas or propane) to remove the final traces of sulphur and then convert copper oxide to copper.

#### 2.8.3.2 Hoboken converter

The Hoboken converter operates on the same blowing principle as the Peirce-Smith Converter but the large escape of gas that usually occurs when the converter is tilted for charging and tapping the slag and crude copper is avoided.

The effluent gas is sucked off through the flue at the end of the converter. The siphon minimises gas escape during all phases of operation. The converter is charged through a small opening at the top of the casing and charging is therefore possible during blowing without tilting the converter because of the shorter process duration. Dilution of the effluent gases due to infiltrated air is small, so that the steady average concentration of $SO_2$ is higher than for the Peirce-Smith converter. However, the $SO_2$ concentration will still vary throughout the cycle. The end result is that there is a smaller loss of $SO_2$ from the converter. The smaller opening used for charging can create problems due to slag buildup.

The Hoboken converter is shown in Figure 2.33.

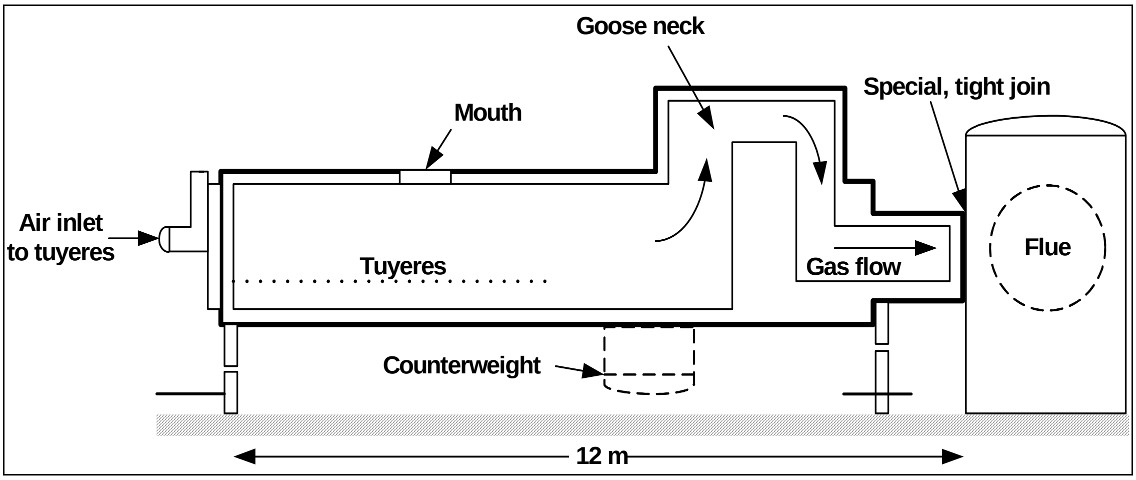


**Figure 2.33: The Hoboken converter**

#### 2.8.3.3 Kennecott/Outotec flash converter

The Kennecott/Outotec flash converter is also used and has been developed further since the original BREF document was written and a second installation is being commissioned. In this case, ground matte produced by a flash smelting furnace is used as the feed material. The

Mitsubishi converting stage and the flash converter are the only continuous converters in metallurgy.

### 2.8.3.4 Other converters

The Ausmelt/ISA Smelt furnace, the TBRC, the converter stage of the Mitsubishi process and the Noranda reactor are also used as converters. These furnaces use molten matte as the feed material and some may be operated continuously. The OBM converter is used for ferro-nickel.

The AOD converter is used for ferro-manganese production using oxygen for decarburisation and argon for degassing in the same manner as in the steel industry [ 243, French comments on MnFe alloys 2008 ].

## 2.8.4 Melting and refining furnaces

### 2.8.4.1 Induction furnaces

Induction furnaces are simple crucibles or channels that are heated by an external electrical coil, channel induction furnaces are mainly used for melting items with large dimensions. In one case, the channel furnace is used to melt aluminium cans.

The induction furnace is shown in Figure 2.34.

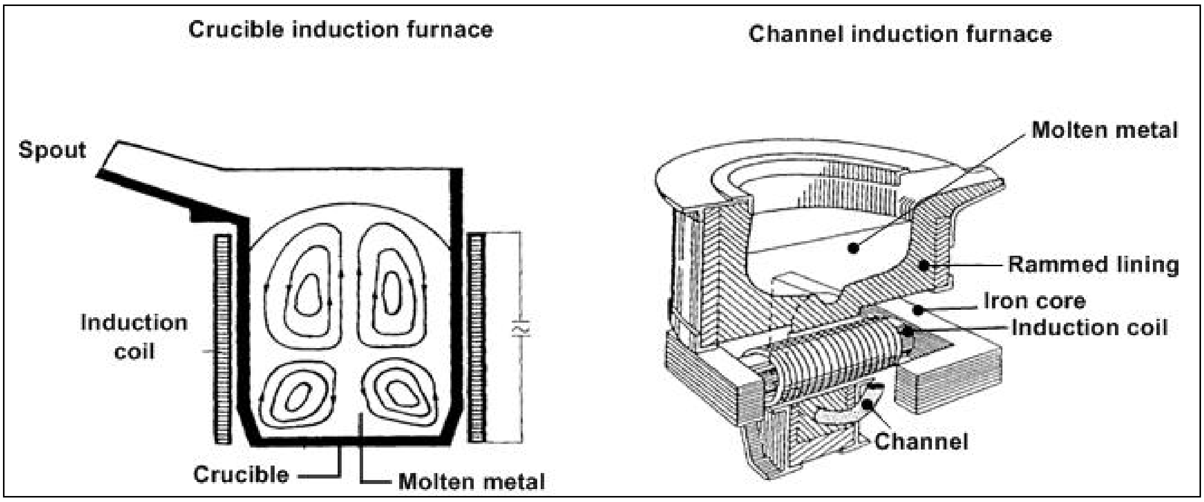


**Figure 2.34: Induction furnaces**

A current is induced in the metal that has been charged into the furnace and heat is generated. The furnaces are equipped with fume extraction hoods and dust abatement that can be used during drossing and pouring operations. Access to an induction furnace for charging and tapping means that a movable hooding system is often used. The hoods are robust so that they can withstand some mechanical impact. Alternatively, efficient fixed or lip extraction is used.

The efficiency of this furnace can be low for some materials but can be increased particularly if the feed material is small. Large items can be cut to improve efficiency and also to allow the fume collection hoods to be deployed properly. Some continuous processes also retain a heel of molten metal in the bottom of the furnace between charges if the operation allows it.

These furnaces are used for small melting capacities of up to 30 tonnes commonly for copper, brass, zinc and aluminium. They may also be operated under vacuum, for example when melting super alloys, high alloyed steel, pure metals and, in some cases, for metal distillation.

The temperature of the furnace can be automatically controlled to minimise the production of fumes when melting volatile or oxidisable metals such as zinc or alloys that contain zinc.

These furnaces are also used to hold molten metal for alloying and casting. The current induced in these furnaces causes the metal to be stirred electromagnetically, which promotes mixing of the charge and any alloying materials that are added.

#### 2.8.4.2 Indirectly heated kettles

Indirectly heated kettles are simple crucibles that are heated externally by the combustion gases from gas or oil combustion, by electricity or for lower temperatures by thermal fluid. Contact with a direct flame is avoided to prevent local hot spots at the base of the crucible and good temperature control can be maintained in the melt so that oxidation and vaporisation of the metal is prevented.

These kettles are used mainly for melting impure lead and lead alloys and zinc and its alloys which do not contain plastic or other organic materials.

#### 2.8.4.3 Shaft furnaces for melting metal

Shaft furnaces are simple vertical furnaces with a collecting hearth (inside or outside the furnace), a burner system at the lower end and a material charging system at the top. The burners are usually gas-fired and are designed to produce an oxidising or reducing atmosphere. This allows the metal to be melted with or without oxidation. Metal is fed into the top of the furnace and is melted as it passes down the shaft. Independent control of the fuel to air ratio is usually provided for each burner. Continuous CO or hydrogen monitoring is also provided for each row of burners and monitors the combustion gases from each burner in turn. Combustion gases are usually extracted and cleaned. An afterburner is used sometimes to decompose any carbon monoxide, oil, VOCs or PCDD/F that are released. The addition of oxygen above the melting zone has been used to provide afterburning in the upper levels of shaft or blast furnaces.

The furnace is used to melt pure metal but occasionally metal that is contaminated with organic material is used. If oily metal is fed into the furnace it passes through the temperature gradient that exists between the charging area and the burners. The low temperature can produce a mist of partially burnt organic material. The shaft furnace is also used to preheat the charge material before smelting.

#### 2.8.4.4 Contimelt process

The Contimelt process comprises two interconnected furnaces, a hearth shaft furnace and a drum (or poling) furnace. The first is a vertical rectangular furnace with a horizontal collecting chamber which is fed with blister or black copper and other raw materials. Oxy-gas burners supply heat and the feed is melted to produce a fire-refined copper and a small amount of slag that is separated.

The Contimelt process is shown in Figure 2.35.

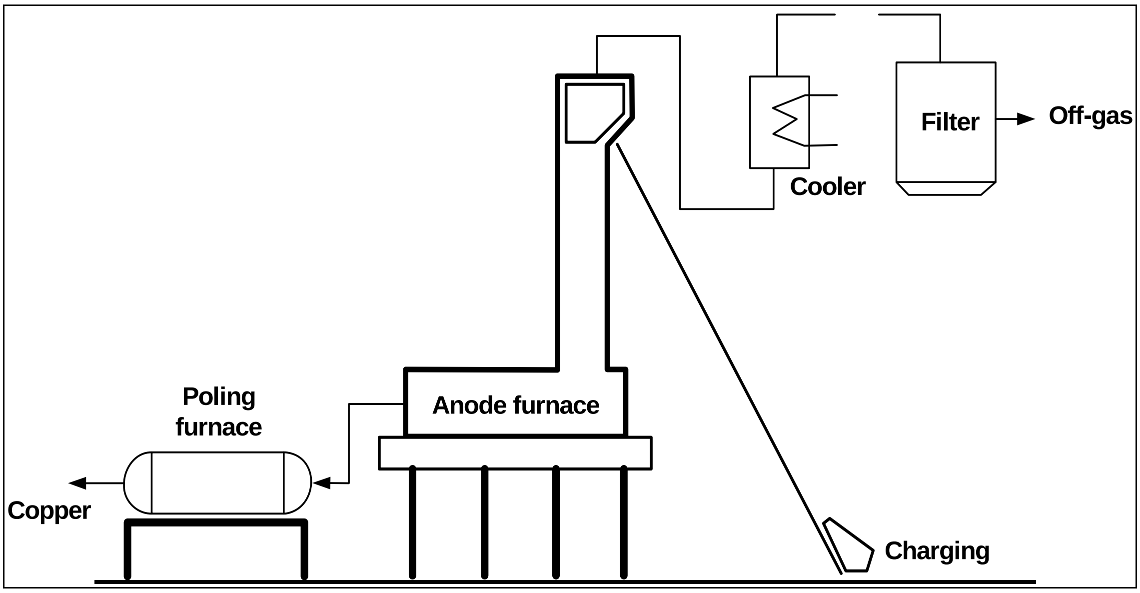


**Figure 2.35: Contimelt Process**
[ 121, Rentz, O. et al. 1999 ]

Molten copper flows via a siphon and a launder to a horizontal cylindrical furnace where it is de-oxidised using natural gas. Refined copper is then cast as anodes. Gases from the second furnace are passed to an afterburner. They are then combined with gases extracted from the first furnace and pass to a waste heat boiler, burner air preheater, cooling stage and finally a fabric filter.

The furnace operating conditions can be controlled to minimise oxidation of the metal. The arrangement allows heat recovery by steam generation or charge preheating.

This is a continuous two-stage process to melt and treat black and blister copper, high grade copper scrap and anode scrap to produce copper anodes. A similar development in the aluminium industry is the Meltower process [ 113, ALFED 1998 ]. This process uses a vertical melting tower and incorporates charge preheating using the hot exhaust gases.

#### 2.8.4.5 Electron beam furnaces

The very high melting temperatures of refractory metals like tungsten, tantalum or niobium do not allow melting in a normal melting furnace. For high melting point metals, the electron beam furnace has been developed using accelerated electrons as an energy source to impart their energy into the furnace charge. The electron beam melting furnace is used to produce high-purity inclusion-free metals. The ability to melt high-purity metals is due to the perfectly clean high temperature heat source (electrons) and the water-cooled copper hearth. The melted metal freezes against the copper so that the melt is only in contact with its own solid. Electron beam melting and refining is a well-established process for the production of ultra-clean refractory metals.

#### 2.8.4.6 Rotary furnace

The rotary furnace is a refractory-lined rotating cylinder fitted with burner at one end. A charging door is provided at one end and the burner can sometimes be housed in this. Oxy-fuel firing can be used. The furnaces can be either long or short and several variants exist:

- short rotary furnace for the smelting of secondary lead, precious metals, etc.

- long rotary furnace for the melting and recovery of aluminium scrap, etc.
- Thomas furnace for the melting and refining copper scrap, etc.
- rotary furnace with submerged tuyères for the refining of blister or black copper, slag cleaning, etc.
- tilting rotary furnace: for the melting and recovery of aluminium scrap, lead, dross, etc.
- rotary/rocking furnace also called the Doerschel furnace used for the smelting of secondary lead.

Furnace rotation can be varied to give a complete reaction of the charged material and high efficiency. Raw materials are usually charged via an end door; this is usually enclosed and extracted to prevent fume emissions. The furnaces use oil or gas fuel and oxy-burners are commonly used. Heat from the burner is transferred to the refractory wall and the charge is heated by the refractory during rotation.

Slags and metal produced during the process can be tapped from a tap-hole at the door end or at the mid-point of the furnace. The tapping hole is orientated by partial rotation of the furnace to maintain the separation of the metal and slag. Tapping from the door end allows fumes to be collected from a single enclosure and extraction system. Tilting rotary furnaces are also used, they show improved recovery rates for some feedstocks and are less reliant on fluxes. A variety of metals can be smelted or melted in these furnaces.

#### 2.8.4.7 Reverberatory (closed-well) furnaces

The reverberatory furnaces are used for batch melting, refining and holding a variety of metals, particularly aluminium. They are refractory-lined, rectangular or circular bath furnaces fired by wall or roof mounted burners. They are often operated in a variety of configurations sometimes with a sloping hearth where mixed metal objects can be placed and aluminium is separated from other metal components such as iron to prevent the contamination of the batch of aluminium. They can also vary in the number of wells or chambers that are used [ 234, UBA Copper, lead, zinc and aluminium 2007 ].

Varieties of fuels are used and oxy-fuel burners can be used to increase the melting rate. Extraction and treatment of the combustion gases is used and the furnaces are partially sealed. Hoods and covered launders provide extraction during tapping and charging. Slag or dross can be removed by raking or by tapping.

Many designs have large access doors that allow large objects to be charged. This introduces the problem of sealing and extraction during charging. Water cooling of the doors can reduce this problem by reducing warping of the doors. Sealed charging carriages are used and charging pipes can be used for concentrates. In a similar manner, door sealing can be affected by material being incorrectly charged to the furnace. In some cases, spilt metal or slag can solidify in the opening or in other cases, wire or cable can prevent the doors from closing properly.

The melting efficiency of a reverberatory furnace is not usually high because of poor heat transfer from the burner. Efficiency has been improved in practice by using oxygen enrichment or by using combinations of gas and solid fuel to extend the flame length. The use of regenerative burners reduces energy consumption significantly. Stirring of the contents using electromagnetic systems or pumps can also improve efficiency. The pumped systems can be operated with a side-well to allow the melting of fine metal particles with minimum oxidation.

### 2.8.5 Summary of furnaces in common use

The furnaces used in these industries are summarised in Table 2.10, Table 2.11 and Table 2.12.

| Furnace | Metals used | Material used | Comment |
|---|---|---|---|

| | | | |
|---|---|---|---|
| Steam coil dryer<br>Fluid bed dryer<br>Flash dryer | Copper and some others | Concentrates | |
| Rotary kiln | Most metals for drying;<br>fuming ZnO;<br>calcining alumina, nickel and ferro-alloys;<br>burning film in precious metals;<br>de-oiling copper and aluminium scrap;<br>mercury removal from gas-cleaning precipitates. | Ores, concentrates and various scrap and residues | Drying, calcining and fuming applications<br>Used as an incinerator |
| Fluidised bed reactor | Copper, nickel, cobalt, precious metals, zinc and $Al_2O_3$ | Concentrates and $Al(OH)_3$ | Calcining and roasting |
| Up-draught sintering machine | Zinc and lead | Concentrates and secondary raw materials | Sintering |
| Down-draught sintering machine | Zinc and lead | Concentrates and secondary raw materials | Sintering |
| Steel belt sintering machine | Ferro-alloys, manganese and niobium. | Ore | Other applications possible |
| Herreshoff | Mercury and refractory metals, molybdenum (rhenium recovery) | Ores and concentrates | Roasting, calcining |

**Table 2.10: Drying, roasting, sintering and calcining furnaces**

| Furnace | Metals used | Material used | Comment |
|---|---|---|---|
| Enclosed refractory-lined crucibles | Refractory metals and special ferro-alloys | Metal oxides | |
| Open pit | Refractory metals and special ferro-alloys. | Metal oxides | |
| Baiyin | Copper | Concentrates | |
| Electric arc furnace | Ferro-alloys | Concentrates, ore, secondary materials | |
| Contop/cyclone | Copper | Concentrates, ores | |
| Submerged electric arc furnace | Precious metals, copper and ferro-alloys | Slag, secondary materials, concentrates, ores | For the production of ferro-alloys, the open, semi-closed and closed types are used |
| Rotary | Aluminium, lead and precious metals | Scrap and other secondary raw materials | Oxidation and reaction with substrate |
| Tilting rotary furnace | Aluminium<br>Lead | Scrap and other secondary raw materials<br>Flue dusts that contain lead and secondary material. | Minimises salt flux use<br>Flue dust from primary copper production. Battery recovery |
| Rotary/rocking furnace | Lead | Smelting of secondary lead | Also called the Doerschel furnace |
| Reverberatory and hearth/well furnaces | Aluminium, copper and others | Scrap and other secondary raw materials | Smelting of oxidic copper material, refining |
| Vanyukov | Copper | Concentrates | |
| Ausmelt/ISA Smelt//KRS | Copper and lead | Intermediates, concentrates and secondary raw materials | |
| QSL | Lead | Concentrates and secondary raw materials | |
| Kivcet | Lead and Copper | Concentrates and secondary raw materials | |
| Noranda | Copper | Concentrates | |
| El Teniente | Copper | Concentrates | |
| TBRC *(KALDO)???*<br>TROFF | Copper, lead, tin and precious metals | Most secondary raw materials including slimes | |
| Mini smelter | Copper/lead/tin | Scrap | |
| Blast furnace and ISF | Lead, lead/zinc, copper, precious metals,<br>HC FeMn | Concentrates, most secondary | |
| INCO flash furnace | Copper and nickel | Concentrates | |
| Outotec flash furnace | Copper and nickel | Concentrates | |
| Mitsubishi process | Copper | Concentrates and anode scrap | |
| Peirce Smith | Copper (converter), ferro-alloys, metal oxide production | Matte and anode scrap | |
| Hoboken | Copper (converter) | Matte and anode scrap | |
| Outotec flash converter | Copper (converter) | Matte | |
| Noranda converter | Copper (converter) | Matte | |
| Mitsubishi converter | Copper (converter) | Matte | |

**Table 2.11: Smelting and converting furnaces**

| Furnace | Metals used | Material used | Comment |
|---|---|---|---|
| Induction | Most | Clean metal and scrap | Induced stirring assists alloying. Vacuum can be applied for some metals |
| Electron beam | Refractory metals | Clean metal and scrap | |
| Rotary | Aluminium and lead | Various scrap grades | Fluxes and salts used for complex matrices |
| Reverberatory (also known as hearth or closed-well furnaces) | Aluminium (primary and secondary) | Various scrap grades (An additional side-well can be used for fine metal particles) | Bath or hearth configurations can vary. Melting or holding metal |
| Contimelt | Copper | Copper anode and clean scrap | Integrated furnace system |
| Shaft | Copper | Copper cathode and clean scrap | Reducing conditions |
| Drum (Thomas) | Copper | Clean copper scrap | Melting and fire-refining |
| Heated crucibles (indirect kettles) | Lead and zinc | Clean scrap and raw metal | Melting, refining and alloying |
| Direct heated crucibles | Precious metals | Clean metal | Melting and alloying |

**Table 2.12: Melting furnaces**

## 2.8.6 Electrochemical processes

### 2.8.6.1 Electrowinning

In electrowinning, an electrolytic cell is used consisting of an inert anode of lead or titanium and a cathode, placed in an aqueous electrolyte comprising the metal solution. The cathode is either a thin blank of pure metal (starter sheet) or a former sheet made from stainless steel or aluminium (permanent cathode plate). Metal ions pass from the solution and are deposited onto the cathode, and gases such as chlorine or oxygen are evolved at the anode. Chlorine is collected in a sealed anode compartment but oxygen is usually released and may entrain some of the electrolyte and produce an acid mist, which may need to be collected and returned to the process. Cell hoods and gas-cleaning equipment or the use of beads or a foaming agent are needed to prevent mist from entering the workplace or environment. Depleted electrolyte is normally returned to the process.

Copper, cobalt, nickel, tin, zinc and precious metals are produced in this manner. When using permanent cathode plates, the pure metal deposits can be stripped or scraped off, melted and cast into the required shapes.

### 2.8.6.2 Electrorefining

In electrorefining, an electrolytic cell is used consisting of a cast anode of the metal to be refined and a cathode, placed in an electrolyte comprising the metal solution. The cathode is either a thin blank of pure metal (starter sheet) or a former sheet made from stainless steel (permanent cathode plate). Metal ions are dissolved from the impure anode and pass into the solution from where they are deposited onto the cathode.

Copper, precious metals, lead and tin are refined in this manner. When using permanent cathode plates, the pure metal deposits can be stripped or scraped off, melted and cast into the required shapes.

During Electrorefining, other metals contained in the anodes are separated, less noble metals are dissolved in the electrolyte and more noble metals like the precious metals, selenium and tellurium form an anode slime that settles in the electrolytic cells. Anode slimes are periodically removed from the cells and the valuable metals are recovered. In some cases, anode bags are used to contain the slimes.

A portion of the electrolyte is bled from the system and other metals recovered from it.

#### 2.8.6.3 Molten salt electrolysis

In molten salt electrolysis an electrolytic cell is constructed using inert cathodes and anodes (steel or carbon) so that the high electrolyte temperatures can be withstood. Molten metal is deposited at the cathode and is removed periodically by vacuum or displacement. Gases such as chlorine or oxygen are evolved at the anode; chlorine is collected and recycled or sold. For aluminium, oxygen reacts with the carbon anode, which is continuously consumed.

Molten salt electrolysis can be used to produce aluminium, lithium, sodium and magnesium.

### 2.8.7 Hydrometallurgical processes

Acids and NaOH, sometimes also $Na_2CO_3$ are used to dissolve the metal content of a variety of ores and concentrates before refining and electrowinning. The material to be leached is usually in the form of the oxide, either as an oxidic ore or an oxide produced by roasting [ 134, Metallurgical Consulting Traulsen GmbH 1998 ]. Direct leaching of zinc concentrate is also done at both elevated and atmospheric pressure.

Some copper sulphide ores can be leached with sulphuric acid or other media sometimes using natural bacteria to promote oxidation and dissolution, but very long residence times are used. Air or oxygen or chlorine can be added to leaching systems to provide the appropriate conditions, and solutions that contain ferric chloride are also used. The Hydro Copper and similar processes have been developed to extend the range of ores and concentrates that can be treated by hydrometallurgy [ 308, Hydrocopper 2007 ].

The solutions that are produced are treated in a number of ways to refine and win the metals. Common practice is to return the depleted solutions to the leaching stage, where appropriate, to conserve acids and alkaline solutions.

#### 2.8.7.1 Heap leaching

Open heap leaching is usually carried out at the mine. Material is crushed and ground to allow intimate particle/acid contact and is then formed into natural heaps on an impervious liner. Acid is sprayed onto the heaps and percolates through the mass [ 127, Chadwick, J. 1994 ]. It is collected on the liner and is recirculated to allow the metal content to buildup . Leaching time of a single heap can vary from 100 days for copper oxide ore to 500 days for copper sulphide ore.

Bacteria can be used to enhance the leaching process and improve efficiency and this technique is used for some nickel ores where zinc, cobalt and copper are leached simultaneously and then separated prior to metal recovery [ 284, Talvivaara June 2008 ]. The advantages of bio-heap leaching are that:

- it is based on a naturally occurring process, the bacteria promote leaching of metals from ore to solution;
- irrigation and aeration are the only additional processes;
- there can be substantially lower capital and operating costs than in traditional smelting and refining processes.

### 2.8.7.2 Atmospheric leaching (open tank)

Atmospheric leaching of oxides and concentrates is carried out in open or partially enclosed tanks by recirculating the mixture to maintain the temperature and acid concentration. The system is usually operated in a number of tanks in series. This is followed by sedimentation to separate the residue and purification and winning of the metal solution. Some leach residues can be leached further when the acid strength and temperature are increased. The use of a number of leaching stages can improve the leaching efficiency but can result in the dissolution of more impurities, particularly iron, which subsequently should be removed. The addition of oxygen and mixing it with the leachate by agitation can enhance the process.

### 2.8.7.3 Pressure leaching (autoclaving)

Pressure leaching or autoclaving can be carried out as a complete leaching process or as part of a series of leaching stages. Acid- or alkaline-resistant pressure vessels are used and liquor is recirculated to allow the reactions to proceed. Pressure leaching is also used to leach black copper to separate copper from other metals including precious metals.

Oxygen, air or chlorine can be added to increase oxidation. Pressure reduction stages can result in the production of acid mists and they are designed to contain them.

### 2.8.7.4 Solvent extraction

In solvent extraction, metals can be extracted from aqueous solutions with certain organic solvents that are insoluble in water. The aqueous and organic phases are dispersed in each other and by controlling the pH of the mix and the complexing agent used, the target metal is selectively extracted into the organic phase. After phase separation, a pure metal solution is obtained by re-extracting the metal from the organic phase into a secondary aqueous phase (stripping), from which the metal can be won in different ways [ 309, A MODERN VSF™ SX PLANT 2007 ]. Figure 2.36 shows the principle for such a process to produce copper. Other metals such as cobalt and zinc can also be treated in this way.

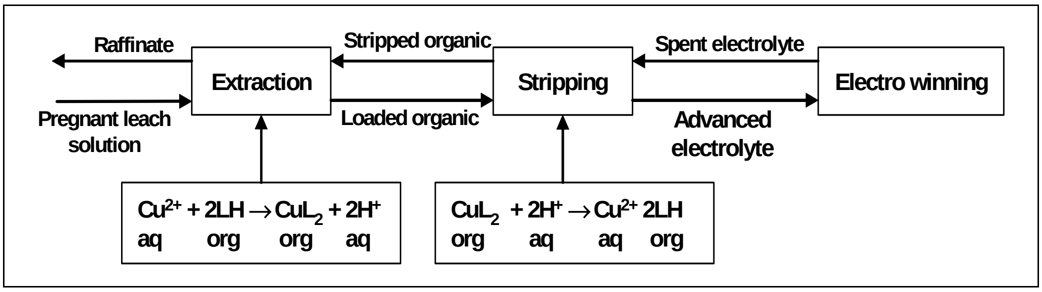


**Figure 2.36: Solvent extraction (SX) processing stages**

Solvent extraction can be used to selectively concentrate and purify solutions that contain zinc from either primary or secondary raw materials. The result is a pure zinc solution that can be used to produce SHG zinc after electrolysis or pure zinc sulphate, zinc oxide or other zinc chemicals.

The Zincex process originally used two different solvent extraction circuits, the first uses an anionic extractant a secondary amine, (Amberlite LA-2) and the second uses a cationic extractant di-2-ethylhexyl-phosphoric acid (D2EHPA) to separate zinc from impurities and also. Increase the zinc concentration to produce a pure zinc sulphate electrolyte. The process has been simplified and enhanced to use only one solvent extraction cycle with D2EHPA and is integrated in the three main stages of leaching, solvent extraction and electrowinning, [ 327, Highlights and hurdles in Zinc production by solvent extraction 2008 ].

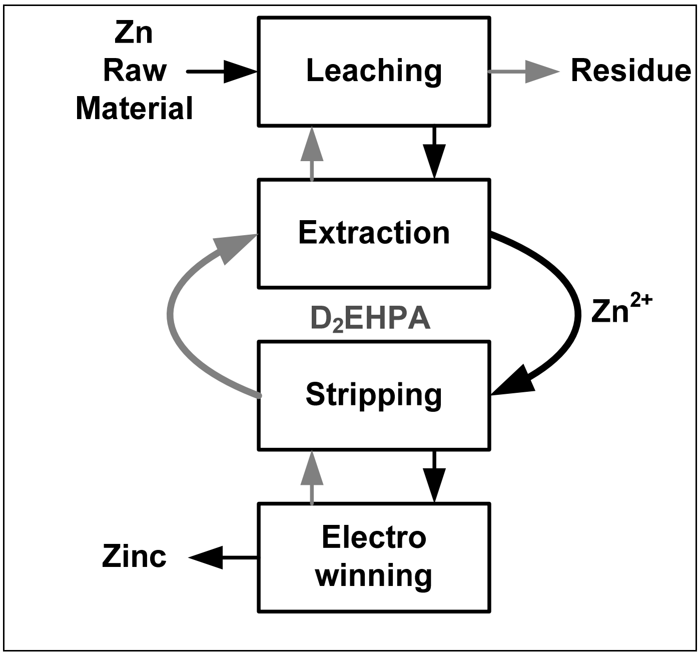


**Figure 2.37: Process diagram of the modified Zincex process**

When applied to primary zinc ores and concentrates, the process involves atmospheric leaching of the raw material , upgrading and purification of the pregnant leach solution by solvent extraction (SX), and zinc recovery by electrowinning (EW). The SX stage is also used to recover zinc from dirty secondary raw materials such as batteries.

# 2.9 Air abatement and recovery techniques

## 2.9.1 Applied processes and techniques

Collected gases are transferred to an abatement plant where contaminants are removed and some components recovered. Dust and acid gases are commonly removed and valuable or toxic metal components are recovered for use in other processes. The design of the abatement process is critical, and factors such as efficiency, suitability of the method and the input and output loading of the material to be collected are used.

The following Section 2.9.2 describes the techniques that have been reported and observed during site visits that are the applied processes and techniques. These are also the techniques to consider in the determination of BAT. More information is given in the techniques described in the metal-specific chapters.

## 2.9.2 Techniques to consider in the determination of BAT

The sections of this document entitled 'Techniques to consider in the determination of BAT' set out techniques considered generally to have potential for achieving a high level of environmental protection in the industries within the scope of the document. The background to the way the techniques are described is given in Section 2.1.2 and Table 2.2.

### 2.9.2.1 Design and control techniques for an abatement plant

**Description**

The choice and design of a suitable abatement technique is particularly important. Several techniques exist and, although some may seem to offer a very high performance, problems may be encountered unless the characteristics, such as the loading and nature of the gases, dust and other components are fully considered. For example, a fabric filter using modern materials is considered to offer better environmental performance than other techniques for dust removal; however, it cannot be considered to be universally applicable due to problems of stickiness and abrasion with some types of dust. These issues are specific to individual sites and materials and the operator should take these factors into account in a professional design brief.

The volume, pressure, temperature and moisture content of the gas are important parameters and have a major influence on the techniques or combination of techniques used. In particular, the dewpoint will be affected by all of these parameters and their variations throughout a production cycle should be taken into account.

The characterisation of the nature of the dust or fume is very important so that it is possible to identify any unusual properties of the dust (hygroscopic, pyrophoric, sticky, abrasive, etc.). The particle size and shape, wetability and density of the material are also factors to optimise the choice of technique. The dust concentration and its variability should also be taken into account producing a reliable, robust design.

Many operators have identified that performance may deteriorate with time as equipment wears and maintenance is needed. Modern systems should be used to continuously monitor performance by direct measurement of the gases emitted (for example, dust, CO, $SO_2$). For example, dust can be monitored by using electrodynamic techniques. This is a technique based on a charge induction principle derived from particle interaction with probe inserted into a stack or duct. Alternatively, critical control parameters can be monitored. Alarm systems should be incorporated into these systems.

**Achieved environmental benefits**

The prevention of emissions of metals, dust and other compounds.

**Cross-media effects**

Energy usage is increased due to an increase in pressure drop in the system. Wet scrubbers and wet ESPs produce an effluent that must be treated before discharge.

**Operational data**

Process operation and control is used extensively in this sector. The following techniques are important:

- Use of reagent metering systems.
- Use of microprocessor control of reagent feed and plant performance. On-line monitoring of temperature, pressure drop, dust or other pollutants emitted, ESP current and voltage and scrubber liquor flow and pH are used. Alarms are provided to indicate operational problems.
- Operators are trained and assessed in the use of operating instructions and the use of the modern control techniques described.
- Levels of supervision are optimised to take advantage of the above and to maintain operator responsibility.
- Use of environmental management and quality systems.
- Use of predictive or other mathematical models to assess trends in operating conditions for example in the copper and aluminium industries, to prevent emissions or to optimise the process.
- Use of robust maintenance systems. There is growing use of dedicated maintenance staff forming part of the operator teams.
- Use of routines to check the reliability of weighing systems.
- Use of filter bag burst detection based on interface between the dust monitor and the cleaning cycle.
- Use of small furnaces to smelt samples of the raw materials so that optimum blends of raw materials and fluxes can be identified and the optimum furnace operation established. This technique is also used to determine the content of metals in each consignment so that purchase prices can be agreed upon.

Good process control is used to achieve these gains and also to maintain safe conditions and to analyse past events and process responses. The implementation of a capable process control system is required for all modern non-ferrous smelting and operating processes, so without a good process control system an operation cannot be considered to be BAT practice.

There are a number of cases (e.g. blast furnaces) where the development and use of modern process control is needed. More work is needed to identify the relevant control parameters and systems.

**Applicability**

These techniques are generally applicable to most plants.

**Economics**

The processes are operating economically and costs, where they are available, are reported in Annex I to this document.

**Driving force for implementation**

Reduction of emissions and possible saving in raw materials.

**Example plants**

Plants in DE, AT, FR, BE, PL.

**Reference literature**

[ 226, Nordic Report 2008 ], [ 103, Farrell, F. 1998 ].

### 2.9.2.2 Dust and particle removal

The following techniques are used for the removal of particles such as dust and fumes from the various processes used by the industry.

#### 2.9.2.2.1 Electrostatic precipitators

**Description**

The electrostatic precipitator (ESP) is used extensively in the industry and is capable of operating over a wide range of temperature, pressure and dust burden conditions. It is not particularly sensitive to particle size, and collects dust in both wet and dry conditions. Corrosion and abrasion resistance is built into the design.

The ESP consists of a series of high voltage discharge electrodes and corresponding collector electrodes. Particles are charged and subsequently separated from the gas stream under the influence of the electric field generated between the electrodes. The electrical field is applied across the electrodes by a small direct current at a high voltage (100kV). In practice, an ESP is divided into a number of discrete zones (up to five zones are commonly used). The ESP is shown in Figure 2.38.

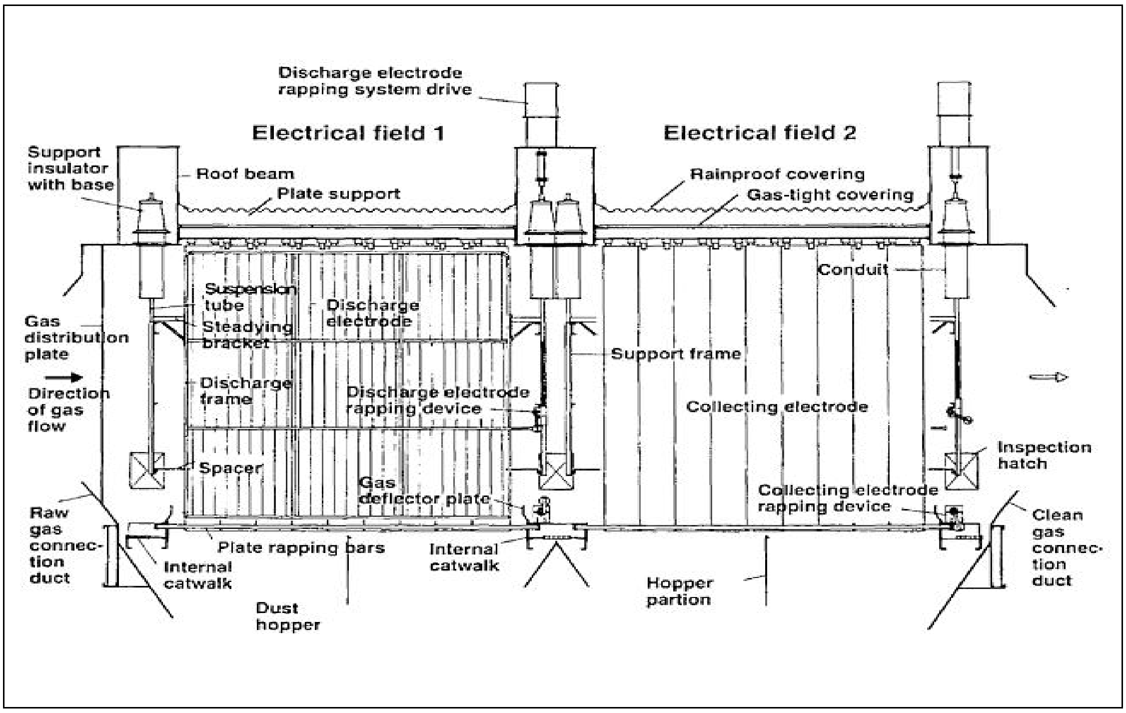


Figure 2.38: Typical arrangement of an electrostatic precipitator (only two zones shown)

Particles are removed from the gas stream in four stages;

- application of an electrical charge to the dust
- placement of the charged dust in an electrical field
- capture of the dust onto the collecting electrode
- removal of the dust from the surface of the electrode.

The discharge electrodes must be rapped or vibrated to prevent dust build-up and their mechanical strength must be compatible with the transmission of the rapping blow or vibration. The mechanical reliability of the discharge electrodes and their supporting frame is important as a single broken wire can short out an entire electrical field of the precipitator.

The performance of an ESP follows the Deutsch formula, which relates efficiency to the total surface area of collector electrodes, the volumetric flowrate of the gases and the migration velocity of the particles. Therefore, for a given dust, maximising the surface area of the collector electrodes is very important and current practice is to use wide electrode spacing. This practice relies in turn on good rectifier design and control.

The industry uses rectifier designs, which includes the use of separate rectifier sections for each zone or portion of a zone of the ESP. This allows the applied voltage to be varied in the inlet and outlet zones to take account of the reduced dust load towards the outlet and gives the ability to operate the zones at progressively higher voltages without sparking. Good design is also practised by using automatic control systems. They maintain the optimum high tension (HT) voltage applied to the electrodes in a particular zone without sparking. An automatic monitor is used to apply the maximum voltage without sparking and constantly varies the HT. Fixed HT power supplies are unlikely to provide optimal collection efficiencies.

**Achieved environmental benefits**
An ESP usually does not achieve final dust concentrations as low as those achieved by a fabric filter. To achieve the best performance from a precipitator, the gas flow through units are optimised to give a uniform flow to prevent gas from bypassing the electrical field. Correct design of inlet ducting and the use of flow distribution devices within the inlet mouthpiece are used to achieve uniform flow at the inlet to the precipitator. Dust emissions in the range of 5 to 20 mg/Nm$^3$ can be achieved depending on the particular application.

**Cross-media effects**
Increase in energy use.

**Operational data**
The resistivity (the inverse of the conductivity) of the dust is particularly important. If it is too low the particles reaching the collector electrode lose their charge easily and dust re-entrainment can occur. When the dust has a high a resistivity, an insulating layer is formed on the electrode, which hinders normal corona discharge and leads to a reduction of the collection efficiency. Most dusts have a resistivity within the correct range and collection can be improved by conditioning the dust. Ammonia and sulphur trioxide are commonly used. The resistivity can also be reduced by reducing the gas temperature or by adding moisture to the gas. Performance data is given in Table 2.15 and Table 2.16.

**Applicability**
This technique is generally applicable to most plants.

**Economics**
The processes are operating economically and costs, where they are available, are reported in Annex I to this document.

**Driving force for implementation**
Reduction of emissions and possible saving of raw materials.

**Example plants**
Plants in DE, AT, FR, BE, PL.
*(What is missing are examples were in the NFM industry |ESP's are applied and what they can achieve similar to table 2.14 in section 2.9.2.2.4. Usually with ESP's concentration from <1 to 20 can be achieved, depending on the type of dust, temperature, resistivity, raw gas concentration, size…)*

**Reference literature**
[ 196, Finkeldei, L. 1999 ], [ 73, Theodore, L. et al. 1992 ], [ 77, Soud, H.N. 1995 ], [ 189, VDI 1998 ], [ 195, Lurgi, A.G. et al. 1991 ].

#### 2.9.2.2.2 Wet electrostatic precipitator

**Description**
Wet electrostatic precipitators operate on the same principles. In this case, the collected dust is removed from the collector plates or tubes by the liquid film formed by condensing water and precipitated collected acid mist. In the case of a high solids content, built-in atomising nozzles can be used to spray water continuously into the precipitator to prevent the formation of sludge deposits on the collecting electrodes. The spray increases the liquid film on the collecting electrodes and reduces its solids content. In addition, wet precipitators are equipped with flushing systems. Flushing is carried out intermittently. The high voltage supply is interrupted during the flushing process. They offer advantages with certain dusts that adhere to conventional plates or when other components in the gas stream interfere with the operation, for example, in the case of a cool, damp gas. A liquid effluent is produced that requires further treatment. The wet ESP is shown in Figure 2.39.

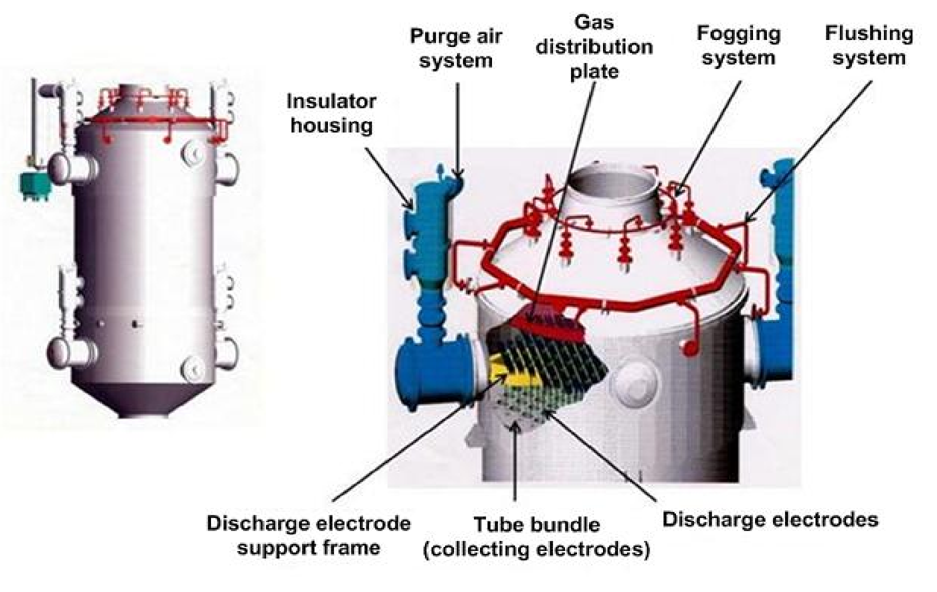


**Figure 2.39:** **Wet electrostatic precipitator**

**Achieved environmental benefits**
The prevention of emissions of metals, dust and other compounds.

**Cross-media effects**
Energy use is increased. Waste water is produced that should be treated to prevent the discharge of metals and other substances to water.

**Operational data**
Performance data is given in Table 2.15 and Table 2.16.

**Applicability**
This technique is generally applicable to most plants. Wet ESPs or moving electrode ESPs can be used for difficult dusts or moist gases.

**Economics**
The processes are operating economically and costs, where they are available, are reported in Annex I to this document.

**Driving force for implementation**

Reduction of emissions and possible saving in raw materials.

**Example plants**
Plants in DE, AT, FR, BE, PL.
*(What is missing are examples were in the NFM industry wet ESP's are applied and what they can achieve similar to table 2.14 in section 2.9.2.2.4.*

**Reference literature**
[ 195, Lurgi, A.G. et al. 1991 ], [ 196, Finkeldei, L. 1999 ], [ 73, Theodore, L. et al. 1992 ], [ 77, Soud, H.N. 1995 ], [ 189, VDI 1998 ].

#### 2.9.2.2.3 Cyclones

**Description**
Cyclones were installed in many of the processes in the 1980s and are still in widespread use. The cyclone is an inertial gas-cleaning device. Dust becomes separated from the gas stream when the direction of gas flow is changed and the dust continues in the original direction by virtue of its inertia and is deposited onto a collection surface. The cyclone is shown in Figure 2.40.

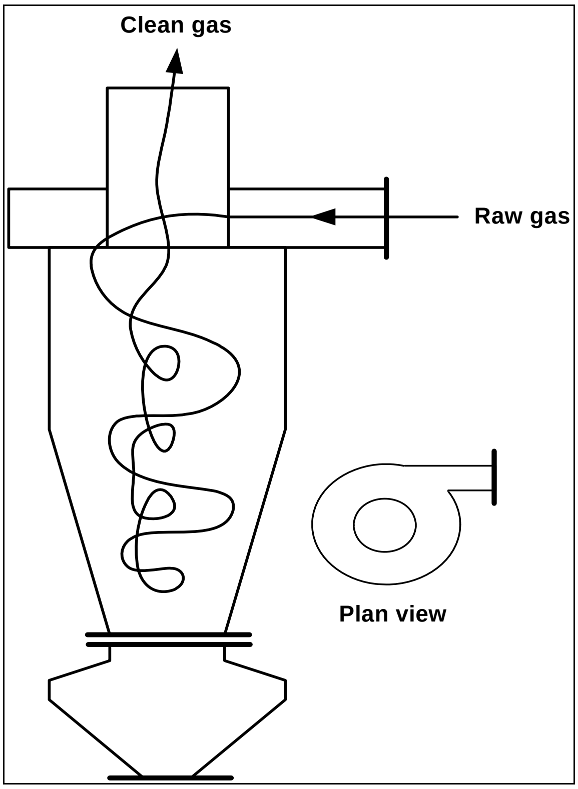


**Figure 2.40: Arrangement of a cyclone**

The inlet gas is channelled into a spiral flow. Centripetal forces operating within the spiral provide the change of direction, and the particles above a critical mass will be deposited onto the cyclone walls.

**Achieved environmental benefits**
The prevention of emissions of metals, dust and other compounds.

**Cross-media effects**
There is an increase in energy use.

**Operational data**

Performance data is given in Table 2.15 and Table 2.16.

**Applicability**
Cyclones are not generally suitable for controlling emissions directly from the processes in this industry sector. The efficiency in collecting fine dust is too low to deal effectively with furnace emissions. Operational experience has shown that they are not capable of meeting modern release standards. However, cyclones are used effectively as a primary collector in conjunction with another technique, particularly on larger processes where throughput can vary.

**Economics**
The processes are operating economically and costs, where they are available, are reported in Annex I to this document.

**Driving force for implementation**
Reduction of emissions and possible savings in raw materials.

**Example plants**
Plants in BE, DE, AT, FR, BE, PL.
*(What is missing are examples were in the NFM industry Cyclones are applied and what they can achieve similar to table 2.14 in section 2.9.2.2.4.*

**Reference literature**
[ 73, Theodore, L. et al. 1992 ], [ 77, Soud, H.N. 1995 ], [ 189, VDI 1998 ], [ 195, Lurgi, A.G. et al. 1991 ], [ 196, Finkeldei, L. 1999 ], [ 214, VDI (D) 1990 ].

### 2.9.2.2.4 Fabric or bag filters

**Description**
Fabric filter systems are used for many applications within this industry sector, due to their high efficiency in controlling the fine dust encountered in melting operations. Settling and cooling chambers but also waste heat recovery boilers are used before baghouses to reduce the likelihood of fires, to condition the particles and to recover the heat content of the off-gas before dedusting.

The fabric filter with various cleaning systems is shown in Figure 2.41, Figure 2.42 and Figure 2.43.

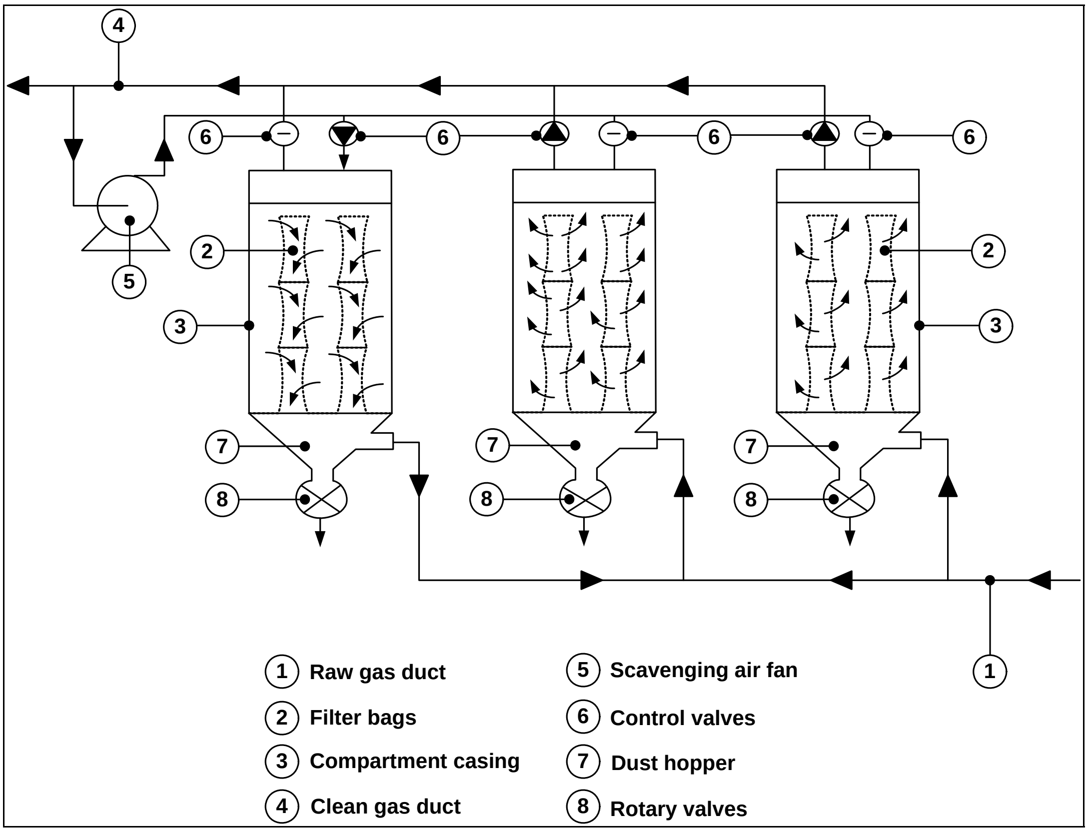


Figure 2.41: Reverse airflow fabric filter (with one compartment in the cleaning cycle)

The basic principle of fabric filtration is to use a fabric membrane which is permeable to gas but which will retain the dust. The bags are usually supported on a metal frame and each bag will incorporate a method of sealing into the baghouse structure. Initially, dust is deposited both on the surface fibres and within the depth of the fabric, but as the surface layer builds up, it itself becomes the dominating filter medium. As the dust cake thickens, the resistance to gas flow is increased. Periodic cleaning of the filter media is therefore necessary to control the gas pressure drop across the filter. The direction of the gas flow to be treated can be either from the inside of the bag to the outside or from the outside of the bag to the inside.

Fabric filters are normally classified according to the method by which the filter media are cleaned. Regular dust removal from the fabric is important in order to maintain effective extraction efficiency, but it also influences the operating life of the fabric.

The most common cleaning methods include reverse airflow, mechanical shaking, vibration, low pressure air pulsing and compressed air pulsing. Acoustic horns are also used for the cleaning of bags. The normal cleaning mechanisms do not result in the fabric returning to its pristine condition and the particles deposited within the depth of the cloth help to reduce the pore size between the fibres, thus enabling high efficiencies to be achieved on submicron fumes.

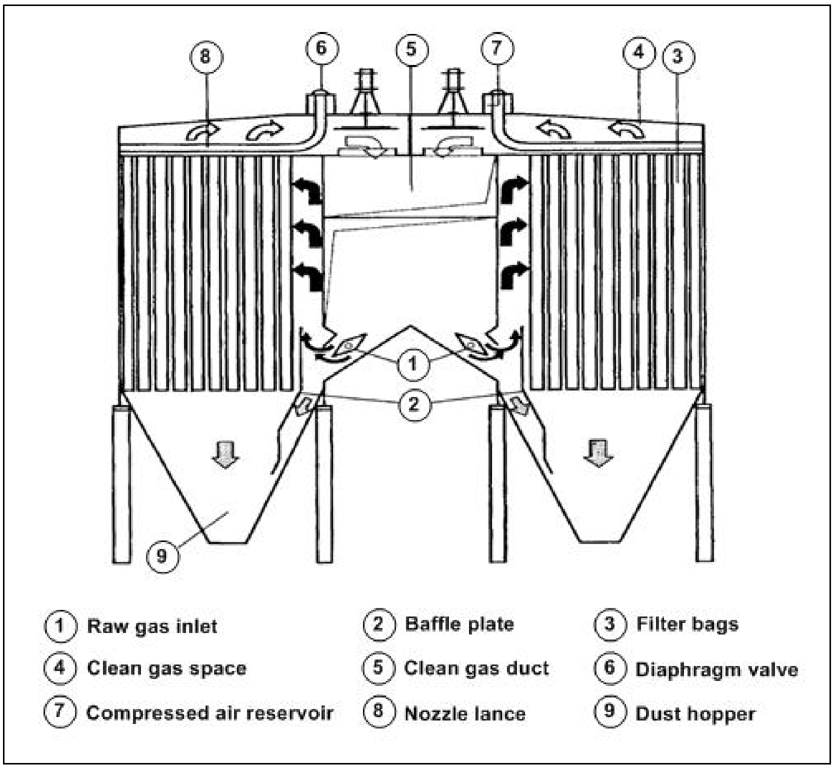


**Figure 2.42:** **Reverse pulsed jet cleaning system**

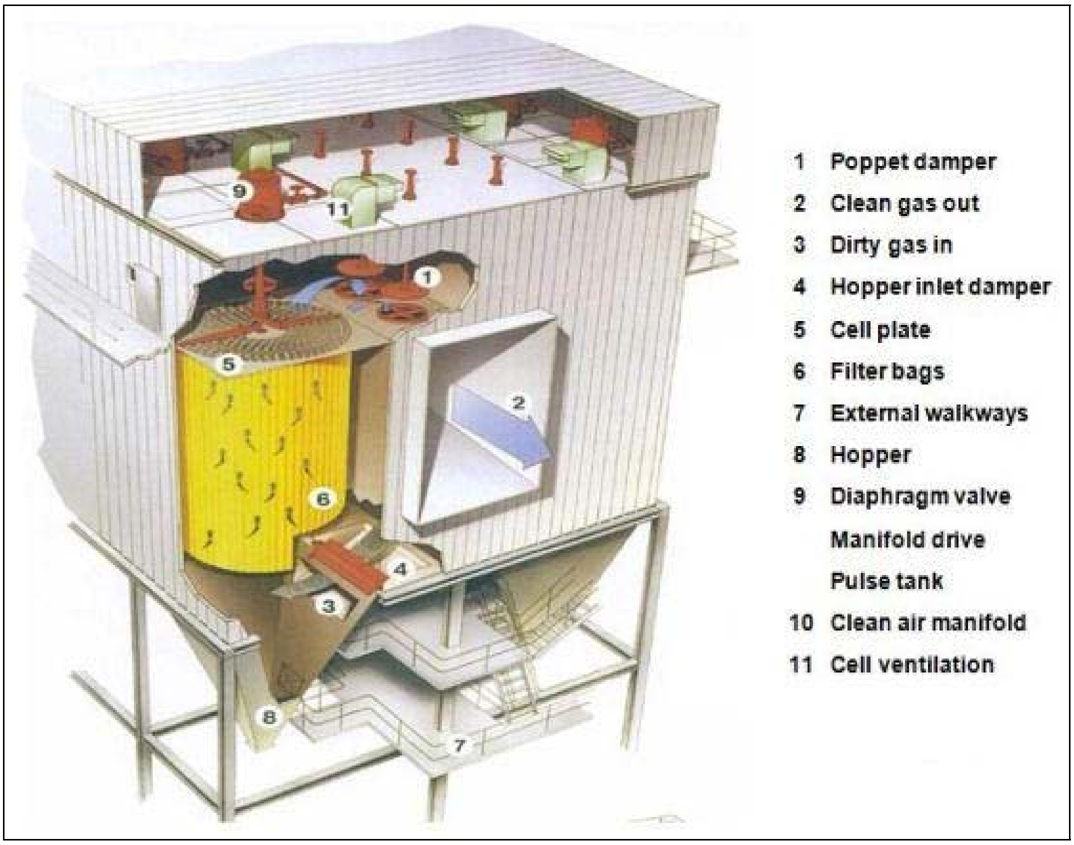


**Figure 2.43: Low pressure air pulsing cleaning system**

Fabric filters are designed on the basis of anticipated filtration velocity which is defined as the maximum acceptable gas velocity flowing through a unit area of fabric ($m^3/s \div m^2$ expressed in m/s). Filtration velocities generally lie in the range of 0.01 to 0.04 m/s according to the application, the filter type and the cloth.

Fabric selection takes into account the composition of the gases, the nature and particle size of the dust, the method of cleaning to be employed, the required efficiency and economics. The gas temperature is also considered, together with the method of gas cooling, if any, and the resultant water vapour and acid dew point.

Characteristics of the fabric considered include chemical resistance, fibre form and type of yarn, fabric weave, fabric finish, abrasion and flex resistance, strength, collecting efficiency, cloth finishes and cloth permeability.

Wear of the filter bags results in a gradual reduction in performance, which can be measured. Damage or catastrophic failure of several bags is a danger when corrosion occurs, abrasive material is filtered or when there is the danger of fire. Simple on-line monitoring systems such as pressure drop indicators or dust telltale devices give only a rough indication of performance.

Triboelectric or optical devices are used to measure the trend in the dust emitted from the baghouse to identify possible failure and they can be used to detect dust peaks during a cleaning cycle. When these measurements are integrated with a zoned cleaning system, the zone that contains damaged bags can be identified and local repairs can be made [ 123, Robson, T.G. et al. 1998 ]. Temperature measurement and alarms are also used.

Baghouse filters in some ferro-alloy processes use pressure filters with fans on the dirty fume/gas side. Developments have led to a closed suction filter with fans on the clean gas side. This technique is used in most of the other metal sectors and combines the advantages of gentle bag cleaning which means longer bag life, low operating and maintenance costs and, due to the closed filter, a defined gas volume.

**Achieved environmental benefits**
The prevention of emissions of metals, dust and other compounds are achieved.

**Cross-media effects**
There is an increase in energy use. Waste may be produced if the collected dust cannot be returned to the process. *(waste is always produced if the dust can not be returned to the processDelete or add in other sections if needed)*

**Operational data**
For correct operation one or more of the following features should be applied:

- Particular attention to the choice of filter material and the reliability of the mounting and sealing system. Good maintenance should be practised. Modern filter materials generally are more robust and have a longer life. The extra cost of modern materials is more than compensated for by the extra life in most cases.
- The addition of lime or other reactants (e.g. activated carbon) in order to capture gaseous components such as $SO_X$ or to remove PCDD/F.
- An operating temperature above the dewpoint of the gas. Temperature-resistant bags and mountings are used at higher operating temperatures.
- Continuous dust monitoring using dust impingement, optical or triboelectric devices to detect filter bag failure. The device should interact if possible with the filter cleaning system so that individual sections, which contain worn or damaged bags, can be identified.
- The use of gas cooling and spark arresting where necessary. Cyclones are considered to be suitable methods of spark arresting. Most modern filters are arranged in multiple compartments and damaged compartments can be isolated if required.

- Temperature and spark monitoring can be used to detect fires, inert gas systems can be provided or inert materials (e.g. lime) may be added to the off-gas where there is a danger of ignition.
- Pressure drop can be monitored to control the cleaning mechanism.

A number of different fabric filter designs using different kinds of filter materials exist, which, all in principle all achieve low emission values and that means dust emissions of below 5 mg/Nm$^3$. The use of the membrane filtration techniques (surface filtration) results additionally in an increasing bag life, high temperature limit (up to 260 ºC) and relatively low maintenance costs. The membrane filter bags consist of an ultra-fine expanded Teflon® membrane laminated to a backing material. The particles in the off-gas stream are captured on the bag surface. Rather than forming a cake on the inside or penetrating into the bag fabric, particles are repelled from the membrane thus forming a smaller cake. This technique is applicable for all new and existing plants and may also be used for the rehabilitation of existing fabric filters [ 141, Elkem Asa 1998 ].

These synthetic filter cloths such as Gore-Tex® and Tefaire® (Teflon/fibreglass) have enabled fabric filters to be used in a wide range of applications and to have an extended life. The performance of modern filter materials under high temperatures or abrasive conditions is good and cloth manufacturers can help to specify the material for specific applications. With the correct design and suitable type of dust, very low dust emissions (as low as 0.1 mg/m$^3$) may be achieved in special cases, but consistent levels of <1 – 5 mg/m$^3$ could be expected in most applications depending on the dust characteristics. Greater reliability and a longer life repays the expense of modern fabrics. Achieving these levels is important as the dusts contain significant levels of metals.

To prevent leakage of unpurified gases to the atmosphere, the effect of warping of the distribution manifolds and the correct sealing of the bags should be taken into account in accordance with good practice.

A comparison of the most commonly used parameters of different filter systems is shown in Table 2.13.

| Parameter | Pulse jet filter | Membrane fibreglass filter | Fibreglass filter |
|---|---|---|---|
| Air to cloth ratio | 80 to 90 m/h | 70 to 90 m/h | 30 to 35 m/h |
| Temperature limits | 250 ºC | 280 ºC | 280 ºC |
| Bag type | Polyester/Nomex® | Gore-Tex® Membrane/fibreglass | Fibreglass |
| Bag size | 0.126 × 6.0 m | 0.292 × 10 m | 0.292 × 10 m |
| Cloth area per bag | 2.0 m$^2$ | 9.0 m$^2$ | 9.0 m$^2$ |
| Cage | Yes | No | No |
| Pressure drop | 2.0 kPa | 2.0 kPa | 2.5 kPa |
| Bag life | Up to 30 months | 6 to 10 years | 6 to 10 years |

**Table 2.13: Comparison between different fabric filter systems**
[ 141, Elkem Asa 1998 ]

Performance data for dust removal using fabric filters is given in Table 2.14.

| Plant | Dust mg/Nm$^3$ | | Comment |
|---|---|---|---|
| | Inlet | Outlet | |
| Hoboken, BE<br>new batch process | | 1 – 3 | Precious metals, copper and lead. Dust is used in another process. |
| Atlantic Copper, ES | | 5 – 20 | Ancillary processes |
| Boliden, Harjavalta, FI | | 0.2 – 4 | Ancillary processes |
| KGHM | | 0.1 – 5 | Ancillary processes |

| | | | |
|---|---|---|---|
| Aurubis, Hamburg, DE Secondary fume collection | 1500 | < 2 | Lime addition prior to fabric filter. Dust is used in process. |
| Aurubis, Lunen, DE | 10000 – 30000 (3) | 1 – 5 | |
| Brixlegge, AT | | 0.75 (1) | *This value is for the converter furnace, there are more for the anode furnace 2,3; Asarco furnace 0.5; melting hall dedusting 5.12; slag production 0.3 mg/Nm3. All these are measured after FF and are Half hourly mean values.* |
| Kovohuty, SK | | 13.5 | |
| Elmet, ES | | 5 – 11 | |
| Metallo-Chimique, BE | | 0.7 – 3 | |
| Affinage de Lorraine, FR | | 0.3 | At measured $O_2$ content |
| German secondary Al plants, DE | 1500 | 0.1 – 15 | ELVs reported |
| AMAG, AT | | 0.7 – 1.7 | |
| French secondary lead smelters, FR | | 0.1 – 4.4 | |
| NL lead refining, NL | | 0.0004 | |
| Stolberg rotary furnace, DE | | < 3.5 | Ancillary processes |
| Lead battery de-sulphurised paste, DE | | < 5 | ELVs reported |
| Lead battery de-sulphurised paste, DE | | < 1 – 5 | ELVs reported |
| Whole battery, DE | | < 1 – 5 | ELVs reported |
| KGHM lead smelter, PL | | 2.2 – 5 | |
| KGHM Glogow I Prim. Copper, anode furnace and refining furnace (2) | | 0.1 – 5 | Measured once a month |
| UK lead smelters, UK | | 0.3 – 16 | 2.24 annual average |
| Beerse, BE<br>whole battery smelter[rr3] | 650 | < 1 | |
| Bergsöe, SW<br>Lead smelter | | < 1 | Dust is re-used in the process. |

**Table 2.14: Performance data for dust removal using fabric filters [249] [256]**

(1) [505] (see in the copper folder

(2) [506] (see in the copper folder)

(3) [507] extract of [234]

*Many of these filters are tailor made or include special features for simultaneous removal of other pollutants than dust. The examples should be included in the specific metal section. In general ESP, FF, scrubbers don't have to be described again entirely. Crossreferring to other section is sufficient. See also the Iron and Steel BREF.*

*Better and more examples should be provided. In to many cases the included values refer to ELVs. This is not acceptable.*

**Applicability**

All of these techniques are suitable -for most new processes. However, due to their tendency to blind in certain circumstances (i.e. with sticky dusts or in air streams close to the dew point) and their sensitivity to fire, they are not suitable for all applications. They may also be applicable to existing fabric filters and can be retrofitted. In particular the bag sealing system can be improved during annual maintenance periods and filter bags can be changed for more modern fabrics during the normal replacement pattern which can also reduce future costs.

**Economics**
The processes are operating economically and costs, where they are available, are reported in Annex I to this document.

**Driving force for implementation**
There are reduction of emissions and possibly saving of raw materials.

**Example plants**
Plants in DE, AT, FR, BE.

**Reference literature**
[ 195, Lurgi, A.G. et al. 1991 ], [ 196, Finkeldei, L. 1999 ], [ 73, Theodore, L. et al. 1992 ], [ 77, Soud, H.N. 1995 ], [ 141, Elkem Asa 1998 ], [ 217, VDI (D) 1997 ], [ 103, Farrell, F. 1998 ].

#### 2.9.2.2.5 Ceramic and metal mesh filters

*Ceramic and mesh filters are usually applied very rarely for industrial dust removal. If they are applied the information should be given in the relevant Metal specific section and not in genarl here. Since this section gives no indication where exactly mesh and ceramic filters are applied the deriving of BAT and BAT-AELs is not possible.*

**Description**
There are several examples where these filters are used in the correct application in this industry and very high dust removal efficiencies are achieved. Fine particles including $PM_{10}$ are removed.

Low density ceramic filters operate in a similar manner to fabric filters as far as operating principles, general arrangement and cleaning operations are concerned. Instead of cloth bags and their metal supports, rigid elements that resemble candle filters are used. They have a high degree of thermal resistance and it is often the limitations of the housings that determine the upper operating temperature. Expansion of the support system as the temperature rises is also a major factor as the sealing of the filter elements in the housing can be affected, resulting in leaks from the dirty gas stream into the clean gas stream. On-line failure detection systems are used in the same way as fabric filters. Ceramic and mesh filters are not flexible like a fabric filter. When cleaning them with an air pulse, the fine dust will not be removed as effectively as with a cloth filter, resulting in a buildup of fines within the filter and thus reducing the capacity of the filter. This effect is more likely to happen with very fine dust.

Ceramic filters are made from aluminosilicates and can be pre-coated with a variety of materials to improve chemical or acid resistance or remove other pollutants. The filter elements are relatively easy to handle when new but become brittle after exposure to heat and can therefore be broken during maintenance or by rough attempts to clean them.

**Achieved environmental benefits**
Emissions of metals, dust and other compounds are prevented.

**Cross-media effects**
There is an increase in energy use. Waste may be produced if the collected dust cannot be returned to the process.

**Operational data**
The presence of sticky dust or tar is a potential problem as this may not be cleaned from the element during the normal cleaning cycle and would cause a significant increase in pressure drop. The effect of temperature on the material to be collected is therefore an important factor in the design of a plant. With the correct design and suitable dust, very low dust emissions of

below 0.1 mg/Nm$^3$ are achieved. Achieving these levels is important as the dusts contain significant levels of metals.

Similar performances at high temperatures have also been reported using a redesigned metal mesh filter. The development allows the rapid establishment of a dust cake layer after cleaning while the zone is off-line.

Filters that are correctly designed, constructed and sized for the application and incorporate the following features:

- Particular attention paid to the choice and the reliability of the housing, mounting and sealing systems.
- The use of temperature resistant housing and mountings.
- Continuous dust monitoring using dust impingement, optical or triboelectric devices to detect filter failure. The device should interact with the filter cleaning system if possible so that individual sections which contain worn or damaged elements, can be identified.
- Gas conditioning provided where necessary.
- The use of pressure drop to monitor and control the cleaning mechanism.

Performance data is given in Table 2.15 and Table 2.16.

**Applicability**
The techniques are suitable_-for most new *(What means new in this context?)* processes. However, due to their tendency to blind in certain circumstances (i.e. with sticky dusts or in air streams close to the dew point) they are not suitable for all applications. They may also be applicable to existing ceramic filters and can be retrofitted. In particular the sealing system can often be improved during normal maintenance periods.

**Economics**
The processes are operating economically and costs, where they are available, are reported in Annex I to this document.

**Driving force for implementation**
There is a reduction of emissions and possible saving raw materials.

**Example plants**
Plants in BE, DE, AT, FR, UK.

**Reference literature**
[ 195, Lurgi, A.G. et al. 1991 ], [ 196, Finkeldei, L. 1999 ], [ 73, Theodore, L. et al. 1992 ], [ 77, Soud, H.N. 1995 ], [ 226, Nordic Report 2008 ], [ 103, Farrell, F. 1998 ].

#### 2.9.2.2.6 Wet scrubbers

**Description**
Particle collection by wet scrubbing occurs by three main mechanisms: inertial impacting, interception and diffusion. The particle size to be collected is an important factor and the wetability of the material to be collected can also be significant.

The radial flow wet scrubber is shown in Figure 2.44.

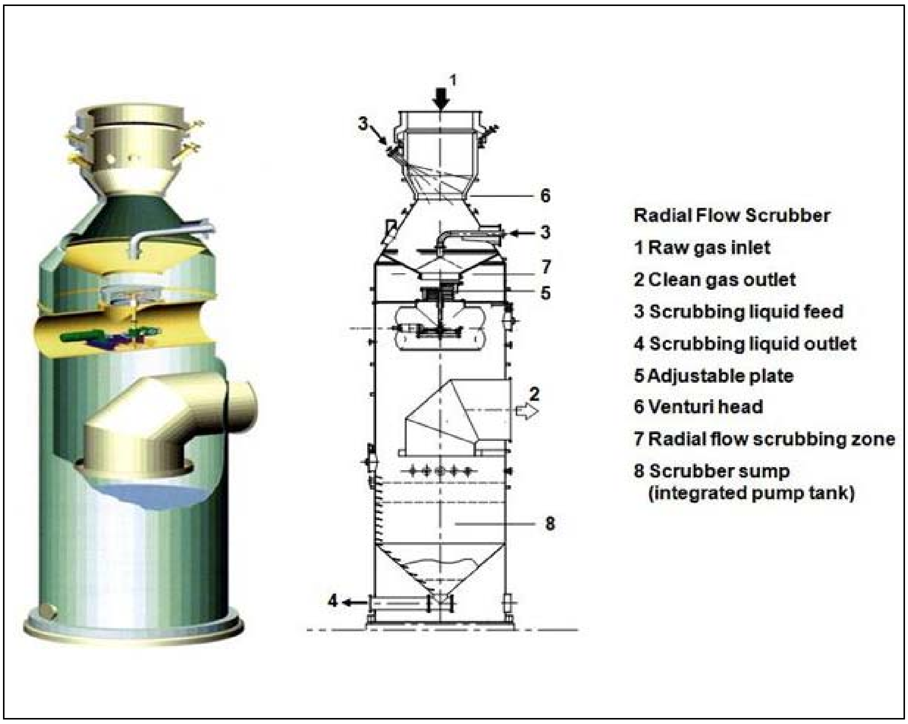


**Figure 2.44:** **Radial flow wet scrubber**

Wet scrubbers are used for cooling, saturating and pre-cleaning gases, e.g. when arranged upstream of wet electrostatic precipitators. Typical examples are the venturi scrubber or the radial flow scrubber with an adjustable pressure drop. Wet scrubbers are used in many different non-ferrous metal production processes, for instance copper, zinc and lead. Scrubber design is based on the relationship of gas and liquid velocity and of gas volume and liquid quantity. These parameters determine the pressure drop across the scrubber and thus the collecting efficiency.

Cascade or venturi wet scrubbers are often used for the dedusting of CO-rich off-gases from sealed electric arc furnaces, the gas is then used as high CV gas and is not emitted without further treatment. It is also used to treat gases from a steel belt sintering machine, the dust is very abrasive but easily wetted and emissions of <4 mg/Nm$^3$ are achieved, as the use of a scrubber allows gas cooling to be achieved at the same time as dust removal. Fabric filter life would be severely restricted and rapid fabric wear would result in poor performance.

**Achieved environmental benefits**
The prevention of emissions of metals, dust and other compounds.

**Cross-media effects**
There is an increase in energy use. Waste may be produced if the collected material cannot be returned to the process. A waste water is produced that needs additional treatment to prevent the discharge of metals to water.

**Operational data**
Scrubbers are used when they are correctly designed, constructed and sized for the application *(I don't understand this part of the sentence)* and when the nature of the dust or the gas temperature precludes the use of other techniques or when the dust is particularly suitable for removal in a scrubber. Their use can also be considered when gases need to be removed simultaneously with dust or when they form part of a chain of abatement techniques, for example in dedusting prior to a sulphuric acid plant. Sufficient energy should be applied to ensure the wetting and interception of the particles.

Wet scrubbers should incorporate a monitoring system for pressure drop, liquor flow and (if acid gases are being abated) pH. The scrubbed gases should exit the scrubber to a mist eliminator.

Performance data is given in Table 2.15 and Table 2.16.

**Applicability**

Experience shows that the efficiency of wet scrubbers is strongly dependent upon the particle size and their total energy usage, particularly upon the pressure drop across the collection zone. Moreover, provided the liquid is evenly dispersed within the scrubber, similar pressure drops will often give similar efficiencies on the same dust for quite different scrubber designs. Thus, it is not possible to design a wet scrubber that has high efficiencies without a high energy consumption unless the dust concerned is particularly easy to wet. A variety of designs for high energy scrubbers exist based on radial flow, jet, venturi and cascade principles. Scrubbers have an application with dusts that are difficult to remove with other techniques. In general, the gases are then used in another process (e.g. as a fuel gas) and are not emitted. They are also used in conjunction with wet ESPs to cool and clean gases before conversion in a sulphuric acid plants and to absorb acid gases.

**Economics**

The processes are operating economically and costs, where they are available, are reported in Annex I to this document.

**Driving force for implementation**

Reduction of emissions and saving of raw materials.

**Example plants**

Plants in DE, AT, FR, BE, PL.

*(What is missing are examples were in the NFM industry wet scrubbers are applied and what they can achieve similar to table 2.14 in section 2.9.2.2.4.From the data provided i.e. from polish plants the performance of wet scrubbers can be much worse (also see table 2.15).*

**Reference literature**

[ 196, Finkeldei, L. 1999 ] [ 195, Lurgi, A.G. et al. 1991 ], [ 226, Nordic Report 2008 ], [ 103, Farrell, F. 1998 ].

#### 2.9.2.2.7 Overview of dust abatement techniques

An overview of dust abatement techniques is given in Table 2.15 below.

| Description | Achieved Environmental Benefits (emission mg/Nm$^3$) | Cross-media effects | Operational data (Potential Problems) | Applicability | Driving force for Implementation | Example plants | References |
|---|---|---|---|---|---|---|---|
| Fabric filters | <1 - 5 | NA if dust is re-used | Clogging, fires, sealing.<br>Maximum operating temperature 250 °C. | Most with good sealing and modern fabrics | Good performance for suitable dusts.<br>Potential to recycle dust to process | Secondary lead batteries - DE | [ 215, VDI (D) 1997 ] |
| Wet electrostatic precipitator | <1 – 5<br>Optically clear | Source of effluent | Wire breakage and shorting.<br>Maximum operating temperature 80 °C | Improved performance for wet gases | Good performance for suitable dusts, low pressure drop but effluent produced | Sulphuric acid plants - ES, DE, FI | [ 189, VDI 1998 ] |
| Electrostatic precipitator | 5 - 20<br>(<50 as pre-abatement) | NA if dust is re-used | Variation in particles, wire breakage & shorting.<br>Maximum operating temperature 450 °C. | Most with good control systems and gas distribution | Low pressure drop, reliable, Low maintenance | Lead batteries in Ausmelt/ISA Smelt Plant - BE | [ 189, VDI 1998 ] |
| Wet scrubbers | 4 - 70 | Source of effluent | Lower performance and blockages.<br>Maximum operating temperature 1000 °C inlet. | Precleaning of gases prior to other methods.<br>Only some dusts are suitable.<br>Cleaning fuel gases for combustion or gases for acid plant. | Removal of acid gases and mists | Cascade scrubber for very abrasive dusts.<br>Ferro-chrome sinter plant - FI | [ 216, VDI (D) 1998 ] |
| Ceramic filters | <0.1 – 1 | NA if dust is re-used | Fragility, clogging and sealing.<br>Dust must be suitable.<br>Maximum operating temperature 900 °C. | Higher temperature operation | Very good performance for suitable dusts.<br>Potential to recycle dust to process | | [ 215, VDI (D) 1997 ] |
| Cyclones | 50 - 300 | NA if dust is re-used | Poor performance.<br>Limited efficiency for fine particles.<br>Maximum operating temperature 1100 °C. | Pre-abatement | Precleaning of gases prior to other methods | | [ 214, VDI (D) 1990 ] |

**Table 2.15: Overview of dust abatement techniques**

*(I don't think that the VDI guidelines can be applied here to give the actual performance of these abatemnt systems. Concrete examples for the NFM application have to be given. )*

| Abatement type | Application | Measured dust emission ($mg/Nm^3$) | Comment |
|---|---|---|---|
| Fabric filter<br>(180000 - 250000 $Nm^3/h$) | Secondary lead (batteries) | 0.7 to 3.4 (monthly average) | Short rotary furnace, DE |
| Fabric filter<br>(26000 $Nm^3/hr$) | Cadmium battery recycling | <1 (monthly average) | |
| Cascade scrubber | Ferro-chrome plant | <4 | Very abrasive dust; fabric filter not suitable due to bag failures |
| Fabric filter | Lead battery smelting | <1 | |
| Cyclone + ESP<br>+ wet ESP | Lead Batteries in Ausmelt/ISA Smelt Plant | 1 - 2 | |
| Fabric Filter | Ferro-alloy production | 1 - 10 | |
| Regenerative thermal oxidiser (RTO), cooler and fabric filter | Copper industry (secondary)<br>Lead industry (Secondary) | <1<br><2 | |

**Table 2.16: Measured performance of dust removal systems when using various dust abatement techniques with suitable dusts**

*What are the references for these examples??? It can be seen that the performance of a FF can be worse than 5 mg/Nm$^3$ depending on i.e. the kind of metal which is produced.*

The measured levels are quoted in Table 2.16 as ranges. They will vary with time depending on the condition of the equipment, its maintenance and the process control of the abatement plant. The operation of the source process will also influence dust removal performance, as there are likely to be variations in temperature, gas volume and even the characteristics of the dust throughout a process or batch. The achievable emissions are therefore only a basis from which actual plant performance can be judged and the achievable and associated emissions discussed in the metal-specific chapters take account of the suitability of the dusts encountered and the costs/benefits of the particular application of the technique. Process dynamics and other site-specific issues need to be taken into account at a local level.

### 2.9.2.3 Afterburners/Afterburning chambers (see 4th and 5th bullet)

**Description**

Combustion systems are used in the industry to oxidise CO, dust or gaseous carbonaceous material in a gas stream. Several types of combustion systems are used:

- High temperature afterburners, where the gases are typically heated to between 850 and 1000 °C and held for a minimum of 0.5 seconds (provided there are no chlorinated components) and the results can confirm destruction of any VOCs present. Afterburners employ a burner system (not necessarily used continuously).
- Regenerative thermal oxidisers (RTOs) employ a regenerative system to utilise the thermal energy in the gas and carbon compounds by using refractory support beds. A manifold system is needed to change the direction of the gas flow to clean the bed.
- Catalytic incinerators, where the decomposition is carried out on a metal catalyst surface at lower temperatures, typically from 350 to 400 °C.
- Furnaces designed to burn off-gases, e.g. excess CO to recover energy.
- The uptake shaft or exit portion of a furnace can be used as an afterburner if additional oxygen is added at this point.

Afterburners destroy organic compounds including PCDD/F by thermal oxidation and produce carbon dioxide, water, oxides of sulphur and nitrogen, and other combustion products. Further abatement is necessary to remove these products.

Afterburners are particularly useful in de-oiling and de-coating operations, which can produce a high concentration of organic components. The presence of these components in a furnace produces a high volume of combustion products and would result in a very short residence time in a furnace and the emissions of partially combusted gases.

**Achieved environmental benefits**
Prevention of emissions of organic compounds.

**Cross-media effects**
Potential increase in energy use if the heat generated cannot be used.

**Operational data**
Installations that are correctly designed, constructed and sized for the application are techniques to consider to remove VOCs, PCDD/F, organic or carbon particles or combustible gases such as CO or $H_2$. Heat recovery should be used where possible. The main requirements for effective combustion in an afterburner are:

- Residence time in the combustion chamber or regenerative system must be sufficiently long in the presence of sufficient oxygen to ensure complete combustion. Destruction efficiency of 99 % will usually require a residence time of two seconds at the relevant temperature depending on the presence of chlorinated compounds. Lower residence times and temperatures may also result in the complete destruction of VOCs and PCDD/F but this should then be demonstrated on a local level under realistic operating conditions. Gases should be cooled rapidly through the temperature window of PCDD/F reformation. Turbulence is necessary to provide efficient heat and mass transfer in the combustion zone, and to prevent cool spots. This is usually achieved by using burners that generate a swirling combustion flame, and by incorporating baffles in the combustion chamber.
- An operating temperature of 200 to 400 °C above the auto-ignition temperature of the most stable substance, so minimum operating temperatures are above 850 °C. Where the gas stream contains chlorinated substances, temperatures must be increased to 1100 to 1200 °C, and rapid flue-gas cooling is required to prevent the reformation of PCDD/F.
- Catalytic units operate at lower temperatures and flares require turbulence, air, and an ignition source. If necessary, supplementary fuel can be added.
- The burners should have microprocessor control of the air to fuel ratio to optimise combustion.
- The performance of the combination of equipment, operating temperature and residence time should be demonstrated to show effective destruction of the materials present in the feed gas.

**Applicability**
These techniques can be applied to most new and existing afterburner installations. Operating temperatures can be optimised and it is possible that the use of oxygen enrichment rather than air will increase the gas residence time (smaller gas volume) as well as increasing the operating temperature.

**Economics**
The processes are operating economically and costs, where they are available, are reported in Annex I to this document.

**Driving force for implementation**
Reduction of emissions.

**Example plants**
Plants in DE, AT, FR, BE, PL.

**Reference literature**
[ 196, Finkeldei, L. 1999 ], [ 226, Nordic Report 2008 ], [ 211, VDI (D) 1987 ], [ 212, VDI (D) 1995 ], [ 214, VDI (D) 1990 ], [ 103, Farrell, F. 1998 ],. [ 233, Farrell Nordic Mission 2008 ].

### 2.9.2.4 Treatment of gaseous components

*That is not a good heading because also above mentioned systems such as afterburner were supposed to deal with gaseous components.*

Gases such as $NH_3$, $SO_2$, $SO_3$, HF, HCl and $NO_X$ are produced in several processes, for example sulphur dioxide is produced during smelting and hydrogen fluoride is produced during electrolysis. Prevention and reduction techniques are available for these gases [ 213, VDI (D) 1998 ]. Reduction of the emissions of these gases is often possible by process control or by fixing the material in a slag or matte. The use of low-$NO_X$ burners and staged combustion air for furnaces and other combustion plants can prevent the formation of these gases.

Organic and metallic components can also be emitted from some processes and can be adsorbed using similar techniques. *This sentence give no further information. Probably delete.*

The following techniques are used to remove gaseous components. More information is given in the metal-specific Chapters 3 to 12.

#### 2.9.2.4.1 Wet scrubbing systems

*(See 2.9.2.2.6: Wet scrubbers are already described and it is mentioned that simultaneous removal of dust and some gaseous components is possible. Combine 2.9.2.4.1 with the previous section on wet scrubbers).*

**Description**
Wet scrubbing systems are used in the industry to remove gaseous components at low concentrations, to remove particles and also to control temperature (by adiabatic cooling). Whilst the basic technology for these applications is similar, the design criteria for dust and gaseous component removal are very different. Wet scrubbing systems are often used for all three processes simultaneously and so the design is inevitably a compromise and significant cross-media effects, such as the production of additional waste water may result depending on the application.

Various scrubbing media are used ranging from seawater to alkali solutions. The application for which a scrubber is used determines the factors that should be measured to monitor performance. The parameters that are used include; pressure drop and liquor flow, temperature, turbidity, conductivity and pH. Potentially significant cross-media effects exist and need to be taken into account locally.

**Achieved environmental benefits**
The prevention of emissions of metals, dust and other compounds.

**Cross-media effects**
There is an increase in energy use. A waste water is also produced that needs additional treatment to prevent the discharge of metals to water.

**Operational data**
Scrubbers that are correctly designed, constructed and sized for the application are techniques to consider to remove low concentrations of sulphur dioxide (less than 2 %) and other acid gases such as HF and HCl that may be produced.

Wet scrubbers should incorporate a monitoring system if possible for pressure drop, liquor flow and pH, the scrubbed gases should exit the scrubber to a mist eliminator. Weak acid liquors produced by scrubbers should be re-used, recovered if possible or treated to reduce emissions to water.

**Applicability**
This technique is generally applicable to most plants.

**Economics**
The processes are operating economically and costs, where they are available, are reported in Annex I to this document.

**Driving force for implementation**
A reduction of emissions and possible recovery of raw materials.

**Example plants**
Plants in DE, AT, FR, BE, PL, ES, UK, NO, SE, US, IT, BG, RO.

**Reference literature**
[ 11, Hatch Associates Ltd 1993 ], [ 13, HMIP (UK) 1994 ], [ 226, Nordic Report 2008 ], [ 103, Farrell, F. 1998 ].

#### 2.9.2.4.2 Dry and semi-dry scrubbers

**Description**
Adsorption techniques such as dry scrubbing are used to absorb acid gases and adsorb metallic or organic components. Lime, magnesium hydroxide, limestone, zinc oxide and alumina are frequently used for both applications and dual alkaline scrubbers are used elsewhere in the world. Activated carbon (or coke) is used to remove metal (mercury) and organic substances, for which it is usually more effective.

Adsorption is achieved using packed towers or by injecting the reagent into the gas stream and using a reactor tower. Fabric filters are most frequently used downstream to collect the partially reacted scrubbing medium and provide a further surface area for further absorption to take place. The scrubbing medium can be recycled several times within the scrubbing network to allow full use of the absorptive and adsorptive capacity. In the case of alumina and zinc oxide, they are subsequently used in the main process. Fluorides absorbed by alumina are recovered by the electrolysis process.

A variant on dry scrubbing is semi-dry scrubbing. In this case a slurry of the reactant (usually lime) is injected into a reactor with the gas stream. The water is evaporated, provided the gas temperature is high enough and the gaseous components react with the particles. The particles of the reacted reagent are then removed from the gas stream. Dry scrubbing is often less effective than wet or semi-dry scrubbing, particularly with less reactive gases such as $SO_2$. The effectiveness of the reactant is often related to the reactivity of the reagent and suppliers of lime can often produce material at a reactivity that is suitable for certain applications.

When these processes are used to remove $SO_2$, they are known as flue-gas desulphurisation techniques (FGD). They are used to reduce the $SO_2$ content of gases from anode furnaces and other low strength sources and for tail gas scrubbing of the gases from a sulphuric acid plant. Gypsum is produced when wet methods are used and can be sold in some circumstances.

**Achieved environmental benefits**
The prevention of emissions of metals, dust and other compounds.

**Cross-media effects**

There is an increase in energy use. Waste may be produced if the collected material cannot be returned to the process.

**Operational data**
Scrubbers using the correct reagent that are correctly designed, constructed and sized for the application are techniques to consider to remove low concentrations of sulphur dioxide (less than 2 %) and other acid gases such as HF and HCl that may be produced. Dry scrubbers using activated carbon are techniques to consider to remove organic matter such as PCDD/F or to remove mercury. Scrubbers should also use one or more of the following techniques depending on the application:

- Dry and semidry scrubbers should incorporate suitable mixing and reaction chambers.
- Particles generated in the reaction chamber should be removed in a fabric filter or ESP.
- The partially reacted scrubbing medium can be recycled to the reactor.
- The spent scrubbing medium should be used in the main process if possible. For example alumina and zinc oxide can be used in their respective processes.
- Semi-dry scrubbers should incorporate a mist eliminator if mists are produced.

**Applicability**
This technique is generally applicable to most plants.

**Economics**
The processes are operating economically and costs, where they are available, are reported in Annex I to this document.

**Driving force for implementation**
The reduction of emissions and possible saving raw materials.

**Example plants**
Plants in DE, AT, FR, BE, PL, NL.

**Reference literature**
[ 11, Hatch Associates Ltd 1993 ], [ 13, HMIP (UK) 1994 ], [ 226, Nordic Report 2008 ], [ 103, Farrell, F. 1998 ], [ 233, Farrell Nordic Mission 2008 ]:

#### 2.9.2.4.3 Techniques to prevent the formation of and to treat $NO_X$

*This again is an example where the given information is quite specific and should be relocated next to the relevant metal section (secondary copper, secondaryaluminium)*
*Crosscheck with section 2.9.2.9.*

**Description**
The production stages usually rely on high temperatures but are also associated with the use of oxygen. This reduces the partial pressure of nitrogen in the flame and reduces nitrogen oxide formation provided that nitrogen is not present in great amounts in the very hot areas. Typical levels for the emissions of nitrogen oxides for secondary copper are reported to be in the range of 20 to 400 mg/Nm$^3$ depending on the furnace and type of operation. For $NO_X$, the use of highly efficient processes (e.g. Contimelt) requires a balance to be established locally between energy use and achieved value. Other furnaces in the secondary aluminium sector that use oxy-fuel burners can also show a reduction in $NO_X$, the range for these processes is 50 to 500 mg/Nm$^3$. *But in the Al section is stated that with oxy-fuel burner the NOx emissions may or may not increase. See section 4.2.4.1.4.*

Nitrogen oxides can be produced in significant amounts during acid digestion using nitric acid in the dissolution of silver. High concentrations of nitrogen oxides are treated in scrubbers so that nitric acid can be recovered; various oxidising agents are used to promote conversion and recovery as nitric acid. Residual nitrogen oxides can be removed by catalytic means such as selective or non-selective catalytic reduction if very high $NO_X$ concentrations occur continuously [ 161, Bobeth, A. 1999 ]. Table 2.17 shows emissions of nitrogen oxide from several processes.

**Achieved environmental benefits**
Prevention of emissions of oxides of nitrogen.

**Cross-media effects**
No cross-media effects were reported.

**Operational data**
The use of pure oxygen in a burner leads to a reduction of nitrogen partial pressure in the flame and therefore thermal $NO_X$ formation may be reduced. This may not be the case with oxygen enrichment in or near the burner, or if there is significant leakage of air into the furnace as the higher gas temperature may promote thermal $NO_X$ formation. In the latter case, oxygen can be added downstream from the burner to reduce this effect and maintain the improvement in melting rate. Table 2.17 shows emissions of $NO_X$ from several processes.

| Production site | Emission source | Range $NO_x$ mg/Nm$^3$ as $NO_2$ | Comment |
|---|---|---|---|
| Aurubis, Lunen, DE<br>Secondary copper | Shaft melting furnace Cu | 60 - 110 | Oxy-fuel |
| Aurubis, Lunen, DE<br>Secondary copper | Anode furnace Cu | 100 - 350 | Upper range is the ELV |
| Aurubis, Lunen, DE<br>Secondary copper | KRS furnace | 10 - 100 | Oxy-fuel |
| Brixlegge, AR<br>Secondary copper | Melting furnace | 21 – 300 | Oxy-fuel |
| AMAG, Austria.<br>Aluminium production | Reverberatory furnace | 15 - 310 | Oxy-fuel??? |
| AMAG, Austria.<br>Aluminium production | Rotary Furnace | 10 - 157 | |
| Un named DE.<br>Aluminium production | Swarf dryer | 40 - 350 | Upper range is the ELV |
| AMAG, AT.<br>Aluminium production | Swarf dryer | 69 – 101 | |
| AMAG, AT.<br>Aluminium production | Tilting rotary furnace | 11 - 36 | Oxy-fuel |
| KGHM, Poland<br>Precious metals | Kaldo furnaces | 3 – 230 | Oxy-fuel |
| Un named DE<br>Secondary lead | Secondary smelter | < 50 | |
| Affinage de Lorraine, FR<br>Aluminium production | Rotary furnaces | 28 – 160 | Oxy-fuel |
| Elkem, Thamshavn, Norway<br>Ferro Alloys | EAF | 230 – 400 | |

**Table 2.17: Emissions of nitrogen oxide from several processes**
[ 234, UBA Copper, lead, zinc and aluminium 2007 ], [ 194, Mezger, G. 1999 ], [ 256, Plant visit report AMAG 20071114.doc 2007 ], [ 249, Austria Brixlegge Report 2007 ], [ 276, French PCDD/F Report 2008 ], [ 233, Farrell Nordic Mission 2008 ].

**Applicability**
Oxy-fuel firing is a technique that can be applied to most of the combustion and pyrometallurgical processes in use. The full benefit is achieved with new plants where the combustion chamber and abatement systems can also be designed for the lower gas volumes. The technique is also applicable to existing plants and can in many cases be retrofitted.

**Economics**

The economical advantages of oxy-fuel are mainly related to improvements in terms of production rate. In the secondary aluminium sector in 1999 the fixed costs were around EUR 145/t for two furnaces (22561 tonnes produced/year). The higher productivity allowed by using oxy-fuel burners would result in a cut in these costs to around EUR 122/t (22651 x 145/27000). There is therefore a potential saving of EUR 23/t for a production rate of 27000 t/y.

Some data on costs involved in oxy-fuel firing for secondary aluminium production are given in Table 2.18.

| Parameter | Benefits/costs | Comment |
|---|---|---|
| Melting time | - 2.45 h/charge | Reduced batch melting time |
| Productivity | + 0.84 t/h | Increased productivity of the furnace |
| Gas consumption | - 80 $m^3/t$<br>(tonne of oxygen) | Reduced consumption of gas |
| $O_2$ consumption | + 126 $m^3/t$ | Additional consumption of oxygen |

**Table 2.18: Data on costs involved in oxy-fuel firing for secondary aluminium production**
[ 276, French PCDD/F Report 2008 ]

**Driving force for implementation**
Reduction of emissions, saving energy.

**Example plants**
Plants in DE, AT, FR, BE, UK.

**Reference literature**
[ 234, UBA Copper, lead, zinc and aluminium 2007 ], [ 194, Mezger, G. 1999 ], [ 256, Plant visit report AMAG 20071114.doc 2007 ], [ 249, Austria Brixlegge Report 2007 ], [ 276, French PCDD/F Report 2008 ], [ 122, ETSU 1994 ], [ 103, Farrell, F. 1998 ].

### 2.9.2.5 Gas recovery systems

*This again is an example where the given information is quite specific and should be relocated next to the relevant metal section*

**Description**
In addition to the use of wet, dry and semi-dry scrubbing systems to remove the gaseous components reported above, this industry makes extensive use of recovery systems to recover gases from process gas streams. HCl can be absorbed in water and $SO_2$ or $NO_X$ can be absorbed in water or hydrogen peroxide.

The following examples are used in the industry to close the material cycles:

- The hydrochloric acid loop for processes involving dissolution, hydrochloric acid (HCl), is used in combination with excess chlorine. By using evaporation and collection in water, an azeotropic acid (in concentrations of about 20 wt-% ~~w/w)~~) is obtained. This is re-used in different parts of the process.

- The nitric acid loop: silver and palladium are often dissolved in nitric acid ($HNO_3$). A significant quantity of nitrogen oxide off-gases (NO and $NO_2$) can be captured with oxygen or hydrogen peroxide in special cascade scrubbers. Problems are encountered by the long time needed to oxidise small quantities of NO and the reduction of gas absorption by exothermic reactions. Therefore cooling and several combined scrubbers are necessary to reach the limit values avoiding brown fumes from the stack. The resulting nitric acid from the first scrubber usually has concentrations of about 45 % by weight and can be re-used in several processes.

- The chlorine loop: chlorine is used in wet processes to dissolve metals and in dry chlorination steps at elevated temperatures to refine them. In both cases closed systems are used, e.g. using U-tubes with water and sealed electrolytic cells. Chlorine gas can be recovered or hypochlorite solutions produced. Hypochlorite is also used as an oxidising agent in scrubber solutions for various refining processes.

- The ammonium chloride loop: the relatively low solubility of ammonium chloride ($NH_4Cl$), in evaporated solutions at room temperature makes it possible to re-use crystalline precipitates of this salt.

**Achieved environmental benefits**
Prevention of emissions of acid gases and other compounds

**Cross-media effects**
There is an increase in energy use. A waste water may be produced which will require treatment.

**Operational data**
No data has been reported but the metal-specific chapters provide some information.

**Applicability**
This technique is generally applicable to most plants.

**Economics**
The processes are operating economically and costs, where they are available, are reported in Annex I to this document.

**Driving force for implementation**
A reduction of emissions and a saving of raw materials.

**Example plants**
Plants in DE, AT, FR, BE.

**Reference literature**
[ 11, Hatch Associates Ltd 1993 ], [ 13, HMIP (UK) 1994 ], [ 103, Farrell, F. 1998 ].

#### 2.9.2.6 Techniques to remove hydrocarbons and VOCs

*This again is an example where the given information is quite specific and should be relocated next to the relevant metal section. Much of the included information has been already mentioned under 2.9.2.3 afterburner. The description covers different types of techniques but the subsequent information on operational data, applicability and costs refers only to afterbruners.*

**Description**
Total carbon and VOCs are produced by poor combustion and during various operations such as storage of hydrocarbons, removal of CO and hydrocarbons produced during process operations, degreasing of components, solvent extraction processes and from the breathing of tanks used to store solvents and fuel. Materials may be aromatic, aliphatic, chlorinated organic or water based. The ecotoxicity varies and this is taken into account so that the most benign material is used and to determine the abatement system that should be used on a site by site basis. Containment is practised to prevent emissions and mixers/settlers can be used that minimise contact with air. Solvent or fuel vapours need to be extracted and removed from the exhaust gases.

The techniques used to remove or destroy VOCs are afterburners, regenerative afterburners, ESPs and scrubbers detailed above and concentrations of <10mg/Nm$^3$ can be achieved. Combinations of the techniques are used where there is a wide range of hydrocarbons present. Biofilters and reactors are also used [ 156, VDI (D) 1976 ]. Activated carbon traps and chiller/condenser systems are used which allow the material to be recovered for re-use. In one solvent extraction process, ventilation air is cooled and removes solvent down to a level of 0.2 kg per tonne of cobalt produced. VOCs can also be emitted during the delivery of solvents, etc. Back venting of displaced gases is used to minimise the emission of VOCs.

**Achieved environmental benefits**
Prevention of emissions of hydrocarbons and VOCs.

**Cross-media effects**
There is an increase in energy use if the heat generated cannot be used.

**Operational data**
Installations that are correctly designed, constructed and sized for the application are techniques to consider in the determination of BAT for the removal VOCs or combustible gases such as CO or $H_2$. Heat recovery should be used where possible. The main requirements for effective combustion in an afterburner are:

- Residence time in the combustion chamber or regenerative system must be sufficiently long in the presence of sufficient oxygen to ensure complete combustion. Destruction efficiency of 99 % will usually require a residence time of two seconds at the relevant temperature depending on the presence of chlorinated compounds. Lower residence times and temperatures may also result in the complete destruction of VOCs and PCDD/F but this should then be demonstrated on a local level under realistic operating conditions. Gases should be cooled rapidly through the temperature window of PCDD/F reformation. Turbulence is necessary to provide efficient heat and mass transfer in the combustion zone, and to prevent cool spots. This is usually achieved by using burners that generate a swirling combustion flame, and by incorporating baffles in the combustion chamber.
- An operating temperature of 200 to 400 °C above the auto-ignition temperature of the most stable substance, so minimum operating temperatures are above 850 °C. Where the gas stream contains chlorinated substances, temperatures must be increased to 1100 to 1200 °C, and rapid flue-gas cooling is required to prevent the reformation of PCDD/F.
- Catalytic units operate at lower temperatures and flares require turbulence, air, and an ignition source. If necessary, supplementary fuel can be added.
- The burners should have microprocessor control of the air to fuel ratio to optimise combustion.
- The performance of the combination of equipment, operating temperature and residence time should be demonstrated to show effective destruction of the materials present in the feed gas.

VOCs can be emitted if oily material is used as feed and can account for 5 - 100 g per tonne of copper or between 1 and 10 mg/Nm$^3$ [ 249, Austria Brixlegge Report 2007 ]. VOCs may also be emitted from solvent degreasing or solvent extraction processes.

Table 2.19 shows emissions of hydrocarbons and VOC from several non-ferrous metal production processes.

| Emission source | Range as carbon, mg/Nm$^3$ | Technique |
|---|---|---|
| Copper secondary smelting, remelting/refining processes | 1 – 50 | Optimised combustion |
| Hydrocarbon from anode production using RTO | 2 – 5 | RTO with pre-treatment of gases |
| Material storage and | <25 | Cooling and condensor |

| | | |
|---|---|---|
| handling of pitch in anode manufacture | | |
| Ferro-alloy processes<br>Precious metal processes | <5 | Semi-closed furnace |
| Solvent extraction (PM, Co, Ni Cu) | 1 – 30 | Cooling and condenser, sealed or covered reactors or carbon or biofilter |

**Table 2.19: Emissions of hydrocarbons and VOC from several non-ferrous metal production processes**

[ 234, UBA Copper, lead, zinc and aluminium 2007 ], [ 242, Nl Anode Input 2008 ], [ 226, Nordic Report 2008 ].

**Applicability**

These techniques can be applied to most new and existing afterburner installations. Operating temperatures can be optimised and it is possible that the use of oxygen enrichment rather than air will increase the gas residence time (smaller gas volume) as well as increasing the operating temperature.

**Economics**

Several RTO installations are operating viably. Maintenance costs are reported to be EUR 74000 per year, gas EUR 3.9 million per year, electricity EUR 530000 per year. The other processes are operating economically but no costs have been submitted.

**Driving force for implementation**

A reduction of emissions and saving raw materials.

**Example plants**

Plants in DE, AT, FR, BE.

**Reference literature**

[ 234, UBA Copper, lead, zinc and aluminium 2007 ], [ 242, Nl Anode Input 2008 ], [ 226, Nordic Report 2008 ], [ 76, Soud, H.N 1993 ], [ 157, Winter, B. et al. 1999 ], [ 103, Farrell, F. 1998 ], [ 233, Farrell Nordic Mission 2008 ], [ 348, French input for Aluminium 2010 ].

### 2.9.2.7 Removal of other impurities

In addition to their interference with the recovery of sulphuric acid and sulphur dioxide, other non-ferrous metals that are present in the ores and concentrates have an adverse environmental impact. They need to be removed if they have not been already. They also have a value and so they are recovered separately from the metal of prime interest. Additional purification stages are therefore used to remove and recover them and these are reported in the metal-specific chapters.

#### 2.9.2.7.1 Other metals

*All information is much to general and of little help and use. Probly delete and use parts where appropriate.*

**Description**

Pyrometallurgical processes are used to remove impurities from the desired metal by volatilising and/or slagging other metals. For example zinc, bisthmuth, lead, tin, cadmium, arsenic and gallium may be volatilised under the operating conditions in the furnace and are fumed from the melt. The choice of operating temperature influences this stage of the process and these metal oxides can be collected using an appropriate dust removal technique. The metals are then recovered from the collected flue dusts in a number of ways. Slag cleaning furnaces and slag fuming processes are also operated to remove volatile metals that are collected as flue dusts. These flue dusts and other residues therefore form the raw materials for a variety of metals.

Volatile metals and their oxides are also found in dusts and residues from other processes for example dust from steel making. These residues provide the raw material for other processes to recover zinc and other volatile metals. In these processes, a rotary kiln (Waelz kiln) or an Ausmelt/ISA Smelt furnace is used to fume the metal and enrich zinc and lead in a mixed oxide which can then be recovered in other pyrometallurgical processes.

Tanks and other equipment used in hydrometallurgical plants are mostly ventilated to atmosphere to ensure a safe workplace. This ventilation air may contain an acidic mist that contains metal compounds from the solution. Removal techniques comprise wet scrubbers or demisters. The demister elements are placed in the gas stream in the vent stack or on top of the cooling towers and the separated solution flows back into the main reservoir.

**Achieved environmental benefits**
Prevention of emissions of metals and their recovery. *(Isn't this misleading. For me it read as if emissions and recovery should be avoided.*

**Cross-media effects**
There is an increase in energy use. Waste or waste water may be produced if the collected material cannot be returned to the process.

**Operational data**
No data has been reported but the metal-specific chapters provide some information.

**Applicability**
This technique is generally applicable to most plants.

**Economics**
The processes are operating economically and costs, where they are available, are reported in Annex I to this document.

**Driving force for implementation**
A reduction of emissions and a saving of raw materials.

**Example plants**
Plants in DE, AT, FR, BE, PL.

**Reference literature**
[ 226, Nordic Report 2008 ], [ 103, Farrell, F. 1998 ].

### 2.9.2.8 Mercury

*This again is an example where the given information is quite specific and should be relocated next to the relevant metal section.*

**Description**
Mercury is volatile at the temperatures encountered in most abatement processes and other techniques may be needed to remove it [ 25, OSPARCOM 1996 ] [ 136, Fugleberg, S. 1999 ]. In the case of mercury removal before a sulphuric acid plant, any residual mercury will be present in the acid that is produced, the product specification is normally <0.1 to 0.5 ppm and is equivalent to ~ 0.02 mg/$Nm^3$ in the cleaned gas and all processes listed below are reported to achieve this[r4]:

- Boliden-Norzink process: this process is based on a wet scrubber using the reaction between mercuric chloride and mercury to form mercurous chloride (calomel), which precipitates from the liquor. The process is placed after the washing and cooling step in the acid plant, so the gas is dust and $SO_3$ free and the temperature is about 30 °C. The gas is scrubbed in a packed bed tower with a solution of $HgCl_2$. This reacts with the metallic mercury in the gas and precipitates it as calomel, $Hg_2Cl_2$. The calomel is removed from the circulating scrubbing solution and partly regenerated by chlorine gas to $HgCl_2$, which is then recycled back to the washing stage. The mercury product bleed is either used for mercury production or stored[r5]. Mercury chloride is a very toxic compound of mercury and great care should be taken when operating this process.

- Bolchem process: this process step is located in the acid plant like in the Boliden-Norzink process, but the removal is effected by 99 % sulphuric acid. This acid comes from the absorption part of the acid plant and it oxidises the mercury at ambient temperature. The resulting acid that contains mercury is diluted to 80 % and the mercury is precipitated as sulphide with thiosulphate. After filtering off the mercury sulphide, the acid is returned to the absorption stage. No acid is therefore consumed in the process.
- Outotec process: in this process the mercury is removed before the washing step in the acid plant. The gas at about 350 °C, is led through a packed bed tower where it is washed countercurrently with 90 % sulphuric acid at about 190 °C. The acid is formed *in situ* from the $SO_3$ in the gas. The mercury is precipitated as a selenium chloride compound. The mercury sludge is removed from the cooled acid, filtered and washed and sent to the production of metallic mercury. Part of the acid is then recycled to the scrubbing step. In a revision to this process, mercury is removed from the gases by washing with a solution of selenium ions when selenium metal is produced along with mercury selenide.
- Sodium thiocyanate process: this process is used at a zinc roaster. The $SO_2$ gas is washed with a solution of sodium thiocyanate and the mercury is removed as sulphide. Sodium thiocyanate is regenerated, the reaction is shown in the following formula.

$$3Hg + 8SCN- + 4\ H + + SO_2 \Rightarrow 2(Hg(SCN)4)2- + HgS + 2H_2O$$

- Activated carbon filter (Lurgi process): this is an adsorption filter using activated carbon to remove mercury vapour from the gas stream.

The Boliden-Norzink and Outotec processes detailed above are most commonly used, but other processes have been reported elsewhere [ 25, OSPARCOM 1996 ], [ 330, Helja Patent 1985 ].

- Selenium scrubber: this is also based on a wet scrubber and uses the reaction between amorphous selenium in sulphuric acid and mercury to remove high concentrations of mercury vapour.
- Selenium filter: a dry scrubbing process which uses amorphous selenium to react with mercury vapour to form mercury selenide.
- Lead sulphide process: a dry scrubbing process using lead sulphide nodules as the medium removes mercury from the gas stream.
- Tinfos/Miltec process: a mercury cleaning process, which is based on oxidation of mercury in the off-gas using sodium hypochlorite. After oxidation in a washing tower, the mercury is precipitated as mercury sulphide (HgS) by the addition of disodium sulphide. The mercury sulphide is removed from the process in a press filter. The sludge that contains mercury is treated as hazardous waste and disposed of in a sealed disposal site. The mercury emissions are reduced by approximately 94 %. The mercury cleaning plant at Tinfos is thoroughly described by Haaland et. al. at Infacon 9 [ 226, Nordic Report 2008 ].
- Lurgi mercury cleaning process: the Lurgi mercury removal unit consists of an electrostatic precipitator to remove residual dust and tars, a gas heater, a packed bed absorber, a fan-damper system to control the gas flow through the unit and extensive gas analysis nitrogen purge equipment to maintain low oxygen levels in the gas. The heater is required to warm the gases to the optimum temperature of 60 - 85 °C; lower gas temperatures result in lower reaction rates and moisture condensation in the packed bed, higher temperatures can result in sulphur being lost from the absorbent. Eramet commissioned a mercury removal unit in 2001 and reports trouble free operation since. Gas flowrates through the unit are around 15000 $Nm^3$/hour. Mercury absorption efficiency is 98 %. After allowing for plant startups, etc, 94 % of the total mercury in the raw gases is captured. Absorber mass is changed after about 8 months of operation and is

disposed of in a secure disposal. Only trace amounts of mercury report to the scrubber water [ 226, Nordic Report 2008 ][r6].

- Boliden-Contech process: selenium coated spheres are used in a packed bed. The method works but the experience in the Scandinavian ferro-alloy industry is limited for this technique.
- The Dowa process where mercury is adsorbed onto pumice stones coated with lead sulphide.

Two other processes are available to reduce the mercury content in sulphuric acid produced during the production of non-ferrous metals and their use is based on a need to improve the quality of the acid rather than on environmental effects:

- Superlig ion exchange process: this process uses ion exchange to remove mercury from the product acid and achieves a concentration of mercury of <0.5 ppm.
- Potassium iodide is added to the acid, which should be at least 93 % strength, at a temperature of about 0 °C. Mercury iodide, $HgI_2$, is then precipitated.

**Achieved environmental benefits**

The product specification is normally <0.1 to 0.5 ppm in sulphuric acid and is equivalent to <0.02 mg/Nm$^3$ in the cleaned gas. The[r7] prevention of emissions and recovery of mercury and the production of mercury-free sulphuric acid. Regulation EC 1102/2008 classifies mercury and mercury compounds produced during the production of non-ferrous metals as waste with effect from 15 March 2011.

**Cross-media effects**

There is an increase in energy use. A solid or liquid waste is produced that will require disposal[r8].

**Operational data**

No data has been reported but the metal-specific chapters provide some information.

**Applicability**

This technique is generally applicable to most plants.

**Economics**

The processes are operating economically and costs, where they are available, are reported in Annex I to this document.

**Driving force for implementation**

A reduction of emissions and the production of saleable acid.

**Example plants**

Plants in DE, AT, FR, BE, PL.

**Reference literature**

[ 226, Nordic Report 2008 ], [ 25, OSPARCOM 1996 ], [ 136, Fugleberg, S. 1999 ], [ 218, VDI (D) 1997 ], [ 292, Kojo et al. 2006 ], [ 103, Farrell, F. 1998 ].

#### 2.9.2.9 Use of oxygen enrichment in combustion ~~systems~~air

*Check if this heading is correct. Crosscheck with section 2.9.2.4.3.*

*This again is an example where the given information is quite specific and should be relocated next to the relevant metal section. This technique is applied in many furnaces. These furnaces are no combustion systems.*

**Description**

Oxygen enrichment of the combustion air is frequently used in the production processes for non-ferrous metals. The processes use tonnage oxygen directly or in the furnace body. This enrichment is used to allow autothermal oxidation of sulphide-based ores, to increase the capacity or melting rate of particular furnaces and to provide discrete oxygen-rich areas in a furnace to allow complete combustion separately from a reducing zone.

The use of oxygen can give both financial and environmental benefits provided that the plant can accommodate the extra heat released. There is a possibility that higher concentrations of nitrogen oxides can be produced with oxygen enrichment but the associated reduction in gas volume usually means that the mass is reduced. Further discussion will be made in the relevant metal chapters.

**Achieved environmental benefits**
The prevention of emissions of metals, dust and other compounds.

**Cross-media effects**
Positive, an overall reduction in energy use is possible.

**Operational data**
Oxygen can achieve the following improvements:

- The increase in the heat released in the furnace body allows an increase in the capacity or melting rate and a reduction in the quantity of fuel used and an associated reduction in greenhouse gas emissions. It is possible to operate some processes autothermally and vary the extent of oxygen enrichment "on-line" to control the metallurgical process and prevent emissions.
- A significant reduction in the volume of process gases produced as the nitrogen content is reduced. This allows a significant reduction in the size of downstream ducts and abatement systems and prevents the loss of energy involved in heating the nitrogen.
- An increase in the concentration of sulphur dioxide (or other products) in the process gases allows conversion and recovery processes to be more efficient without using special catalysts.
- The use of pure oxygen in a burner leads to a reduction of nitrogen partial pressure in the flame and therefore thermal $NO_X$ formation may be reduced. This may not be the case with oxygen enrichment in or near the burner, or if there is significant leakage of air into the furnace as the higher gas temperature may promote thermal $NO_X$ formation. In the latter case, oxygen can be added downstream from the burner to reduce this effect and maintain the improvement in melting rate.
- The production of tonnage oxygen on site is associated with the production of nitrogen gas separated from the air [ 115, ETSU (UK) 1996 ]. This is used occasionally for inert gas requirements on site. Inert gases are used for abatement systems when pyrophoric materials are present (e.g. dry Cu concentrates), for degassing molten metal, for slag and dross cooling areas and for fume control of tapping and pouring operations.
- Injection of oxygen at discrete points in a furnace downstream of the main burner allows temperature and oxidising conditions to be controlled in isolation from the main furnace operations. This allows the melting rate to be increased without an unacceptable increase in temperature. An example is the provision of an integral afterburning zone in a blast furnace.

**Applicability**
This is a technique that can be applied to most of the combustion and pyrometallurgical processes in use. The full benefit is achieved with new plants where the combustion chamber and abatement systems can also be designed for the lower gas volumes. The technique is also applicable to existing plants and can in many cases be retrofitted.

**Economics**

Some data on costs involved in oxy-fuel firing for secondary aluminium production are given in Table 2.20.

Gas consumption savings of EUR 12/t are reported which, on the basis of an expected production of 13500 t/year (one furnace), represents an annual saving of EUR 152000. Oxygen consumption represents an additional cost of EUR 12/t, which represents an annual cost of EUR 152000.

The economical advantages are therefore mainly related to improvements in terms of production rate. In 1999 the fixed costs were around EUR 145/t for two furnaces (22561 tonnes produced/year). The higher productivity allowed by using oxy-fuel burners would result in a cut in these costs to around EUR 122/t (22651 × 145/27000). There is therefore a potential saving of EUR 23/t for a production rate of 27000 t/y.

| **Parameter** | **Benefits/costs** | **Comment** |
|---|---|---|
| Melting time | - 2.45 h/charge | Reduced batch melting time |
| Productivity | + 0.84 t/h | Increased productivity of the furnace |
| Gas consumption | - 80 $m^3$/t<br>(tonne of oxygen) | Reduced consumption of gas |
| $O_2$ consumption | + 126 $m^3$/t | Additional consumption of oxygen |

**Table 2.20: Techno-economic comparison of an oxy-fuel burner compared to an air-fuel burner**

### Driving force for implementation

Reduction of emissions, saving energy.

### Example plants

Plants in DE, AT, FR, BE, UK.

### Reference literature

[ 122, ETSU 1994 ], [ 276, French PCDD/F Report 2008 ], [ 103, Farrell, F. 1998 ].

## 2.10 Dioxins and furans

*The structure and hierarchy does not fit. Dust, VOC, Mercury, NOx are four digit headers. Why are Dioxins at a 2 digit header level. Make consistant. The info an Dioxin generation and removal should also be relocated to relevant metal specific sections.*

### 2.10.1 Sources and formation of polychlorinated dibenzo dioxins and furans (PCDD/F)

In this document, dioxins and furans are referred to together as PCDD/F.

PCDD/F are formed by gas-phase reactions with chlorinated organic precursors. Apart from a carbon source, which is always present, only small amounts of chlorine in the input materials (30 - 300 ppm in typical ores and a few ppm in metals) or in the fuels (commercial coke has, for example a chlorine content of around 0.05 % by mass) will be sufficient for PCDD/F to form. Processes prone to PCDD/F formation include, for instance, combustion processes, ore sintering, metal smelting and, hence, also pyrometallurgical processes. The greater part of PCDD/F formation occurs through de novo synthesis as the off-gas is being cooled through the temperature window of approximately 400 to 200 °C in the presence of reactive carbon, chlorine, oxygen and a catalytically active metal like copper.

The main sources of PCDD/F formation in non-ferrous metallurgy may be [ 306, Environment Dioxins Report 2007 ]:

- smelting secondary copper, aluminium and lead (dirty input materials, that contain chlorine and organics, no adequate operation conditions or gas-cleaning )
- melting and alloying metals, in particular in the presence of copper and when heated with gas under substoichiometric conditions.

Minor sources of PCDD/F formation are:

- foundries
- smelting secondary copper, aluminium and lead (clean input materials, optimised operation and/or flue-gas-cleaning ).

Sources that are not well known are:

- other sintering processes, as applied at a relatively modest scale to non-ferrous ores
- sources that are probably negligible are other processes, fitted with well-designed, well operated thermal or catalytic post-combustion or deNOx catalysis, and without subsequent heat recovery.

However, whether and to what extent PCDD/F will be emitted with the off-gas not only depends on the fuels used and materials processed (e.g. metals with catalytic properties), but is primarily a matter of process control (mass transfer conditions) and the specific off-gas conditions (e.g. temperature, residence time in the different temperature windows, $SO_2$ content). PCDD/F are also relevant to the production of metals in processes that need chlorination such as the electrolytic production of magnesium from seawater and dolomite.

This industry relies on sources of secondary raw materials from the scrap industry. Although there are agreed scrap grades, the impurities present may lead to the formation of PCDD/F during incomplete combustion or by de novo synthesis. The presence of PCDD/F in EAF dust and the presence of polychlorinated biphenyls on transformer scrap and other materials are potential direct sources of PCDD/F. The aim should be to operate at or below 0.1 ng ITEQ/Nm$^3$ should be used when PCDD/F contamination is present.

The presence of oils and other organic materials on scrap or other sources of carbon (partially burnt fuels and reducing agents, such as coke), can produce fine carbon particles which react with inorganic chlorides or organically-bound chlorine in the temperature range of 250 to 500 °C to produce PCDD/F. This process is known as de novo synthesis and is catalysed by the presence of metals such as copper or iron. Pre-selection or treatment of the feed material to minimise the amount of precursors or organic matter is therefore a very important measure to prevent the formation of PCDD/F.

High levels of $SO_2$ are reported to inhibit de novo synthesis in municipal solid waste incinerators where the formation of $CuCl_2$, which is said to act as a catalyst for de novo synthesis, is inhibited by the formation of $CuSO_4$ [ 278, Hunsiger et alles 2007 ]. This effect might be applicable in the non-ferrous metals sector and could influence the sequence of $SO_2$ removal.

## 2.10.2 Techniques to consider in the determination of BAT for the prevention and destruction of PCDD/F

The sections of this document entitled "Techniques to consider in the determination of BAT" set out techniques considered generally to have potential for achieving a high level of environmental protection in the industries within the scope of the document. The background to the way the techniques are described is given in Section 2.1.2 and Table 2.2.

### 2.10.2.1 Examples of techniques to consider

**Description**

Although PCDD/F are destroyed at high temperatures (above 850 °C) in the presence of oxygen, the process of de novo synthesis is still possible as the gases are cooled through the “reformation window”. This window can be present in abatement systems and in cooler parts of the furnace, e.g. the feed area. Care taken in the design of cooling systems to minimise the residence time in the window is practised to prevent de novo synthesis. Sufficient oxygen should be present in the hot gases and oxygen injection can be used to ensure complete combustion. PCDD/F are easily adsorbed onto solid matter and may be collected by all environmental media such as dust, scrubber solids and filter dust.

Possible methods for reducing the emissions of PCDD/F are given below:

- Active coke technique: the addition of activated carbon to calcium hydrate (or lime, sodium bicarbonate, etc.) has proven to be an effective adsorbent in secondary aluminium smelting plants using feedstock that contains metal with organic contamination. Active carbon is also used in a primary copper smelter where a number of other metals are also recovered, the fine grained active carbon binds the PCCD/F and is removed in fabric filters or ESPs. The quantity and composition of the additive depend to a large extent on the process conditions and the origin and composition of the input materials. To reduce the need for an adsorbent, it may be useful to return all or some of the filter dust to the process. Moreover, the adsorbent required must be adapted to the emission behaviour of the plant. With respect to sorbent consumption, optimised solutions must be individually tested in relation to the smelting technology employed in each case.
- Combustion conditions: improvements of the combustion conditions can include the use of enriched air or pure oxygen, enhanced or improved mixing of oxygen with combustibles, the raising of the combustion temperature or the residence time at high temperature.
- Thermal post combustion or afterburner: incinerating the off-gas followed by a rapid quench of the hot gas also minimises PCDD/F formation. Catalytic oxidation systems are also available for the destruction of PCDD/F.

- Reducing the organic contents: removing organic contaminants (e.g. machining oil, coatings) of the feed are also a measure to reduce PCDD/F formation.
- Oxygen injection in the upper zone of a furnace: the process concerned has no room to allow an afterburner to be fitted. There are some restrictions in the degree of gas mixing achieved but the overall performance is acceptable.
- Modification to furnace charging systems: modifications have been made to give small, even additions of raw materials in semi-closed furnaces. This reduces furnace cooling during charging, maintains higher gas temperatures, optimises the process and prevents the reformation of PCDD/F [ 233, Farrell Nordic Mission 2008 ].
- High efficiency dust filtration to remove the dust. PCDD/F. PCDD/F may be absorbed onto dust and can be removed using high efficiency dust filtration. It has been reported that fabric filters that incorporate a catalytic layer are available.

**Achieved environmental benefits**
The destruction of PCDD/F as well as the destruction of CO and other carbon compounds.

**Cross-media effects**
The energy used to produce oxygen. The collected dusts may have high PCDD/F concentrations and may need to be disposed of or treated carefully by returning dusts to the furnaces.

**Operational data**
In a secondary aluminium plant using a tilting rotary furnace, exhaust gases are treated with an afterburner and then with sorbalite (lime hydrate and activated carbon). In the same installation a rotary furnace is used and dust and fume is treated with $NaHCO_3$ and activated carbon. The filter dust is collected and can be treated with the salt slag from the furnace. There is also a closed-well furnace and these gases are treated with sorbalite. The measured emissions are well below 0.1 ng I-TEQ/$Nm^3$. Some emission results are given in Table 2.21 below.

| Plant | PCDD/F ng I-TEQ/$Nm^3$ | Comment |
|---|---|---|
| Hoboken, BE new batch process | 0.001 | Precious metals, copper and lead. Dust is used in another process. |
| Aurubis, Lunen, DE | 0.001 – 0.4 | |
| Brixlegge, AT | 0.6 – 0.9 | Secondary copper with RTO |
| Metallo-Chimique, BE | 0.01 | |
| Affinage de Lorraine, FR | 0.07 | At measured $O_2$ content |
| German plants secondary Al plants, DE | 0.1 – 0.5 | ELVs reported |
| AMAG, AT | < 0.1 | |
| Lead battery de-sulphurised paste, DE | 0.1 – 0.4 | ELVs reported |
| Lead battery de-sulphurised paste, DE | 0.1 – 0.4 | ELVs reported |
| Whole battery, DE | 0.1 – 0.4 | ELVs reported |
| Ferro-alloys, AT | 0.0004 | |

**Table 2.21: PCDD/F emissions for some metal industry installations**
[ 178, UBA (A) 1998 ], [ 229, Umicore etc 2007 ], [ 234, UBA Copper, lead, zinc and aluminium 2007 ], [ 256, Plant visit report AMAG 20071114.doc 2007 ], [ 249, Austria Brixlegge Report 2007 ], [ 276, French PCDD/F Report 2008 ].
*Values included should not refer to ELVs. Try to get more and better real measured data. For dioxins companies tend to give the lowest and the highest values. What is needed is a range, an average, a 97th percentile.*

These value ranges should be viewed in terms of the accuracy involved in sampling and analysing these very low levels of PCDD/F, in particular how the results for any of the congeners that are below the limit of detection are reported.

**Applicability**

The techniques given above are all techniques to consider depending on the application, and they can all be incorporated into existing processes. The most effective and economically viable technique will depend on the specific site, safety aspects and operational stability as well as economic factors. Emission levels of better than 0.5 ng I-TEQ/Nm$^3$ can be achieved using one or more of these techniques to the clean gas side of the system. Lower values better than 0.1 ng I-TEQ/Nm$^3$ can be achieved by a combination of these techniques.

**Economics**

No data has been reported for all processes but the technique used in FR for secondary aluminium reports the following costs:

- Total investment costs were around EUR 485000 for both oxy-fuel burners and the lignite coke injection. The cost of coke injection alone was EUR 183000.
- The measurement and control operational cost was EUR 36400.
- There were also cost savings that amounted to EUR 23 per tonne, which represents EUR 300000/year. Consequently, the payback is lower than two years.

**Driving force for implementation**

Compliance with environmental permits.

**Example plants**

AT, DE, FR.

**Reference literature**

[ 121, Rentz, O. et al. 1999 ], [ 234, UBA Copper, lead, zinc and aluminium 2007 ], [ 256, Plant visit report AMAG 20071114.doc 2007 ], [ 249, Austria Brixlegge Report 2007 ], [ 276, French PCDD/F Report 2008 ], [ 178, UBA (A) 1998 ].

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## 2.11 Sulphur Dioxide

*This section might stay here since it has a more outstanding character compared to other pollutants.*

### 2.11.1 Formation of sulphur dioxide

Sulphur dioxide is produced during the drying and smelting of sulphidic concentrates and other material. Calcining, smelting, converting and other operations produce sulphur dioxide at varying concentrations and the removal systems used depend on the concentration encountered.

Sulphur that is present in raw materials can be incorporated into slags or mattes using appropriate reagents, mattes can be used in the processes. Sulphur that is not captured in the matte or slag from a smelting process is usually present as $SO_2$ and can be recovered as elemental sulphur, liquid $SO_2$, gypsum or sulphuric acid. The presence of markets for these products influences the choice of the end-product but the most environmentally safe option is to produce gypsum or elemental sulphur in the absence of reliable outlets for the other products. Sulphur dioxide is produced from the roasting and smelting of sulphide concentrates and the associated conversion processes. These processes are operated so that the maximum concentration of sulphur dioxide is produced to improve the efficiency of sulphur recovery. The recovery of sulphur eliminates cross-media issues.

#### 2.11.1.1 General principles of sulphur dioxide removal

**Techniques for gases with up to 1 % sulphur dioxide**

1. Lime injection followed by a fabric filter.
2. The Wellman-Lord regenerable process which involves the reaction of weak gases with sodium sulphite and water to produce sodium bisulphite. Concentrated sulphur dioxide can be stripped from this solution and liquid sulphur dioxide produced or other products made such as sulphur.
3. Scrubbing with an amine or polyether-based solvent which can absorb sulphur dioxide, which is then desorbed and sent as a side-stream to a sulphuric acid plant or removed by a reaction with water to produce sulphuric acid or liquid sulphur dioxide (Asarco, Solinox or Cansolv processes).
4. Peracidox process; oxidation with hydrogen peroxide to produce sulphuric acid.
5. Sulfacid process; oxidation with an active carbon catalyst to produce sulphuric acid.
6. Flue-gas desulphurisation (FGD) in a dry or semi-dry scrubber using lime or wet limestone to produce gypsum or other desulphurisation products. This technique is used extensively in power plants.
7. Double alkaline scrubbing with caustic soda absorption and gypsum precipitation.
8. Seawater scrubbing.
9. Alumina absorption and gypsum precipitation (Dowa process).
10. Magnesium sulphate precipitation.
11. Wet or dry scrubbing with zinc oxide to produce zinc sulphite or sulphate which can be treated in a zinc leaching stage.

**Techniques for gases with higher concentrations of sulphur dioxide are described below**

Sulphur dioxide is produced at higher concentrations during the sintering, roasting and smelting of a wide range of sulphidic ores and concentrates. The metals produced are copper, nickel, lead, zinc, molybdenum and several mixed metal streams. The techniques used to treat these higher strength gases are listed below:

1. Absorption of sulphur dioxide in cold water (e.g. cold seawater) followed by vacuum stripping and recovery as liquid sulphur dioxide. These processes are used in conjunction with a sulphuric acid plant to recover sulphur dioxide that is not dissolved. The potential for the production of liquid sulphur dioxide depends on the existence of a local market.

2. Production of sulphuric acid. The production of sulphuric acid by burning sulphur to produce sulphur dioxide is a well established chemical process. These installations benefit from a constant, high concentration of the gas and therefore have fewer process limitations. Gases from a roaster or smelter do not have these characteristics and are more difficult to operate and may not achieve the same level or consistency of conversion.

The smelter gases from the furnace are cleaned and cooled and may be dried Figure 2.45 (see also Section 4.4.11 of the LVIC-AAF BREF [ 339, BREF LVIC-AAF 2007 ]). The sulphur dioxide in the gas is then converted to sulphur trioxide in a contact process when the gases are passed through a vanadium pentoxide catalyst bed. Sometimes the catalyst is doped with caesium oxide, which improves performance particularly when the $SO_2$ concentration is low and variable or when the temperature is low. The plant design should allow operation at lower temperatures (depending on heat exchanging performance). See the LVIC-AAF BREF [ 339, BREF LVIC-AAF 2007 ] Section 4.4.4. Improved catalysts are used to increase the conversion efficiency in single and double contact plants.

In a **single contact plant,** the gases pass through a series of three or more catalyst beds to obtain high conversion efficiency. The production of sulphur trioxide is exothermic and if the sulphur dioxide content is high enough to generate sufficient heat, the gases are cooled between each pass. With gases that have a low sulphur dioxide content, heat may have to be added before the passes. The sulphur trioxide formed is then absorbed in 98 % sulphuric acid, which is then diluted to give sulphuric acid. The WSA process is a development of the single contact plant and can achieve up to 99.3 % conversion. The process is described in Section 2.11.3.3.

The presence of sulphur trioxide inhibits the conversion of sulphur dioxide and a **double contact process** is therefore most commonly used to achieve more efficient sulphur dioxide conversion when the sulphur dioxide content of the gas is sufficiently high. In this case, sulphur trioxide is absorbed into 98 % sulphuric acid after the second or third pass, allowing conversion of more sulphur dioxide in the subsequent passes. This is followed by a further sulphur trioxide absorption stage. The use of a double contact plant increases the removal efficiency of sulphur dioxide from 98 % to >99.7 % [ 130, Eurometaux Copper Industry 1998 ]. It has also been reported that if the plant design allows operation at a lower temperature (depending on the heat exchanger performance) the use of a caesium-doped catalyst can improve this to greater than 99.97 % under very special conditions [ 137, Riekkola-Vanhanen, M. 1999 ], [ 240, Nl Input on Zn production 2008 ]. Catalysts decrease in effectiveness as they age and the effect can lead to a 0.1 % reduction in conversion over a three year operating period [ 339, BREF LVIC-AAF 2007 ]. The double contact plant is shown in Figure 2.46.

Conversion to double contact is complex and expensive (see also Section 2.11.3.3) but it is possible to use a single contact plant with tail gas desulphurisation to achieve lower residual $SO_2$ concentrations. Gypsum can be produced for external sale or alternatively zinc sulphite (or sulphate) can be produced which can be used in the zinc leaching stage. These options can allow energy savings and lower waste generation but the cost must be compared to conversion using local conditions. If there is no market for gypsum, the costs for landfilling gypsum need to be considered.

Dust removal before the contact process is essential to protect the catalyst and to produce a pure acid. This reduces the concentration of most metals, for example zinc, to acceptable levels in the acid that is produced and prevents the poisoning of the catalyst. The pretreatment of the gas stream usually involves several stages depending on the contaminants present in the gas stream. The stages can include cooling with heat recovery, a hot electrostatic precipitator, scrubbing to remove mercury, etc. and a wet electrostatic precipitator. The weak acid generated in the gas-cleaning section contains typically 1 - 50 % $H_2SO_4$. Halides will also be present as HCl (10 - 5000ppm) and HF (10 - 1000 ppm including $H_2SiF_6$). In the Polish plant Głogow 2, there is a high level of fluoride in the gas entering cooling and washing scrubber (500-2000 ppm). A system is used to remove fluoride from the gas stream by dosing a solution of sodium silicate into the scrubber circuits. The acid may also contain metals such as copper, zinc and iron (individually up to 2500 ppm), mercury (up to 1900 ppm) and lead (up to 50 ppm). Arsenic may be present up to levels of 10000 ppm. Other elements, such as aluminium, nickel, chromium, cadmium, bismuth, antimony, etc. may also be present depending on the contaminants present in the smelter feed. The weak acid will also be saturated with $SO_2$ (typically between 2000 and 5000 ppm depending on the $SO_2$ strength). This acid can be decomposed and the gases passed to the acid plant can be neutralised to produce gypsum for sale, treated and disposed of or used, e.g. if there is a leaching process nearby.

The sulphuric acid production process removes any residual dust and metals before the contact stage so that they not are transferred to the acid that is produced. The removal of dust and metals before the contact process (see Figure 2.45) means that these are not significant components in the gases emitted to air [ 234, UBA Copper, lead, zinc and aluminium 2007 ]. Acid mists can be emitted from the stack and candle filters or wet scrubbers can be used where they are needed to eliminate these mists. It is reported that high fluoride levels in the gas reduces the mist elimination efficiency of candle filters [ 103, Farrell, F. 1998 ] (see also the LVIC-AAF BREF [ 339, BREF LVIC-AAF 2007 ]).

Any $NO_X$ that is present in the gases treated in the sulphuric acid plant is absorbed in the acid that is produced. If the concentrations are high then a brown acid is produced and this may not be acceptable to potential customers. The problem is therefore one of potential sales. When sulphuric acid is brown due to organic compounds, hydrogen peroxide can be added to remove the colour.

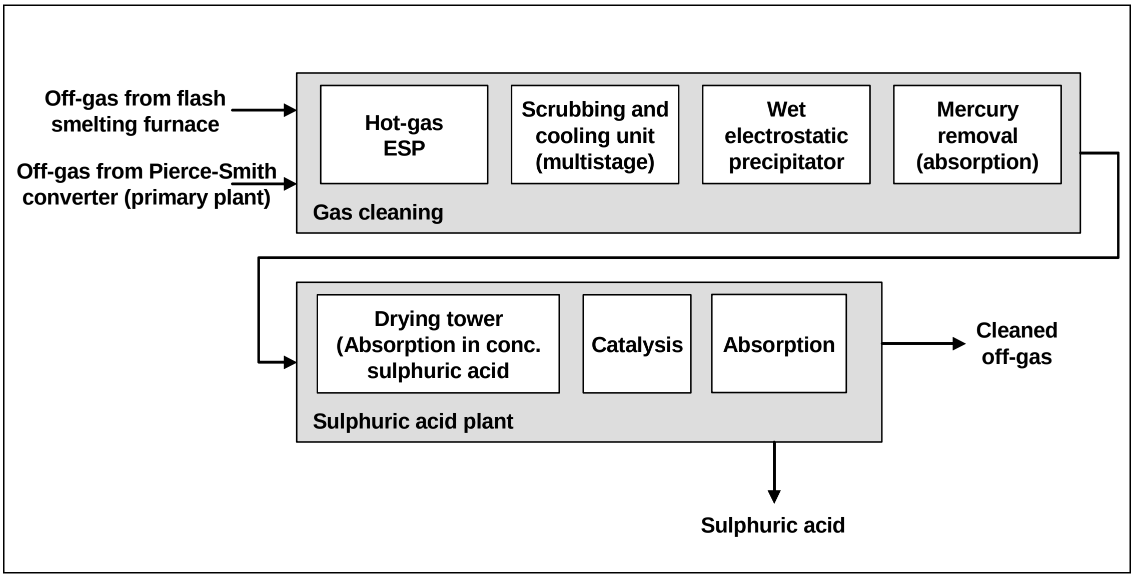

**Figure 2.45: Typical gas-cleaning train for a sulphuric acid plant**

The off-gas from the flash furnace entering the acid plant of Głogów 2 in Poland contains a high level of $NO_X$ (up to 1000 ppm), so to maintain the required level of 5 ppm in the produced acid, there are two systems for decomposing the nitrogen oxides. One of them doses hydrazine to the drying and absorbing acid circuits, the other one decomposes nitrogen compounds from the mist eliminators condensate by diluting and blowing with $SO_2$-rich gas (Lurgi method) [ 238, ECI Copper Installations 2008 ]. A plant in the Netherlands uses SCR in the first pass to achieve the same quality of acid and the final emission of $NO_X$ is quoted as 10 ppm [ 240, Nl Input on Zn production 2008 ].

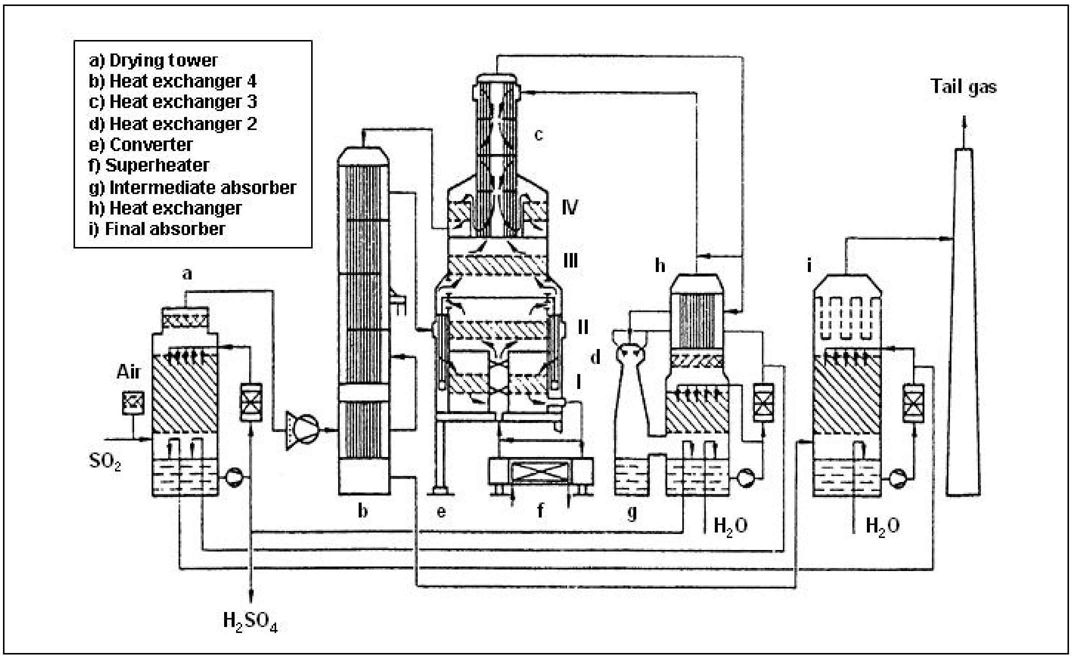

**Figure 2.46:** **Typical double absorption sulphuric acid plant**

Process control based on the measurement of $SO_2$ in the off-gas leads to a delayed reaction of the process. In the non-ferrous metal sector, the oxygen level can be used for process control but makes the control of the sulphuric acid plant far more complex than for sulphur burning [ 234, UBA Copper, lead, zinc and aluminium 2007 ].

Sulphuric acid plants in this sector that have highly variable $SO_2$ inlet concentrations need to be operated at temperatures that are 20 °C below the maximum catalyst temperatures so that the catalyst is not deactivated. The effect is shown in Figure 2.47. Catalysts can also fail if the temperature is too low and therefore it is very important to keep the temperature level sufficiently high to prevent the catalysis from switching off quickly which occurs at low $SO_2$ inputs. The level of temperature is about 10 - 30 °C higher in comparison with steady-state operation, causing a significant decrease of the conversion rate. The temperature operating window for a sulphuric acid plant in this sector is therefore more restricted than in a sulphur burning plant.

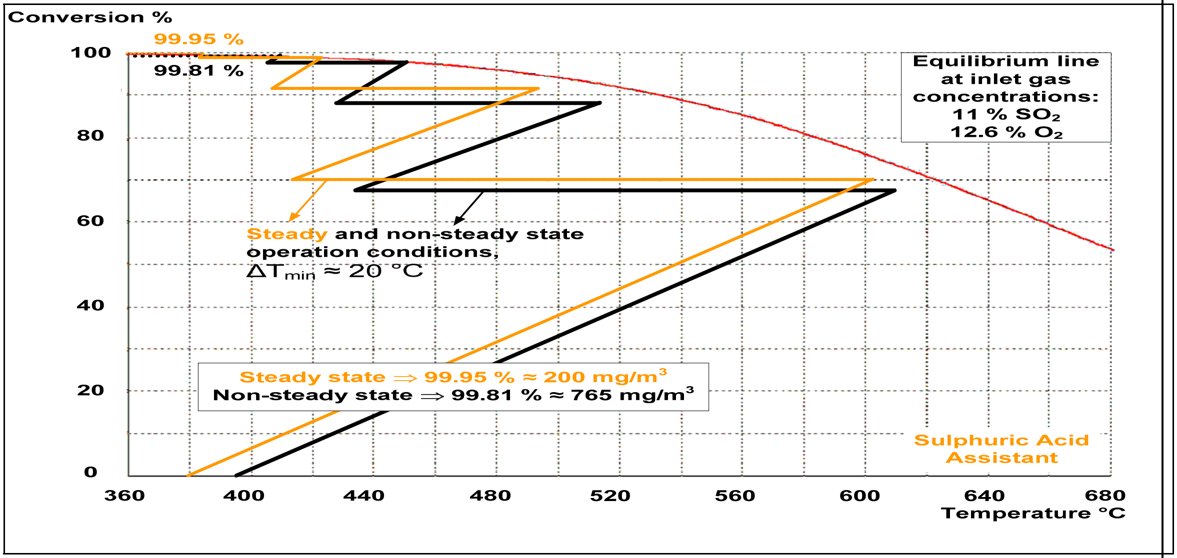

**Figure 2.47:** **Comparison of steady and non-steady-state $SO_2$ inlet concentrations on conversion efficiency**

[ 313, UBA DE Sulphur dioxide conversion 2009 ]

The emission of sulphur dioxide from sulphuric acid plants is proportional to the conversion rate provided that the sulphur dioxide content of the feed gas is constant (respectively proportional to the sulphur dioxide content of the feed gas) [ 313, UBA DE Sulphur dioxide conversion 2009 ]. Data is given in the LVIC - AAF BREF [ 339, BREF LVIC-AAF 2007 ] for the conversion rate and outlet $SO_2$ concentrations for a number of inlet gas strengths. However, because of missing information from the TWG of the LVIC-AAF BREF [ 339, BREF LVIC-AAF 2007 ], the calculated number for other double contact/double absorption plants (680 mg/Nm$^3$) does not take into account the reduction in gas volume that results from the absorption of $SO_3$ during the process. The correct equation for the calculation of the inlet concentration and the conversion rate is given in Figure 2.48

$$C_{SO_2,out} = \frac{(1-\eta_{SO_2})\times\rho_{SO_2}\times C_{SO_2,inlet}\times 10^6}{(1-1.5\times C_{SO_2,inlet})}$$

**Figure 2.48: Equation for the calculation of the inlet concentration and the conversion rate ή is the conversion rate and $\rho$ is the density**

The data for existing plants in the LVIC-AAF BREF [ 339, BREF LVIC-AAF 2007 ] was calculated at 99.8 % conversion using an inlet strength of 11 % $SO_2$ and an off-gas concentration of 680 mg/Nm$^3$ is predicted. The equivalent result when using the correct graph gives a predicted off-gas concentration of 770 mg/Nm$^3$ using the same conversion rate and inlet gas concentration [ 313, UBA DE Sulphur dioxide conversion 2009 ] [ 314, UBA DE Sulphur dioxide volume reduction data 2009 ]. As a consequence, the concentration given in Table 2.24 of the LVIC-AAF BREF for other double contact/double absorption plants (680 mg/Nm$^3$) is now 770 mg/Nm$^3$. The missing data has now been provided and the corrected graph is shown as Figure 2.49.

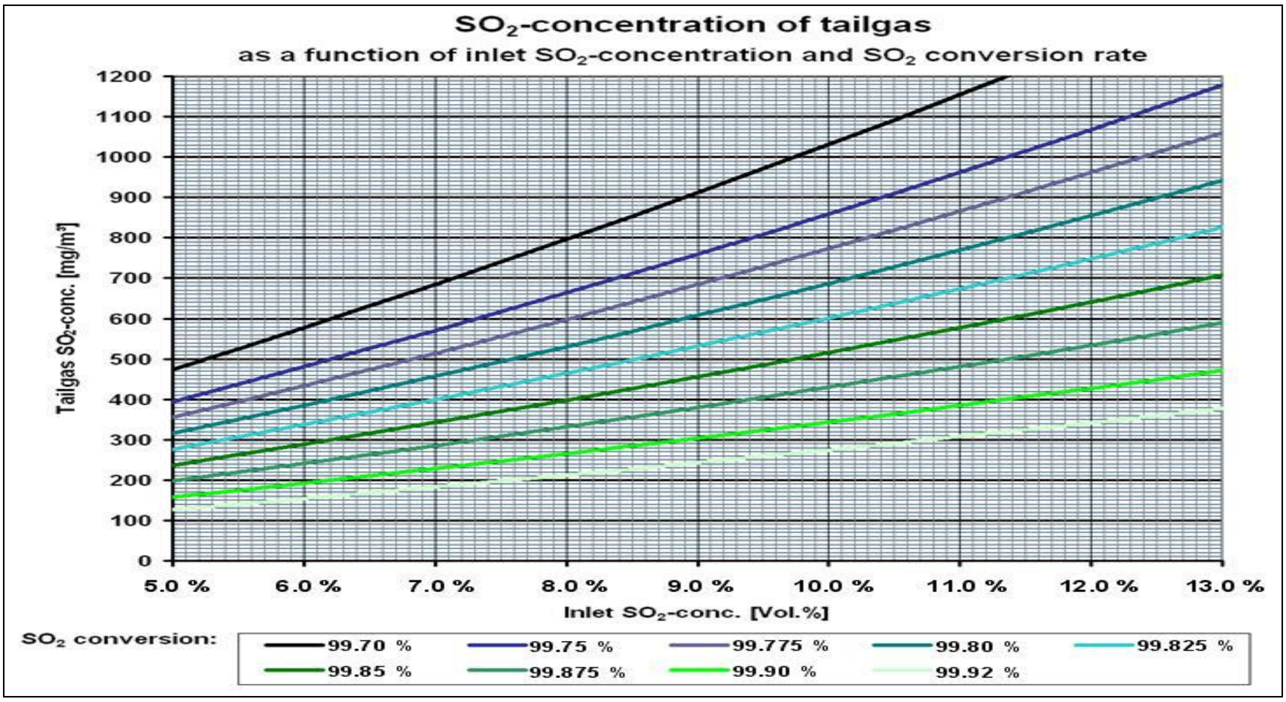

**Figure 2.49: Conversion of $SO_2$ to sulphuric acid**
[ 313, UBA DE Sulphur dioxide conversion 2009 ]

### 2.11.2 Current emission and consumption levels

The performance of the EU-27 sulphuric acid plants associated with the production of non-ferrous metals is shown in Table 2.22, Table 2.23 and Table 2.24 [ 238, ECI Copper Installations 2008 ], [ 230, FF Mission report 2007 ], [ 229, Umicore etc 2007 ], [ 233, Farrell Nordic Mission 2008 ] [ 231, FF Mission 2007 ]. Other relevant data is reported in the BREF for LVIC-AAF [ 339, BREF LVIC-AAF 2007 ].

| **Sulphuric Acid Plant Data (With additional abatement measures where shown in Process Type and plants operating normally)** | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Company** | **$SO_2$ Source** | **Line** | **Capacity (t/d)** | **Process Type** | **Number of Beds** | **Cs promoted Catalyst** | **Inlet $SO_2$ Vol. (%)** | **Conversion Rate (%)** | **$SO_2$ year av. (mg/m³)** | **$SO_2$ day av. (mg/m³)** | **$SO_2$ max. 1/2 h. av. (mg/m³)** |
| Atlantic Copper, Huelva | Flash smelter and PS Converter | 1 | 2200 | Double Contact Double Absorption | 5 | partial fourth bed | 5 to 11.5 | 99.7 to 99.83 | 500 – 700 | 400 – 800 | up to 1000 |
| | | 2 | 600 | | 4 | last bed | 5.5 to 8.5 | 99.7 | 500 – 700 | 400 – 800 | up to 1200 |
| | | 3 | 1300 | | 5 | none | 5 to 10 | 99.7 to 99.8 | 500 – 800 | up to 900 | up to 1200 |
| Aurubis AG, Pirdop | Flash smelter and PS Converter | 1 | 1862 | Double Contact Double Absorption | 4 | last bed | 7.4 to 11.3 | 99.7 to 99.8 | 864 | 600 – 1000 | up to 1150 |
| | | 2 | 1862 | | 4 | first and last bed | 7.4 to 11.3 | 99.7 to 99.8 | | | |
| KGHM Głogów 1 | Hoboken converter | | 700 | Double Contact Double Absorption | 4 | none | 4.5 to 8 | 99.8 | | 300 – 800 | |
| KGHM Głogów 2 | Flash furnace (for Cu), Kaldo furnace (for Ag) | | 900 | Double Contact Double Absorption | 4 | none | 6 to 8 | 99.9 | | 300 – 800 | |
| Boliden Harjavalta | Cu: flash smelter + PS converters, Ni: Flash Smelter | 1 | 2400 | Double Contact Double Absorption | 4 | first bed | 7 to 12 | 99.8 to 99.9 | 350 | 500 | up to 600 |
| | | 2 | 1000 | | 4 | first bed | 8 to 13 | 99.7 to 99.8 | 800 | 1000 | up to 1200 |
| Aurubis AG, Hamburg | Flash smelter and PS Converter | 1 | 1300 | Double Contact Double Absorption | 4 | first and last bed | 5 to 12 | 99.7 to 99.8 | 500 to 800 | up to 900 | up to 1200 |
| | | 2 | 1300 | | 4 | first and last bed | 5 to 12 | 99.7 to 99.8 | | | |
| | | 3 | 1300 | | 5 | first bed | 5 to 12 | 99.8 | | | |
| Asturiana de zinc Xstrata zinc | Roaster | 1 | 300 | Double Contact Double Absorption | 4 | none | 7 to 8 | 99.5 | 1015 | | |
| | | 2 | 450 | | 4 | none | 7 to 8 | 99.5 | 1398 | | |
| | | 3 | 850 | | 4 | none | 7 to 8 | 99.7 | 1014 | | |
| | | 4 | 900 | | 4 | last bed | 7 to 8 | 99.7 | 715 | | |

| Sulphuric Acid Plant Data (With additional abatement measures where shown in Process Type and plants operating normally) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Company** | **$SO_2$ Source** | **Line** | **Capacity (t/d)** | **Process Type** | **Number of Beds** | **Cs promoted Catalyst** | **Inlet $SO_2$ Vol. (%)** | **Conversion Rate (%)** | **$SO_2$ year av. ($mg/m^3$)** | **$SO_2$ day av. ($mg/m^3$)** | **$SO_2$ max. 1/2 h. av. ($mg/m^3$)** |
| Xstrata Zink Nordenham | ZnS roaster | 1 | 590 | Double Contact Double Absorption | 4 | partial first and third bed | 5 to 8.5 | 99.5 to 99.7 | | | up to 1300 |
| Nyrstar Balen | Fluidised bed roaster (zinc conc.) | F5 | 850 | Double Contact Double Absorption | 4 | last bed + top layer third bed | 8 to 9.5 | 99.5 to 99.6 | 800 to 1200 | | up to 1500 |
| Nyrstar Auby | Fluidised bed roaster (zinc conc.) | 1 | 570 | Double Contact Double Absorption | 4 | | 8 to 8.5 | 99.5 to 99.7 | 900 to 1200 | | |
| Kemira Kokkola | Boliden Kokkola roaster, | 1 | 1000 | Double Contact Double Absorption | 4 | none | 6 to 9 | 99.6 to 99.8 | | | up to 400 |
| Ruhr Zink Datteln | Roaster | 1 | | Double Contact Double Absorption | 4 | | | 99.6 | | | up to 1370 (<30 $SO_3$) |
| Boliden Odda | Zn-Smelter | 1 | 370 | Double Contact Double Absorption | 4 | partial first and third bed | 7 - 8 | 99.2 | 900 - 1500 | n..d | |
| | | | | With Sea water scrubber | | | | | | 50 – 300 Based on two spot samples per year | |
| BBH Stolberg | QSL-Pb smelter | | 360 | Double Contact Double absorption | 4 | top layer first bed + complete fourth bed | 5 to 12 | 99.6 to 99.7 | 1000 | | 1370 |

**Table 2.22 Double contact/double absorption sulphuric acid plants associated with non-ferrous metal production**
[ 238, ECI Copper Installations 2008 ], [ 230, FF Mission report 2007 ], [ 229, Umicore etc 2007 ], [ 233, Farrell Nordic Mission 2008 ] [ 231, FF Mission 2007 ].

| Sulphuric Acid Plant Data (With additional abatement measures where shown in Process Type and plants operating normally) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Company** | **$SO_2$ Source** | **Line** | **Capacity (t/d)** | **Process Type** | **Number of Beds** | **Cs promoted Catalyst** | **Inlet $SO_2$ Vol. (%)** | **Conversion Rate (%)** | **$SO_2$ year av. (mg/m³)** | **$SO_2$ day av. (mg/m³)** | **$SO_2$ max 1/2 h av. (mg/m³)** |
| Boliden Rönnskar | Roaster, smelter, flash smelter, P.S. converter | | 2000 | Double Contact Double Absorption | 5 | last bed | 7 to 10.5 | 99.97 | 100 – 160 | | |
| Boliden Rönnskar | Roaster, smelter, flash smelter, P.S. Converter | | | Cold Sea Water Plant | | | 7 to 10.5 | | 120 – 220 | | |
| Umicore Hoboken | ISA Smelt | | 360 | Double Contact Double absorption | 4 | last bed | min. <1<br>max. 7 to 10 | >99.7 | 80 | 140 – 180 | up to 300 |
| KCM S.A. Plovdiv | Zn roaster | 1 | 440 | Double Contact Double Absorption | 4 | last bed | 6 to 7.5 | 99.8 to 99.85 | 140 – 280 | | up to 360 |
| Nyrstar Budel | Fluidised bed roaster (zinc conc.) | 1 | 1000 | Double Contact Double Absorption | 5 | yes | 5 to 7.2 (low variation inlet conc.) | Up to 99.97 | 50 – 80 | | |

**Table 2.23: Sulphuric acid plants with lower $SO_2$ inlet concentration associated with non-ferrous metal production which have been upgraded**
[ 238, ECI Copper Installations 2008 ], [ 230, FF Mission report 2007 ], [ 229, Umicore etc 2007 ], [ 233, Farrell Nordic Mission 2008 ] [ 231, FF Mission 2007 ].

| Sulphuric Acid Plant Data (With additional abatement measures and plants operating normally) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Company** | **$SO_2$ Source** | **Line** | **Capacity (t/d)** | **Process Type** | **Number of Beds** | **Cs promoted Catalyst** | **Inlet $SO_2$ Vol. (%)** | **Conversion Rate (%)** | **$SO_2$ year av. (mg/m³)** | **$SO_2$ day av. (mg/m³)** | **$SO_2$ max. 1/2 h av. (mg/m³)** |
| KGHM Legnica | Shaft furnace, Hoboken converter | 1 | 210 | Single Contact Single Absorption and Solinox plant | 4 | none | 5 to 12 | 96 to 98 | | 200 – 600 | |
| | | 2 | 210 | | 4 | none | 5 to 12 | 96 to 98 | | 200 – 600 | |
| Nyrstar Balen | Fluidised bed roaster (zinc conc.) | F4 | 320 | Single absorption with ZnO scrubber | 4 | Last bed | 4.5 to 7 | 98.8 to 99.1 | | 600 to 900 | up to 1700 |
| Sadaci | Roaster | | | Single contact WSA condenser | 3 | Alkali metal oxide | 2 | 99.3 | | 320 – 450 | |

**Table 2.24: Single contact sulphuric acid plants associated with non-ferrous metal production**

*How can the daily SO2 concentration be so low with the comparably low conversion rates??*

[ 238, ECI Copper Installations 2008 ], [ 230, FF Mission report 2007 ], [ 229, Umicore etc 2007 ], [ 233, Farrell Nordic Mission 2008 ] [ 231, FF Mission 2007 ].

## 2.11.3 Techniques to consider in the determination of BAT for sulphur capture

The sections of this document entitled 'Techniques to consider in the determination of BAT' set out techniques considered generally to have potential for achieving a high level of environmental protection in the industries within the scope of the document. The background to the way the techniques are described is given in Section 2.1.2 and Table 2.2.

The following techniques are techniques to consider for sulphur recovery [ 23, DFIU-University Karlsruhe 1996 ]: *(Capture as in the heading or recovery??)*

The techniques to consider in the determination of BAT for the production of sulphuric acid are reported in Section 4.4 of the LVIC-AAF BREF [ 339, BREF LVIC-AAF 2007 ]. The following techniques should also be considered and used for the future review of the BREF on Large Volume Inorganic Chemicals – Ammonia, Acids and Fertilisers.
*(This not the appropriate place for such a comment. This should be put under concluding remarks and recommendations in order to make sure that it will be considered.*

- the LUREC® process
- the BAYQIK® process
- the SOLINOX® process
- operation with increased $SO_2$ inlet concentration (see Section 2.21.1.1)

The following sections describe the techniques to consider in the determination of BAT for the removal of sulphur dioxide from non-ferrous metal smelter off-gas in addition to those reported in the LVIC-AAF BREF [ 339, BREF LVIC-AAF 2007 ].

### 2.11.3.1 Double contact/double absorption sulphuric acid plants operating under varying gas conditions

**Description**
The double contact sulphuric acid plant comprises a gas-cleaning and washing section, and the contact plant with 4 passes. It uses a modern catalyst promoted by caesium oxide.

12 - 15 m³/h of weak acid (5 % $H_2SO_4$) is produced in the washing section and is sent for neutralisation but in some circumstances can be used by thermal decomposition of the acid bleed.

**Achieved environmental benefits**
Some sulphuric acid plants operating under varying gas conditions are shown Table 2.25. A high conversion rate for sulphur dioxide is achieved resulting in reduced emissions (see Table 2.26). More than 99.8 % conversion is achieved by a recently upgraded installation over a long averaging period [ 331, FGD process for NFM and Site Visits by FF 2009 ].
*(Five of the included example plants show conversion efficiencies of 99.7% in the given range. )*

| Sulphuric Acid Plant Data (With additional abatement measures where shown in Process Type and plants operating normally) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Company** | **$SO_2$ Source** | **Line** | **Capacity (t/d)** | **Process Type** | **Number of Beds** | **Cs promoted Catalyst** | **Inlet $SO_2$ Vol. (%)** | **Conversion Rate (%)** | **$SO_2$ year av. ($mg/m^3$)** | **$SO_2$ day av. ($mg/m^3$)** | **$SO_2$ max. 1/2 h av. ($mg/m^3$)** |
| Atlantic Copper, Huelva | Flash smelter and P.S.Converter | 1 | 2200 | Double Contact Double Absorption | 5 | partial fourth bed | 5 to 11.5 | 99.7 to 99.83 | 500 – 700 | 400 – 800 | up to 1000 |
| | | 2 | 600 | | 4 | Last bed | 5.5 to 8.5 | 99.7 | 500 – 700 | 400 – 800 | up to 1200 |
| | | 3 | 1300 | | 5 | none | 5 to 10 | 99.7 to 99.8 | 500 – 800 | up to 900 | up to 1200 |
| KGHM Głogów 1 | Hoboken converter | | 700 | Double Contact Double Absorption | 4 | none | 4.5 to 8 | 99.8 | 300 – 800 | | 800 |
| KGHM Głogów 2 | Flash furnace (for Cu), Kaldo furnace (for Ag) | | 900 | Double Contact Double Absorption | 4 | none | 6 to 8 | 99.9 | 300 – 800 | | 800 |
| Aurubis AG, Hamburg | Flash smelter and P.S.Converter | 1 | 1300 | Double Contact Double Absorption | 4 | First and last bed | 5 to 12 | 99.7 to 99.8 | 500 to 800 | up to 900 | up to 1200 |
| | | 2 | 1300 | | 4 | First and last bed | 5 to 12 | 99.7 to 99.8 | | | |
| | | 3 | 1300 | | 5 | First bed | 5 to 12 | 99.8 | | | |

**Table 2.25:** **Some sulphuric acid plants operating under varying gas conditions**

| Component | Measured Values | |
|---|---|---|
| Off-gas volume: | 320000 | (Nm$^3$/h) |
| $SO_X$ | 100 - 770 | (mg/Nm$^3$) |
| $SO_3$ | 20 - 50 | (mg/Nm$^3$) |
| $NO_X$ (as $NO_2$) | 20 - 45 | (mg/Nm$^3$) |
| $Cl^-$ (as HCl) | 2 - 7 | (mg/Nm$^3$) |
| $F^-$ (as HF) | 1 - 4 | (mg/Nm$^3$) |
| Residual dust | <2 | (mg/Nm$^3$) |
| Residual dust range | 1 - 7 | (mg/Nm$^3$) |
| Component ranges: | | |
| Cd | <0.01 - 0.02 | (mg/Nm$^3$) |
| Hg | <0.01 - 0.07 | (mg/Nm$^3$) |
| Tl | <0.01 - 0.02 | (mg/Nm$^3$) |
| As | <0.01 - 0.1 | (mg/Nm$^3$) |
| Se | <0.01 - 0.02 | (mg/Nm$^3$) |
| Sb | <0.01 - 0.03 | (mg/Nm$^3$) |
| Pb | <0.01 - 0.15 | (mg/Nm$^3$) |
| Cu | <0.01 - 0.09 | (mg/Nm$^3$) |
| PCDD/PCDF | 0.001 - 0.01 | (ng ITEQ/Nm$^3$) |

**Table 2.26: Performance data for a sulphuric acid plant operating under variable conditions**
[ 238, ECI Copper Installations 2008 ], [ 230, FF Mission report 2007 ], [ 229, Umicore etc 2007 ], [ 233, Farrell Nordic Mission 2008 ], [ 231, FF Mission 2007 ].

*Why does the table includes SOx? In the previous sections on sulphuric acid plants only SO2 was mentioned when the value of 770 mg/Nm3 was used. Furthermore an SO3 values included which should be added when giving a SOx valueor is SO2 meant.*

For existing plants with variable $SO_2$ inlet concentrations, >99.7 % conversion is achieved.
*(How does this fit to the aforementioned 99.8%? )*
The techniques to upgrade existing sulphuric acid plants that were reported in the LVIC-AAF BREF [ 339, BREF LVIC-AAF 2007 ] have been examined and new data has been supplied by Lurgi (Outotec) [ 344, Outotec cost estimation for acid plant retrofitting 2010 ]. They report that the addition of a 5th bed achieves a similar improvement to conversion as the change to a caesium-promoted catalyst in the final bed of a four pass plant.
*What does this mean for the conversion efficiency?? From the tables I don't see any big difference between 4 and 5 beds and if Cs promted beds are used or not.*

### Cross-media effects

The production of solid wastes and weak acid that require treatment and disposal.

### Operational data

Operational data is given in Table 2.26 off-gases from roaster or primary smelter in combination with off-gases from a secondary smelter. $SO_X$ concentration varies between 5 to 12 %.

### Applicability

These techniques are applicable to most existing installations.

### Economics

Cost data in 2002 for a zinc concentrate roaster (550 t/d zinc concentrate), a waste heat boiler and a water treatment plant, a gas-cleaning plant, weak acid treatment and a new double contact double absorption sulphuric acid plant producing 148000 t/yr acid is EUR 40 million.

Other costs for changes to existing plant in the copper sector are given in Table 2.27.

| Year | Technique | Estimated costs | Source |
|---|---|---|---|
| 2009 | Addition of 5th bed (2+2 to 3+2) to an existing plant with a capacity of 120000 $m^3$/hr and 11% $SO_2$ inlet concentration with blower capacity increase | EUR 10 million | Updated costs provided by Lurgi (Outotec) |
| 2009 | Change of catalyst in 4th bed to incorporate caesium promoted catalyst to two existing plants with capacities of 120000 $m^3$/hr and 11% $SO_2$ inlet concentration – excluding costs for changing the heat exchanger | EUR 800000 | Updated costs provided by Lurgi (Outotec) |
| 2009 | $H_2O_2$ scrubber for an acid plant producing 1000000 t/yr of acid | EUR 30 million | Updated costs provided by Lurgi (Outotec) |

**Table 2.27: Costs for changes to existing sulphuric acid plants**

**Driving force for implementation**
The production of sulphuric acid for sale. Required environmental performance.

**Example plants**
Hamburg, DE; Głogow, PL; Huelva, ES.

**Reference literature**
[ 121, Rentz, O. et al. 1999 ], [ 331, FGD process for NFM and Site Visits by FF 2009 ], [ 253, Sulphuric Acid Plants in the European NFM Industry 2008 ].

### 2.11.3.2 Sulphuric acid plants with lower $SO_2$ inlet concentration variations associated with non-ferrous metal production and which have been upgraded

**Description**
A double contact sulphuric acid plant is used to treat the off-gas from an Outotec flash smelting and flash converting furnace with an inlet concentration of 30 - 40 % $SO_2$. The plant has four passes and intermediate absorption after the third pass. A modern catalyst is used. There is a heat recovery system in the form of steam after the first pass.

Other installations in Sweden and the Netherlands use a five pass acid plant. A significant reduction of the concentration of $SO_2$ is achieved (60 to 150mg/Nm$^3$ $SO_2$ in tail gas as annual average) without the use of tail gas scrubbing. The installations report that they are operating with a throughput that is below their designed capacity and the plant in the Netherlands reported emissions of 30 to 80 mg/Nm$^3$ as an annual average with an inlet gas concentration of 7 % $SO_2$. Other changes such as optimising the sequence of gas flow through the passes and using a caesium catalyst in the first and final passes optimise the performance [ 227, IZA Report 2008 ], [ 240, Nl Input on Zn production 2008 ], [ 229, Umicore etc 2007 ], [ 233, Farrell Nordic Mission 2008 ]. Some of the plants are reported to be operating below the designed capacity.

**Achieved environmental benefits**
Maximum conversion of sulphur dioxide to give emissions in the range 60 to 150mg/Nm$^3$ $SO_2$ in tail gas as annual average. *(This range fits only for the NL example. The data from the table below must be considered and than the figures are different. )*

Data from some sulphuric acid plants associated with non-ferrous metal production which have been upgraded are shown in Table 2.28.

| Sulphuric Acid Plant Data (With additional abatement measures where shown in Process Type and plants operating normally) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Company** | **$SO_2$ Source** | **Line** | **Capacity (t/d)** | **Process Type** | **Number of Beds** | **Cs promoted Catalyst** | **Inlet $SO_2$ Vol. (%)** | **Conversion Rate (%)** | **$SO_2$ year av. (mg/m³)** | **$SO_2$ day av. (mg/m³)** | **$SO_2$ max. 1/2 h av. (mg/m³)** |
| Boliden Rönnskar | Roaster, smelter, flash smelter, P.S. converter | | 2000 | Double Contact Double Absorption | 5 | Last bed | 7 to 10.5 | 99.97 | 100 – 160 | | |
| Umicore Hoboken | ISA Smelt | | 360 | Double Contact Double absorption | 4 | Last bed | min. <1<br>max. 7 to 10 | >99.7 | 80 | 140 – 180 | up to 300 |
| KCM S.A. Plovdiv | Zn Roaster | 1 | 440 | Double Contact Double Absorption | 4 | Last bed | 6 to 7.5 | 99.8 to 99.85 | 140 – 280 | | up to 360 |
| Nyrstar Budel | Fluidised bed roaster (zinc conc.) | 1 | 1000 | Double Contact Double Absorption | 5 | yes | 5 to 7.2 (low variation inlet conc.) | Up to 99.97 | 50 – 80 | | |

**Table 2.28: Sulphuric acid plants with lower $SO_2$ inlet concentration associated with non-ferrous metal production and which have been upgraded**

*I don't understand the selection of these examples. In table 2.25 are examples for varying conditions and lower inlets SO2 concentrations. But the variation is sometimes smaller then in the examples in the aforementioned table. The heading of this section includes lower $SO_2$ inlet concentration* ***variations.*** *The term variations is missing in the caption of this table 2.28. But at least for the Umicore plant the variation is extremely high. In the heading it says that these plants have been upgraded. But the plants in section 2.11.3.1 have been upgraded as well quite recently.*

**Cross-media effects**
There is the production of solid wastes and weak acid that require treatment and disposal.

**Operational data**
Dilution to 14 % $SO_2$ at the drying tower inlet, annual average flow 171300 $Nm^3/h$. Over 99.9 % conversion is achieved with recent installations. The plant rely on high, constant sulphur dioxide feeds and use caesium-doped catalyst.

In the Dutch plant, the low iron concentrate allows the calciner to be operated under steady-state conditions and this, combined with a very low variation in the sulphur content, allows an even concentration of $SO_2$ to be produced. This constant gas strength assists the operation of the associated sulphuric acid plant at a high conversion efficiency. The plant is reported to be operating below the designed capacity.

In the Swedish plant, liquid $SO_2$ is also produced and this allows an even gas strength to be maintained. The plant is also reported to be operating below the designed capacity.

**Applicability**
These techniques are applicable to new or modernised installations with low variation of inlet gas concentration.

**Economics**
Economic data was not submitted but the plants are operating viably.

**Driving force for implementation**
The production of sulphuric acid for sale. Required environmental performance.

**Example plants**
Budel, NL; Rönnskar, SE; Hoboken, BE; Plovdiv, BG.

**Reference literature**
[ 137, Riekkola-Vanhanen, M. 1999 ], [ 274, Farrell Mission in DE 2008 ], [ 253, Sulphuric Acid Plants in the European NFM Industry 2008 ].

#### 2.11.3.3 Production of liquid sulphur dioxide from high strength gases

**Description**
Sulphur dioxide is absorbed in cold water (e.g. cold seawater) followed by vacuum stripping and recovery as liquid sulphur dioxide. These processes are used in conjunction with a sulphuric acid plant to recover sulphur dioxide that is not dissolved. The potential for the production of liquid sulphur dioxide depends on the existence of a local market. The process to produce liquid sulphur dioxide is shown in Figure 2.50. Liquid sulphur dioxide is also produced in a cryogenic process.

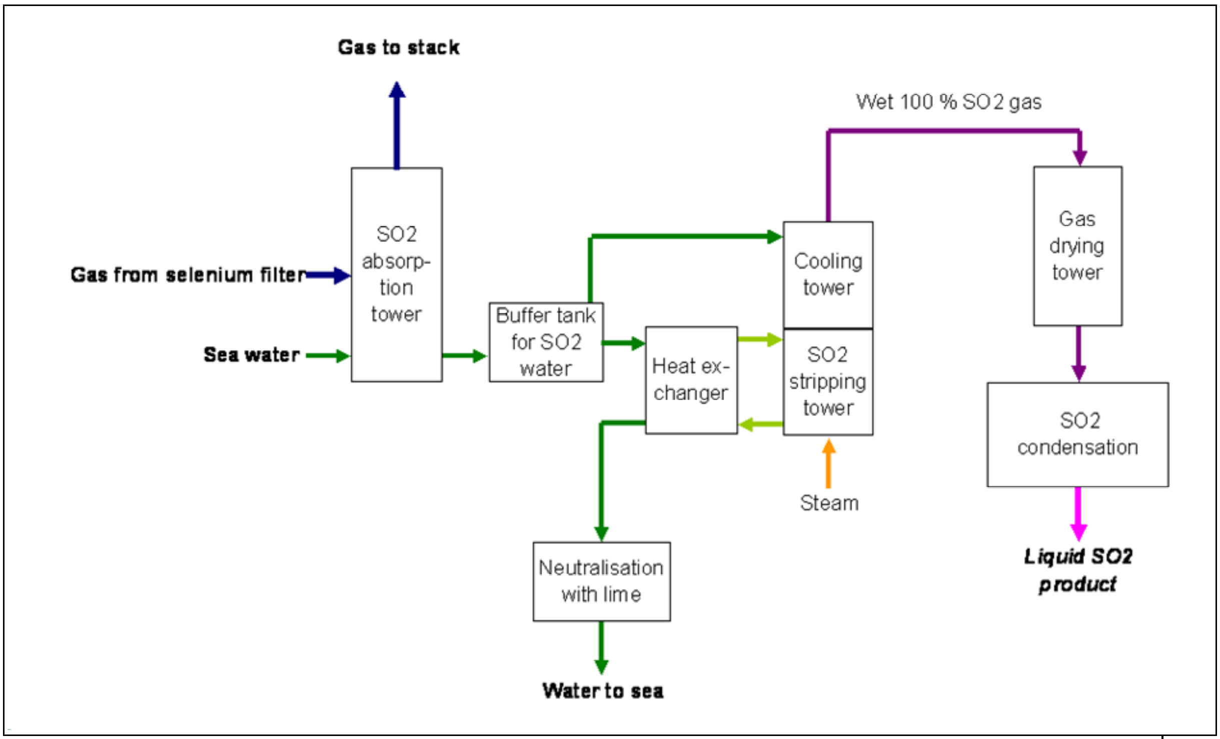

**Figure 2.50:** The process to produce liquid sulphur dioxide

### Achieved environmental benefits

Provision of a supply of sulphur dioxide that can be used to maintain an even inlet concentration to a sulphuric acid plant. The annual average emissions of sulphur dioxide are shown in Table 2.29.

| Year | Tail gas concentration (mg/Nm$^3$) |
|---|---|
| 2006 | 213 |
| 2007 | 155 |
| 2008 | 153 |
| 2009 | 124 |

**Table 2.29:** The annual average emissions of sulphur dioxide
[ 233, Farrell Nordic Mission 2008 ].

### Cross-media effects

No data has been reported.

### Operational data

Non provided.

### Applicability

Applicable to installations where there is a local market for liquid sulphur dioxide.

### Economics

One plant is operating under economic conditions.

### Driving force for implementation

The production of sulphur dioxide for sale.

### Example plants

Boliden, Sweden.

**Reference literature**
[ 233, Farrell Nordic Mission 2008 ].

### 2.11.3.4 Use of flue-gas desulphurisation for low strength gases

Im Deutschen REA!

**Description**

Gases containing sulphur dioxide such as those from a Waeltz furnace installation or an ISF when using Waelz oxide are treated in a flue-gas desulphurisation (FGD) unit that uses a slurry of milled calcium carbonate (limestone, <40 microns) as a $SO_2$ sorbent to produce clean gypsum. Gases are cooled down, dedusted in a fabric filter and the gases are passed to the desulphurisation system. After desulphurisation, the gases are sent to a two-stage drift eliminator and then to the chimney. Pure gypsum is recovered from the slurry produced by the FGD and is sold.

Other scrubbing processes for low strength gases are described in Sections 2.9.2.4.1 and 2.9.2.4.2.
*Such a sentence is not helpful in this section. We are in the techniques to consider section. So cross referring to other tecniques is dispensable.*

**Achieved environmental benefits**

Reduction in $SO_2$ emissions.

**Cross-media effects**

There is the additional use of energy and calcium carbonate. If the sale of clean gypsum is not possible then a waste will be produced.

**Operational data**

The FGD system is composed of a scrubber, absorber and a system to contact the gases with the circulating suspension of limestone. The scrubber operates in co-current phase for cooling, moistening and partial desulphurisation of the gases. This is followed by a counter-current absorption column to reduce the final $SO_2$ concentration below the required level.

The circulating suspension of limestone is pumped from separate tanks which are equipped with mechanical stirrers and the scrubber tank also has a system of aeration. The tanks are sized to allow complete reaction of the absorbed $SO_2$ with $CaCO_3$ suspension, oxidation of sulphur compounds to sulphates and the formation of coarse crystalline residue of synthetic gypsum, $CaSO_4 \cdot 2H_2O$. Compressed air is delivered to the scrubber tank through a pneumohydraulic aerator to improve condition of oxidation of sulphites to sulphates. The reaction slimes from the first absorption stage, containing mainly calcium sulphate (gypsum), are sent to filtration system. The gypsum after dehydration in a filtration press is unloaded directly into a storage box located under the press, from where it is transported to a warehouse, and then sold.

The final $SO_2$ concentration range of 100 - 500 mg/Nm$^3$ is achieved with an FGD input containing 2 - 6 g $SO_2$/Nm$^3$. Final $SO_2$ concentration of 50 - 400 mg/Nm$^3$ is reported as the best performance [ 331, FGD process for NFM and Site Visits by FF 2009 ], [ 346, SO2 low strength treatment - emission data 2010 ].

**Applicability**

Applicable to all processes that have FGD input that contain 2 - 15 g $SO_2$/Nm$^3$ (approx. 0.05 – 0.5%) provided that there is a market for the gypsum that is produced.

**Economics**

For an FGD plant at with a capacity of 85000 Nm$^3$/h and an average inlet $SO_2$ strength of 15 g/Nm$^3$, the capital cost in 2008 was PLN 14000000 which is equivalent to EUR 4000000.

The operating cost is approximately EUR 2100 per day.

**Driving forces for implementation**
The reduction of the impact of $SO_2$ emissions on the environment.

**Example plants**
Miasteczko Śląskie and Bolesław, PL.

**Reference literature**
[ 331, FGD process for NFM and Site Visits by FF 2009 ].

### 2.11.3.5 Solinox® process for sulphur capture from low strength gases (<1 %)

**Description**
The combination of a power station, a single contact sulphuric acid plant and a sulphur dioxide recovery process are used to minimise emissions to air of $SO_2$ from both the fuel and the metal concentrate and to recover energy in the form of heat and carbon monoxide.

**Achieved environmental benefits**
The recovery of heat, CO and a reduction in emissions of $SO_2$.

**Cross-media effects**
The production of solid wastes and weak acid from the gas-cleaning section that require treatment and disposal and an increase in the use of energy.

**Operational data**
Blast furnace off-gases from a copper smelter have a relatively high concentration of carbon monoxide (around 10 % CO) and also contain heat from the process. The off-gases are therefore a valuable energy source but also contain $SO_2$. The gases are transferred to local power plants as additional fuel and to recover the heat content. Off-gases emitted from the power plant therefore contain $SO_2$ from both the blast furnace and the fuel and are treated further in a Solinox plant which uses an adsorption/desorption process to produce a gas that is rich in $SO_2$ (80 %). This gas is converted to sulphuric acid in a single contact plant. The Solinox process has a waste gas that contains less than 200 – 600 mg/Nm$^3$ of $SO_2$ and this is emitted to air [ 238, ECI Copper Installations 2008 ].

The off-gases from the smelter conversion stage have a concentration of $SO_2$ ranging from 5 to 12 %. These are cleaned and then mixed with the strong gas from the Solinox plant and diluted to 12 % and passed to the sulphuric acid plant. This plant produces sulphuric acid and an off-gas that contains 6 to 8 g/Nm$^3$ of $SO_2$ which is then passed to the Solinox plant for recovery.

**Applicability**
This technique is applicable to specific types of concentrates that have low sulphur contents.

**Economics**
No details provided but reported to be expensive.

**Driving force for implementation**
Required environmental performance. Availability of a power plant.

**Example plants**
Legnica, Poland.

**Reference literature**
[ 238, ECI Copper Installations 2008 ].

BAT for sulphur removal is presented in Section 2.20.6 and in the metal specific chapters.

### 2.11.3.6 Sulphur dioxide removal using lime injection

**Description**
Lime is injected in the gas flow with a resulting formation of gypsum. When possible, simultaneous injection of water increases the reactivity of the lime, hence increasing the removal efficiency of the lime. The gypsum and the process dust are removed from the gas flow by a fabric filter which must have sufficient capacity for the additional dust load. The resulting mixture of lime and gypsum can be re-used in other metallurgical or water treatment processes.

Desulphurisation efficiency is influenced by the temperature of the gases (minimum 60°C), the moisture content, and the contact time between lime particles and the gas. Turbulence of the gas flow, high specific surface of the lime particles and the quantity of lime also influence efficiency. A reactor chamber with sufficient residence time can be used to create a turbulent flow if there is space available, but direct injection of lime and water into the gas upstream of a fabric filter is used where there is not sufficient space for a reactor.

Lime injection can be combined with the simultaneous injection of other components, e.g. active carbon for Hg or PCDD/F removal. In existing gas cleaning installations, lime injection can be simple to implement, provided there is a sufficient temperature of the gases and reaction time.

**Achieved environmental benefits**
Dust and $SO_2$ removal is achieved with the same fabric filter. Removal efficiencies range from 50 to 95% *(For both pollutants??What can be achieved for dust and what for SO2?).* Removal rates at the higher end of this range are only possible in ideal conditions in newly-designed, dedicated installations. The addition of lime has a positive effect on dioxin emissions.

**Cross-media effects**
If the gypsum produced is impure it can either be treated/recirculated in the process or disposed of. The impure gypsum can be used in metallurgical processes requiring calcium, e.g. for slag formation or in a waste water treatment facility where the excess lime that didn't react can still be useful. The use of a mixing chamber creates an additional pressure drop, resulting in higher energy use by the fan. The use of energy, lime and water are also cross-media effects.

**Operational data**
A minimum temperature of 60°C is needed for the process to operate effectively. The removal efficiency at a temperature of 150°C and 5% moisture content of the gas is about 45%. When the moisture content increases to 25%, the removal efficiency is increased to 75%. At lower temperatures, the removal efficiency drops to 20 - 40%, and high lime injection rates are needed. Where the gas temperature is close to the dew point, additional water injection is not possible because of the adverse effect on the fabric filter.

Example operational data:

**1) (Hoboken, Belgium).** Newly designed batch process and new gas cleaning system, with varying $SO_2$ concentrations in the process gases. Combined dust abatement and process dust removal system with injection of lime and water in a mixing chamber with residence time of 6 seconds $SO_2$ concentration of the gases vary from 0 up to 1 %. Injection rate: +/- 250 kg/h at 150 °C and moisture content of 30 vol/%. Because of the metal content of the process dust, the flue dust which is removed by the fabric filter is re used in another process. Also the gypsum can be used in this process. Because of lime injection, the filter capacity is 40 % higher than for dust abatement reasons only. A test of dry lime injection in a cool gas showed poor performance and high operating costs and the system was rejected.

2) **Beerse, Belgium.** Existing continuous process with varying $SO_2$ concentrations. Dry lime is injected at two points in the process that have high and low temperatures respectively. Clogging and blocking of the tubes restricts the usable lime injection rate. The mixture of dust and gypsum cannot be recycled internally and the disposal costs for gypsum/dust is high.

**3) Hamburg, Germany**. Secondary fume collection system with added lime injection in a copper smelter. A secondary fume collection system is used to reduce the diffuse emission of dust. A system to inject slaked lime into the gas flow was fitted to reduce the $SO_2$ present in the gas flow. The dust/lime mixture with an average dust and absorbent content of 1500 mg/ $Nm^3$ is removed in a fabric filter with a dust removal efficiency of 99 %. As the system treats secondary fumes, the temperature of the gases is relatively, which affects the removal rate.

**4) Bergsöe, Sweden.** Existing continuous lead smelting process with varying $SO_2$ concentrations using lime injection in the afterburner of a lead smelter. The main process is designed to capture $SO_2$ through the addition of iron to the furnace and the formation of an iron matte. The capture rate by producing matte is approximately 90 %. Further $SO_2$ removal is achieved by the dry injection of lime (~ 60 kg/h) at the afterburner outlet at 1100 °C. The gas flow is 24000 $Nm^3$/h.

Water injection is not possible because of clogging and blocking in pipes and the possible condensation problems in the fabric filters. Higher yields would be possible at the expense of a higher lime injection rate, but lime causes clogging and blocking of the tubes at high injection rate. Due to the lead content of the filter dust, it is recycled to the furnace after dechlorination and the lime content aids slag forming. The cost for the treatment of filter dust is relatively low.

The performance data for the example plants is shown inTable 2.30.

| Plant | $SO_2$ mg/$Nm^3$ | | Dust mg/$Nm^3$ | | Comment |
|---|---|---|---|---|---|
| | Inlet | Outlet | Inlet | Outlet | |
| Hoboken<br>(New batch process) | Up to 1% (= 26600 mg/m3) | 50 – 400 | | | Six second residence time in a reaction chamber. Dust is used in another process |
| Hoboken<br>(Test on secondary fume treatment) | 60 – 250 | 30 – 125 | | | Very high lime use due to low gas temperature. |
| Beerse<br>(Whole battery smelter) | 3000 | 650 | | | Two point injection |
| Hamburg<br>(Secondary fume collection) | 100 – 1500 | 450 – 750 | 1500 | < 2 | Lime addition prior to fabric filter. Dust is used in process |
| Bergsöe<br>(Lead smelter) | 3000 | 400 | | < 1 | Sulphur removed as iron matte and 650 kg/hr lime addition to afterburner. Dust is used in process |

**Table 2.30: Performance data for example plants**
[ 346, SO2 - Lime injection FINAL 4.2.2010 ].

**Applicability**
Optimum conditions can be incorporated in new installations in the copper, lead and precious metals sectors. When using existing gas-cleaning equipment with a fabric filter that is designed to remove process dust, it can be used to capture gypsum if the filter capacity allows for this. When a filter is already used, direct injection is possible when temperature, moisture content and contact time are sufficient. An existing filter installation might be not sufficient because the amount of dust increases drastically and thus might need to be replaced.

**Economics**

Investment cost for plant 1: EUR 550.000 (mixing chamber: EUR 100.00, additional cost for fabric filter: EUR 190.000 , injection system including silo: 2EUR 60.000).

Investment costs for plant 3: EUR 10 million plus approximately EUR 7 million for measures to capture fugitive emissions of the anode furnace and casting wheel.

Simultaneous injection of water decreases the quantities of lime needed as the reaction between $SO_2$ and lime takes place at the surface of the lime particles, a relatively high amount of lime is needed. The quantities that are needed can be reduced by using a lime with a high specific surface and/or by recirculation of the fabric filter dust. Lime cost ranges from EUR 60/ton for calcium hydroxide to EUR 200/ton for expanded calcium hydroxide.

When the flue dust must be disposed of, the cost of this technique can be very high.

**Driving force for implementation**

The treatment of dust and SO2 simultaneously and the utilisation of existing fabric filters.

**Example plants**

Hoboken, BE; Beerse, BE; Hamburg, DE; Bergsöe, SE. *The Bergsoe site is a lead smelter and should be deleted here.*

**Reference Literature**

[ 346, SO2 - Lime injection FINAL 4.2.2010 ].

# 2.12 Effluent treatment and water re-use

## 2.12.1 Main sources of liquid effluent arisings

This section gives an overview on the generation of liquid effluents in a common process. The ways to reduce the volume of waste water, the practice of recycling water and the effluent treatment in a local or central waste water treatment plant are discussed to give an understanding of some of the concepts that may be transferred between the metal groups [ 27, M. Barry et al. 1993 ].

The production of non-ferrous metals by pyrometallurgical and hydrometallurgical methods is associated with the generation of different liquid effluents. The main sources of the most important effluent streams can be classified as shown in Figure 2.51.

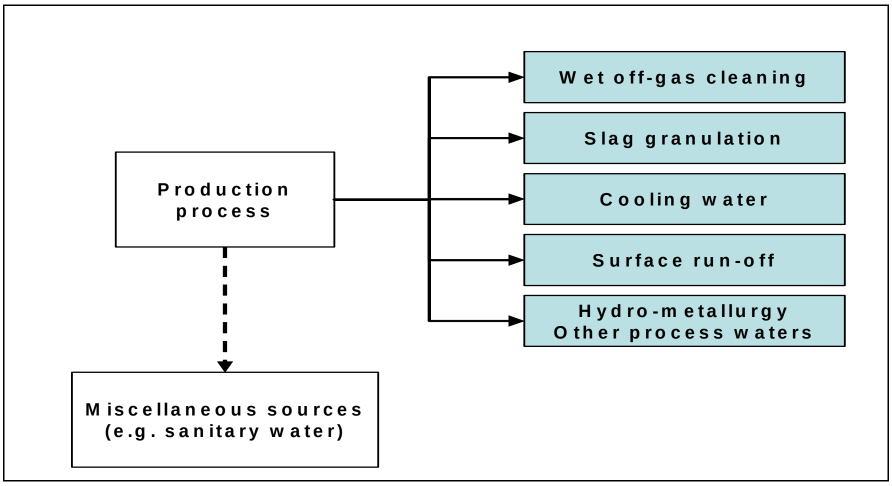

**Figure 2.51: Effluent Classification**

The above waste water streams can be contaminated by metal compounds from the production processes and may have a high environmental impact. Even at low concentrations, some metals like mercury and cadmium are very toxic. This can be illustrated by the fact that mercury and cadmium head the list of priority hazardous substances drawn up at the North Sea Conference of 1984, which called for a 50 % reduction of emissions into the North Sea. The toxic effect of some metal compounds is also due to the fact that under the correct chemical conditions, metals can easily enter natural watercourses as soluble species and be quickly and irreversibly assimilated into the food chain [ 166, Clark, J.H. 1995 ] (see also Section 2.3.2.2 for the MERAG methodology [ 301, MERAG Guidance 2007 ]).

### 2.12.1.1 Effluents from off-gas-cleaning

Wet air pollution control equipment is gradually being replaced by dry control techniques. Dry abatement techniques like fabric filters have the advantage that no sludge or waste water should be treated and the collected dust can often be recycled directly back into the main process, the cross-media issues are therefore reduced in comparison to wet systems.

There are certain cases when wet air cleaning techniques, e.g. wet scrubbers or wet electrostatic precipitators, need to be applied. These are used especially when other abatement systems are not suitable, there is a risk of explosion or combustion from flammable particles and if gaseous substances (for example, sulphur dioxide or trioxide) as well as particles have to be removed from the off-gas stream. Wet electrostatic precipitators are necessary when humid, saturated gases with a high dust content have to be cleaned. For example, during the production of primary zinc and copper, the off-gas from the process, which contains dust and sulphur dioxide, is cleaned by using a scrubber and a wet electrostatic precipitator. Wet electrostatic precipitators are also used to collect the tar mist in the off-gases from an electrode-baking furnace. In wet scrubbers, acceleration and deceleration of the gas stream and the atomised scrubbing liquid produces high turbulence between the gases, the dust and the droplets of liquid. The dust particles are very quickly wetted and chemical reactions are speeded up. A subsequent collector extracts the droplets of liquid and the wetted dust from the gas steam. The contaminated effluent can then be removed for further treatment. If there is no enrichment of soluble components in the washing liquor, removal of the suspended solids by a thickener makes it possible to re-use the washing water. However, in some cases, precipitation of soluble components should be carried out in order to re-use the washing liquid.

The liquid effluent generally requires further treatment, for instance by neutralisation and/or sedimentation for solid-liquid separation. Sometimes specific treatment measures like ion exchange are used to remove very harmful or valuable metal compounds. For example ion exchange is used to recover rhenium from the scrubber effluent that is generated by cleaning the off-gas from a molybdenite roaster. This process is used for both removing a metal compound from the waste water and serves as the most important source for the production of rhenium metal.

Weak acid produced in wet electrostatic precipitators can be treated in a number of ways:

- by concentration and then decomposition in the smelting furnace when $SO_2$ can be recovered in the acid plant;
- the treated liquid can normally be sent back to the wet-cleaning system but a bleed is required to control the composition of the liquor;
- weak acid from these processes can also be re-used in other processes if they are available.

It has been reported that in several cases the process water from the wet scrubbing system of a smelting furnace contains cyanides formed by the reaction of carbon with atmospheric nitrogen. The cyanide level can be reduced by using the scrubbing water for slag granulation, which leads to evaporation and oxidation of most of the cyanides.

Another main effluent stream arises from the removal of mercury from some roaster off-gases. The mercury removal step involves a gas-liquid contact tank with a solution of mercury chloride ($HgCl_2$). This mercury chloride reacts with metallic mercury from the gas to form a solid $Hg_2Cl_2$ precipitate (calomel). The precipitated slurry is removed and oxidised with $Cl_2$ to form the $HgCl_2$ washing solution. Some of the slurry is dewatered by a filter press and sold as $Hg_2Cl_2$ for mercury recovery or disposed of as a special waste.

Effluents from the process are pretreated locally for mercury removal by reaction with zinc dust or by precipitation as HgS before processing in a final effluent treatment plant.

#### 2.12.1.2 Effluent from matte or slag granulation and the production of metal shot and density separation

During the production of non-ferrous metals, the matte, slag and the produced metal will be tapped off from the furnaces. The materials can be granulated separately by pouring into water, using a high pressure water jet or other quench systems to form evenly-sized particles. The granulated metal can then be sold as metal shot. The granulated slag may be used for other purposes and granulated matte can be used in a converter stage. A typical granulation stage is shown in Figure 2.52.

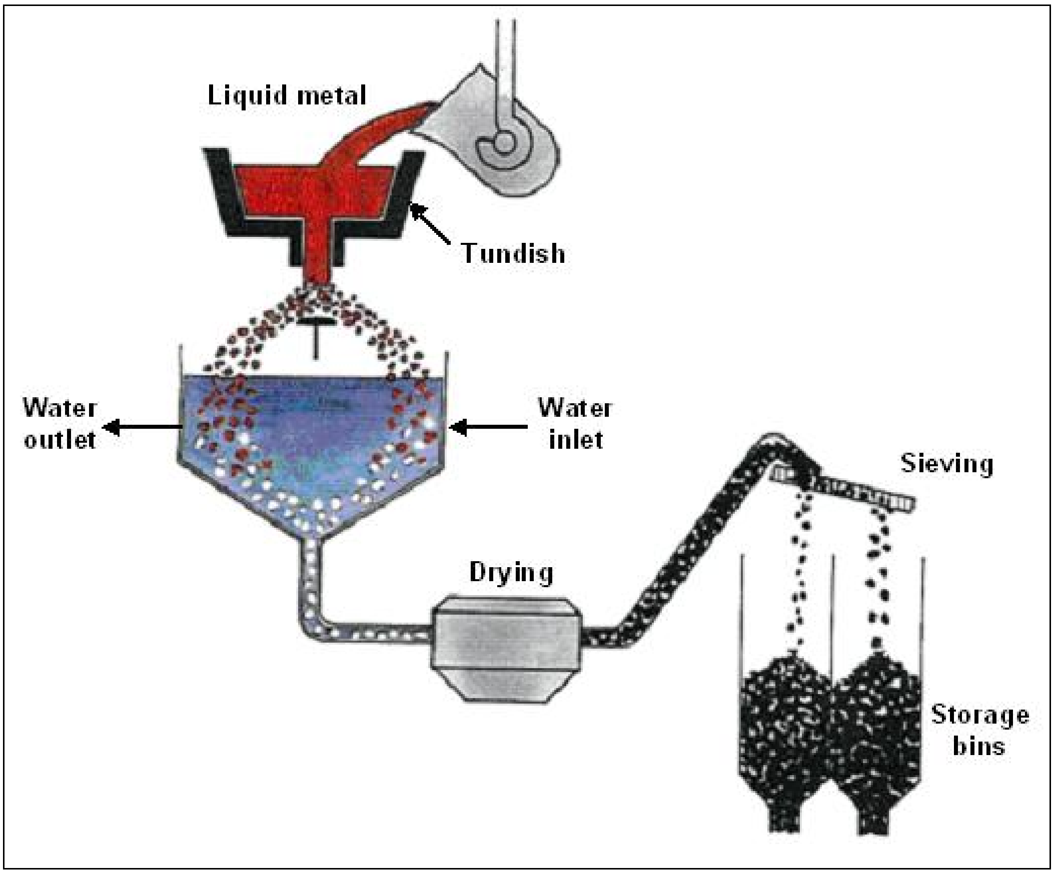

**Figure 2.52: Granulation of molten metal**
[ 149, Schei, A, et al. 1998 ]

The liquid effluent that arises from the granulation step is usually recycled in a closed circuit. To prevent a buildup of suspended solids and metal compounds, a blowdown should be removed from the water circulation system continuously.

Density separation (sink and swim) is also used to separate metals and compounds from light contaminants, for example, the removal of plastic components after shredding. The liquid effluent that arises is usually recycled and floating material is removed. To prevent a buildup of suspended solids and metals a blowdown should be removed from the water circulation system continuously.

The blowdown or effluent is usually sent to a central waste water treatment plant.

#### 2.12.1.3 Cooling water

Cooling water is used on a large scale for the different cooling requirements in metal producing industries. It can be divided into non-contact cooling water and direct contact cooling water as detailed below:

- Non-contact cooling water is used for cooling furnaces, furnace hoods, casting machines, etc. Depending on the location of the plant, cooling can be achieved by a once-through system or a recirculation system with evaporative cooling towers. Water from a once-through cooling system is normally discharged back to the natural source for instance a river or a cooling pond. In this case, the increase of temperature should be regarded before the water is discharged to the natural water body. Non-contact cooling water may also be recycled via cooling towers.

- Direct contact cooling is used during some casting operations. This cooling water is normally contaminated with metals and suspended solids and often arises in large quantities. Due to the specific matrix and in order to avoid dilution effects, direct contact cooling water should principally be treated separately from other waste water.

In order to minimise the impact of cooling on the environment as a whole, the BAT Reference Document on Industrial Cooling System should be used.

### 2.12.1.4 Surface run-off water

Surface run-off water arises from the contamination of rainwater that is collected from building roofs and paved areas at the production facility. Contamination of rainwater occurs when materials such as dust that contain metals from storage, surface deposition, etc. or oils are washed into the drainage system. Contamination of surface water can be prevented or minimised by using good practise for the storage of raw materials as well as by good maintenance and cleaning of the whole production plant.

Surface run-off water may be collected separately. After a sedimentation step or chemical treatment, it can be re-used for other purposes in the production process, for instance as cooling water or for water sprays to prevent dust formation.

### 2.12.1.5 Effluents from the hydrometallurgical process

The main liquid effluent arisings from the hydrometallurgical production of non-ferrous metals are listed in Table 2.31 below.

| Process unit | Operation/source | Use options |
|---|---|---|
| Roaster gas cleaning | Wet cleaning of roaster gases | Waste water treatment plant consisting of precipitation steps sometimes with a removal of metals by using ion exchangers |
| Leaching | General operations including wet gas cleaning | Return to leaching |
| Purification | General operations | Return to leaching or next process step |
| Electrolysis | Cleaning of cells, anodes and cathodes.<br>Spent electrolyte.<br>Electrolyte bleed | Return to leaching.<br>Return to electrolysis after treatment |

**Table 2.31: Potential sources of liquid effluents from the hydrometallurgical production of non-ferrous metals**

The hydrometallurgical production process starts usually with a leaching operation. During leaching, the desired metal and other elements will be liberated from the mineral and go into solution.

Typical leaching reagents and reactions are shown below [ 104, Ullmann's Encyclopedia 1996 ].

- water for water-soluble compounds (copper sulphate)
- sulphuric, hydrochloric, and nitric acids or sodium hydroxide for metal oxides
- complexing agents, e.g. cyanide (gold, silver) or ammonia (copper and nickel minerals)
- reduction of a mineral by a suitable gas or oxidation, for example, manganese dioxide by sulphur dioxide, and nickel matte by chlorine
- acid-base reactions, e.g. recovery of a tungsten complex from tungsten at a high pH.

To increase the amount of the desired metal in the leach liquor, a number of hydrometallurgical purification and enrichment techniques may be used. The target metal may be recovered from the purified solution by using different techniques such as cementation, gaseous reactions, selective precipitation, ion exchange, solvent extraction, crystallisation, evaporative concentration or electrolysis. To ensure a correct balance in some of these processes, it is normally necessary to constantly remove a part of the liquor.

During the production of zinc for instance, electrolyte may be bled to control the buildup of magnesium that may have a detrimental impact on the operation of the electrolytic cells. The flows in the electrolytic cells belong to the same (closed) water circuit as the leaching and purification stages: the sulphuric acid formed during electrolysis is fed to the leaching process and the remaining liquid is purified and fed to the electrolysis process.

The effluent bleed of the electrolytic-leaching-purification circuit is strongly acidic and contains high concentrations of zinc and suspended solids. The volume of the bleed depends strongly on the composition of the zinc concentrates that are used in the roasting. Components that tend to buildup (i.e. are not sufficiently removed from the solution) in the circuit, especially magnesium, will determine the bleed flow.

Many facilities have already demonstrated that effluents generated as electrolyte bleed may be recycled to the leaching operation depending on the contaminants that are present. Electrolyte bleed may also be recycled to electrolysis after the removal of contaminants or minor value elements.

### 2.12.1.6 Other process waters

There are other sources of effluent in this sector.

The most important are:

- the liquors produced during the Bayer process to produce alumina;
- acidic waste waters produced during lead acid battery processing or the processing of precious metals;
- weak sulphuric acid from sulphuric acid plants;
- waste waters from the refining of germanium, gallium, etc.

These waste waters are covered in more detail in the metal-specific chapters but the processes used are sometimes capable of recycling the liquors back into the process or using the acid value in other processes.

Pickling operations are also sources of process waters and the following two examples show how non-acid pickling can be used and how the impact of acid pickling can be minimised.

**Non acid pickling**
This process operates in a sealed circuit. Rod can be pickled in an in-line system that consists of a compartmentalised horizontal steel pipe. A 2.5 to 3.5 % solution of isopropanol alcohol (IPA) in water is used. In copper, the process of converting the cuprous oxide scale in a vapour phase to form copper (left on the rod), is known as the Burns process [ 90, Traulsen, H. 1998 ]. IPA is recovered from the spent solutions for re-use and sludges that contain metal are recovered. Water from the IPA recovery stage is usually sent for waste water treatment.

**Acid pickling**
Acid pickling uses a compartmentalised horizontal system [ 90, Traulsen, H. 1998 ]. In a first stage, the material is pickled with diluted sulphuric acid; then the residual acid is washed in several stages from the metal surface by water sprays followed by drying using compressed air.

Surface pickling is usually performed with sulphuric acid but for some alloys and for metals such as titanium nitric acid, sometimes as a mixture with sulphuric acid, is used in continuous lines or automatic systems. Gas cleaning is used to recover or remove nitric acid fumes; the acid is changed from time to time. Spent acid is sent for treatment and the recovery of metal. The pickling systems are vented for worker protection.

The products are rinsed, the rinse water is sent for treatment, and the sludges are recycled if possible. For surface degreasing of rolled products, detergents are used. The spent water is cleaned by ultra filtration. If organic solvents are used for surface degreasing, a vapour degreasing system is used. In this case, chlorinated hydrocarbons may be present in any waste water treatment sludge that is produced.

An alternative process is used for some copper rod production. After partial cooling in a long water-filled tube, the rod is formed into spirals corresponding to the diameter of the coil. These spirals are spread onto a roller table where the temperature is reduced to 20 ºC by water sprinklers. An acid-resistant alloy conveyor carries these spirals into the pickling tanks where the rod is pickled with a 20 % sulphuric acid solution. The acid pickling system ensures a perfect removal of all oxides from the rod surface. The loops are then washed with rinsing water and finally protected by a wax solution.

Electrowinning can be used to recover the metal dissolved by the pickling acid. The wash solution also may be treated by ion exchange.

#### 2.12.1.7 Miscellaneous sources

In an industrial plant for producing non-ferrous metals, a great number of other sources are involved. Examples are liquid effluents from cleaning stations for trucks delivering raw material; sealing water from pumps; and general operations, including the cleaning of equipment, floors, etc. These liquid effluents are normally collected and treated. Water from the sanitary system is normally discharged to the public sewerage system.

### 2.12.2 Techniques to consider in the determination of BAT

The sections of this document entitled 'Techniques to consider in the determination of BAT' set out techniques considered generally to have potential for achieving a high level of environmental protection in the industries within the scope of the document. The background to the way the techniques are described is given in Section 2.1.2 and Table 2.2.

The applied treatment methods are also techniques to be considered in the determination of BAT. In the case of waste water treatment measures and treatment plants, it is very difficult to define a BAT level in this part of the document. The treatment methods and consequently the achievable emission levels are very much dependent on the specific process and the metals involved [ 207, Noyes, R. 1993 ]. Due to this problem, the techniques will only be described in general by pointing out their advantages and disadvantages. For more detailed information, especially of achievable emission levels, the metal-specific chapters for the different non-ferrous metals should be used.

#### 2.12.2.1 Process-integrated measures

**Description**

Techniques and methods for the re-use of water are already successfully used in the non-ferrous metal industry to minimise the amount of liquid effluent that should be discharged as waste water. The reduction of waste water is sometimes also economically viable because as the amount of discharged waste water is reduced, the amount of fresh water that should be taken from the aquatic environment is also reduced. This also has a beneficial effect on the cross-media issues.

Table 2.32 demonstrates the process steps from which the liquid effluents are already extensively recycled and re-used.

| Recycling and/or re-use of effluents in the non-ferrous metals industries | | | | | | |
|---|---|---|---|---|---|---|
| **Source** | **Production process** | | | | | |
| | **Primary copper** | **Secondary copper** | **Primary lead** | **Secondary lead** | **Primary zinc** | **Ferro-alloys** |
| Slag granulation | ■ | ■ | ■ | | ■ | ■ |
| Wet air pollution control | ■ | ■ | ■ | ■ | ■ | ■ |
| Roasting gas washing effluent | ■ | | ■ | | ■ | |
| Cooling water | ■ | ■ | ■ | ■ | ■ | ■ |
| Anode and cathode rinse water | ■ | ■ | | | ■ | |
| Spent electrolyte | ■ | ■ | | | ■ | |
| Battery breaking | | | | ■ | | |
| Battery classification | | | | ■ | | |
| Lead paste desulphurisation | | | | ■ | | |

**Table 2.32: Examples of recycling and re-use**

Recycling and re-use techniques are process-integrated measures. Recycling involves the recirculation of the liquid to the process where it has been generated. Re-use of an effluent means the recirculation of one source of water for another purpose, e.g. surface run-off may be re-used as cooling water.

Normally a recycling system needs a basic treatment technique or a blowdown of approximately 10 % of the circulating liquid, to prevent a buildup of suspended solids, metals and salts in the recirculation system. For instance cooling water is normally recycled and led in a recirculation system as shown in Figure 2.53 below. The use of biocides should also be taken into account.

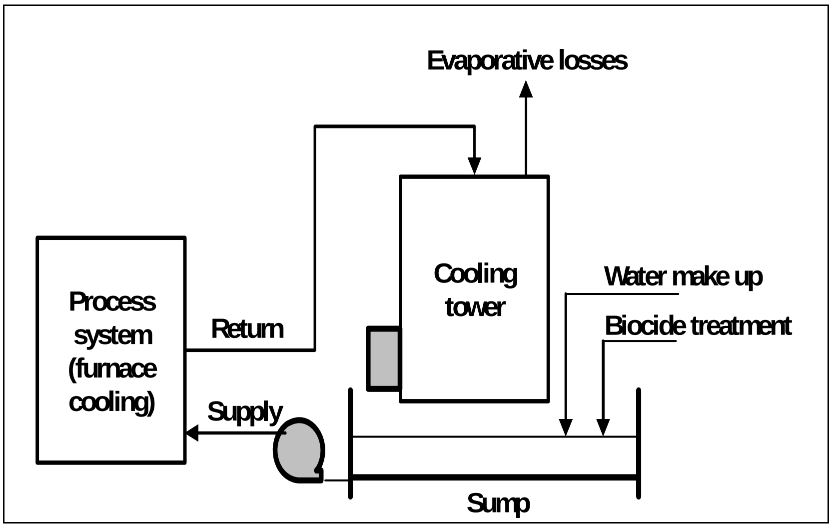

**Figure 2.53: Example of a cooling water recirculation system**

If large quantities of water are available, for example in a coastal site, a flowing cooling water system can be used provided the environmental impact is negligible. Nevertheless effects to the marine environment in the suction area of the flowing cooling water system should be considered. The case for this approach should be made on a site by site basis as the energy costs of pumping and cooling systems should be balanced.

The amount of water discharged is therefore an issue as some installations use extensive water recirculation systems. One copper smelter reported that the daily discharge volume is 3000 $m^3$/d while similar plants that do not recirculate to the same extent discharge more than 100000 $m^3$/d. The mass emissions of pollutants are therefore the factor that should be used when assessing the impact of discharges [ 238, ECI Copper Installations 2008 ].

**Achieved environmental benefits**
The minimisation of waste water can also be supported by good housekeeping, which may advantageously be based on a water management plan.

**Cross-media effects**
None reported.

**Operational data**
See Section 2.12.1[rr9].

**Applicability**
See Section 2.12.1[rr10].

**Economics**
None reported.

**Driving force for implementation**
Reduction of waste water emissions.

**Example plants**
See Section 2.12.1[rr11].

**Reference literature**
[ 238, ECI Copper Installations 2008 ].

### 2.12.2.2 End-of-pipe techniques

Any non-recyclable or non re-usable amounts of water have to be treated in order to minimise the concentration of pollutants like metals, acidic substances and solid particles in the final effluents discharged to the aquatic environment. To reduce the concentration of water pollutants, end-of-pipe techniques, e.g. chemical precipitation, sedimentation or flotation and filtration may be used. These techniques are normally used together in a final or central on-site waste water treatment plant but opportunities can also be taken to precipitate metals before the process stream is mixed with other effluents.

#### 2.12.2.2.1 Chemical precipitation

**Description**
Chemical precipitation is used primarily to remove the soluble metal ions from the liquid effluent. The soluble metals can be precipitated from the waste water by the adjustment of the pH value. A reagent, such as lime, sodium hydroxide, sodium sulphide or a combination of reagents is added to the effluent and forms an insoluble compound with the metal to form a precipitate. These insoluble compounds can then be removed from the water by filtration and

sedimentation. The addition of a coagulant or flocculant that helps to form larger flocs that can be separated more easily, is often used to improve the performance of the system. At least one plant uses a biological process to generate hydrogen sulphide to precipitate the metals as the sulphide.

Precipitation is usually used to remove metals from a waste water stream such as the removal of iron, lead, zinc, chromium, manganese, molybdenum, etc. The hydroxides of metals are usually insoluble, so lime is commonly used for precipitating them.

Similarly, metal sulphides are also insoluble and reagents such as sodium sulphide, sodium hydrogen sulphide and tri-mercapto-sulpho-triazine (TMS) are used in alkaline conditions. $H_2S$ can also be produced biologically using a sulphate-reducing bacteria and the gas is transported to the precipitation stage with a carrier gas. Sulphide precipitation can result in much lower concentrations in the cleaned effluent for certain metals depending on the pH and temperature and the metal sulphide produced can be returned to the smelting stage. Metals such as selenium and molybdenum can also be effectively removed.

Zinc sulphate solutions are treated in a biological conversion stage using hydrogen as an electron donor which is produced by converting natural gas and steam. Zinc sulphide is produced at a rate of 10 tonnes per day and is recycled back to the smelter.

In some cases, the precipitation of a mixture of metals can be carried in two-stages; firstly with hydroxide, followed by a sulphide precipitation. Ferric sulphate can be added after precipitation to remove the excess sulphide.

In order to maximise the efficiency of metal removal, the process should be treated at different pH values with different reactants. The choice of reactant and the pH value is the main consideration for the precipitation of metals. Solubility is also affected by temperature and this should be taken into account.

Another important factor is the valence state of the metal in the water. For example chromium, whose hexavalent form, chromate, is considerably more soluble than the trivalent form. In this case, chromate must be reduced, usually with $SO_2$ at a low pH, for removal of chromium by a precipitation process.

Pentavalent arsenic, $As^V$ is reduced to $As^{III}$ by the reaction with sulphide ions although some $As_2S_5$ may be formed. The reduction of $As^V$ is temperature dependent and rather slow, at least below 50 - 60°C. Trivalent arsenic, $As^{III}$ is precipitated as $As_2S_3$ with sulphide below pH 4 – 5. Precipitated $As_2S_3$ must be separated from the water at pH below 4 – 5. If the pH is raised and $As_2S_3$ is present, there is a risk that the arsenic goes into solution.

In the mining industry, trace metals can be effectively removed from effluents by the addition of ferric salts. Arsenic is removed as either calcium or ferric arsenate by precipitation. ~~Through precipitation, arsenic is removed as either calcium or ferric arsenate.~~ Arsenites can also be precipitated, but they are generally more soluble and less stable then arsenates. Effluent that contains arsenite is generally oxidised prior to precipitation to ensure that the arsenate predominates. Process water from the processing of arsenic bearing ores may contain varying amounts of arsenic (III) and (V) oxyanions, arsenites and arsenate. The presence of such metal ions as copper, lead, nickel, and zinc limit the solubility of arsenic because of the formation of sparingly soluble metal arsenates [ 295, European Commission 2004 ].

The stability and solubility of these arsenates depends on the ratio of iron to arsenic. The larger the ratio, the more insoluble and stable the precipitate. While ferric arsenate is relatively soluble, the basic arsenates with an iron to arsenic molar ratio of eight or more are an order of magnitude less soluble in the pH range 2 to 8.

The precipitation of insoluble ferric arsenates is accompanied by the co-precipitation of other metals such as selenium that involves interactions between the various metals species and the ferric hydroxide precipitate. This makes ferric salts a very effective scavenger for the removal of trace contaminants. Arsenic is precipitated as Fe-As compounds by adding ferric sulphate ($Fe_2(SO_4)_3$). If the pH is 6 or lower, arsenic can be precipitated completely. It is difficult to precipitate nickel and arsenic at the same time, hence a two-stage treatment is required.

The pH dependency of As precipitation compared to the optimum conditions for the precipitation of other metals (Ni, Cu, etc.) means that different optimum pH values exist and minimum values of each metal is not possible with one process.

The final aspect is the possible formation of complex ions, which are generally more soluble. This is common when dealing with waste water that contains ammonia, chloride, fluoride or cyanides along with the metals.

In many plants where metals are being removed, one of the principal problems in reaching the desired effluent limits is the colloidal state of the precipitated materials. This can result from improper neutralisation and flocculation. Various flocculants or coagulants can be used to improve the condition of the precipitated material and suppliers of these materials are able to test the precipitates and specify the correct coagulant.

The efficiency of waste water cleaning by using chemical precipitation is mainly influenced by the following factors:

- the choice of chemical precipitant
- the amount of precipitant added
- the efficiency of removal of the precipitated metal
- the maintenance of the correct pH throughout the treatment process
- the use of iron salts to remove specific metals
- the use of flocculating or coagulating reagents.

**Achieved environmental benefits**

In one site, arsenic is present in the process waste water streams at a level of several g/l. Arsenic is reduced by adding lime followed by settling in order to remove sulphates as gypsum and metals as hydroxides. Arsenic is removed as calcium arsenate to levels of < 50 mg/l. In a second step $FeCl_3$ is added together with lime and arsenic is further reduced after settlement to levels < 0.5 mg/l although there are variations.

Table 2.33 shows the effect of treatment using lime/iron sulphate and NaHS and shows the specific emissions from a primary copper plant.

*In the caption it should be mentioned that these data are for the copper sector only.The table comprises data for primary and secondary copper plants.*

| Component | Primary and secondary copper process water after lime and iron sulphate treatment and settlement | Secondary copper process and surface water after NaHS treatment, settlement and sand filtration |
|---|---|---|
| pH | 9.5 | |
| Cu mg/l | 0.2 – 0.5 | 0.05 – 0.2 |
| Pb mg/l | 0.2 – 0.5 | 0.05 – 0.2 |
| Ni mg/l | 0.2 – 0.5 | 0.05 – 0.2 |
| Zn mg/l | 0.2 – 1.0 | 0.10 – 0.5 |
| As mg/l | 0.1 – 0.2 | <0.01 |
| Cd mg/l | 0.1 – 0.2 | <0.01 |
| Hg mg/l | 0.01 – 0.05 | <0.01 |
| Metal concentrations are based on qualified random samples or twenty four hour flow proportional samples. Variations in effluent composition and source should be taken into account. | | |

**Table 2.33: Example of concentration of some metals after waste water treatment with lime or with NaHS**
[ 238, ECI Copper Installations 2008 ]

| ~~Main components~~ | ~~Cu~~ | ~~Pb~~ | ~~As~~ | ~~Ni~~ | ~~Cd~~ | ~~Zn~~ |
|---|---|---|---|---|---|---|
| ~~Overall pollutant rate (g/t copper produced)~~ | ~~1 - 2.3~~ | ~~0.03 - 0.3~~ | ~~0.05 - 0.23~~ | ~~0.1 - 0.2~~ | ~~0.02 - 0.05~~ | ~~0.16 - 0.8~~ |
| ~~Emission values which are accessible to the authorities~~ | | | | | | |

~~**Table 2.34: Overall pollutant rate of waste water discharges from a primary copper smelter based on measured values from 1996 to 2005**~~
~~[ 234, UBA Copper, lead, zinc and aluminium 2007 ],~~
*The values in table 2.34 are from table 2.37. They are related to annual averages and do not fit to the values presented in table 2.33.*

**Cross-media effects**
None reported.

**Operational data**
See Section 2.12.1 and Table 2.39.

**Applicability**
To ensure the maximum removal efficiency of metals, the most important factor is the maintenance of the choice of precipitant. Table 2.33 shows that the use of sulphide-based reagents can achieve lower concentrations of some metals. Correct pH throughout the effluent treatment process is also of primary importance because some of the metal salts are insoluble only over a very short range of pH values. Outside these ranges, the efficiency of metal removal decreases rapidly, for example zinc will form a soluble anion, zincate, at high pH values.

See Section 2.12.1.

**Economics**
None reported.

**Driving force for implementation**
Reduction of waste water emissions.

**Example plants**
See Section 2.12.1.
*(The crossreference to Section 2.12.1 is not traceable since this section contains many subsections.)*

**Reference literature**
[ 11, Hatch Associates Ltd 1993 ], [ 146, Kemmer, F.N. 1998 ], [ 168, Steil, H.U. et al. 1999 ], [ 234, UBA Copper, lead, zinc and aluminium 2007 ], [ 240, Nl Input on Zn production 2008 ], [ 319, Biotechnology for Sustainable Hydrometallurgy 2003 ], [ 320, Biologically produced Sulphide 2004 ], [ 321, Removal of Selenium and Molybdenum 2007 ], [ 295, European Commission 2004 ], [ 238, ECI Copper Installations 2008 ].
.

#### 2.12.2.2.2 Treatment of weak acid and process water

**Description**
Treatment of waste water comprising weak acid from the sulphuric acid plant or various acidic wash-waters using lime and iron sulphate.

### Achieved environmental benefits

Minimum waste water discharge, reduction in water consumption, production of clean gypsum are achieved.

### Cross-media effects

No cross media effects were reported.

### Operational data

The process outline is shown in Figure 2.54 and the results achieved are given in Table 2.34.

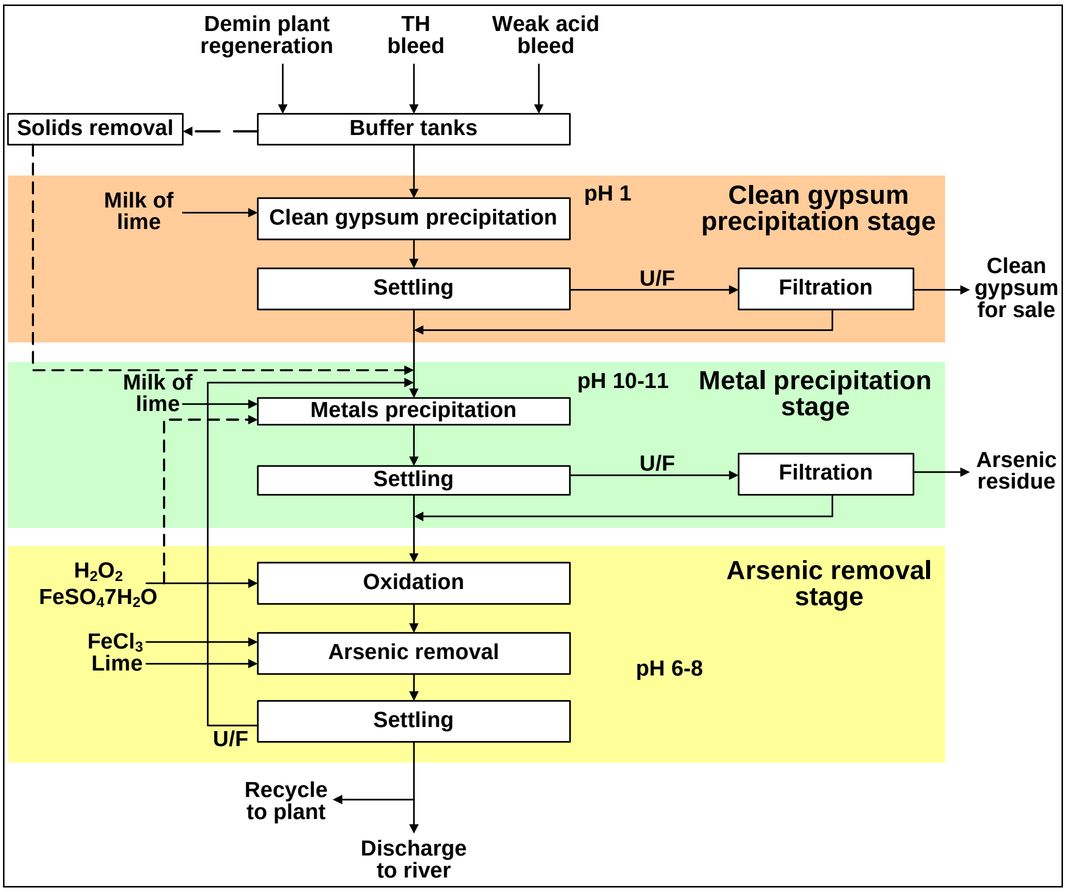

Figure 2.54: Treatment of weak acid

The clean gypsum that is produced contains > 96 % Ca $SO_4.5H_2O$.

| Parameter | Range | Unit |
|---|---|---|
| | Inlet Conditions | |
| Flow | 35 | $m^3/h$ |
| Content | | |
| $H_2SO_4$ | 60 | g/l |
| Cu | 2100 | mg/l |
| Hg | 15 | mg/l |
| As | 2200 | mg/l |
| Pb | 2600 | mg/l |
| Ni | 7 | mg/l |
| Cd | 110 | mg/l |
| Suspended solids | 200 | mg/l |
| | Effluent water(1) | |

| | | |
|---|---|---|
| Flow | 31.2 | m³/h |
| pH | 9.5 | |
| Cu | 0.1 - 0.5 | mg/l |
| Hg | 0.05 | mg/l |
| As | 0.05 - 0.2 | mg/l |
| Pb | 0.1 – 0.5 | mg/l |
| Ni | 0.1 – 0.5 | mg/l |
| Cd | 0.01 – 0.2 | mg/l |
| Gypsum sludge | | |
| Amount | 6 - 7 | t/h |
| Composition | 40 - 50 | %moisture |
| | ~ 30 - 35 | $\%CaSO_4$ |
| | ~ 1 | %As |
| | ~ 1 | % Cu, |
| | ~ 1 - 2 | % Fe, |
| | ~ 0.01 | % Hg, |
| | ~ 1 | Pb, |
| | ~ <0.1 | % Ni, |
| | ~ <0.1 | % Cd. |
| (1) Design data taking variations in effluent into account.<br>The metal concentrations are daily averages based on qualified random samples or twenty four hour flow proportional samples. | | |

**Table 2.34: Performance data for the treatment of weak acid**
[ 238, ECI Copper Installations 2008 ]

**Applicability**
This technique is applicable to most process water systems.

**Economics**
Equipment cost were EUR 2.5 million, installation costs were EUR 4.5 to 5.2 million. Electricity: 200 kWh. Milk of lime (10 %); 15 $m^3/h$. $H_2SO_4$ (10 %); 0.8 $m^3/h$. $FeSO_4.7H_2O$; 80 kg/h

**Driving force for implementation**
Effective treatment of weak acid to produce a saleable product.

**Example plants**
Plants in ES and BG.

**Reference literature**
[ 238, ECI Copper Installations 2008 ].

### 2.12.2.2.3 Treatment of weak acid, process effluent and groundwater

**Description**
One plant uses a biological process to produce sulphide ions. Weak acid which is the bleed from the wet gas-cleaning has a high sulphate concentration (10 - 25 mg/l). The sulphate is reduced to sulphide ions with hydrogen gas and sulphate-reducing bacteria in a biological waste water treatment plant:

$$SO_4^{2-} + 8H^{2+} \xrightarrow{SRB} S^{2-} + 4H_2O$$

The hydrogen is produced out of natural gas and steam in a reformer unit. The zinc and other metals react with $S^{2-}$ and precipitate as a metal sulphide:

$$Me + S^{2-} \rightarrow MeS$$

Sulphate and metal concentrations after this treatment are still too high to be discharged directly and the water is treated in another step together with other waste water from production and groundwater. This also uses sulphate-reducing bacteria to precipitate metals with sulphide, but in this case ethanol, is used as electron donor instead of hydrogen [ 240, Nl Input on Zn production 2008 ]

The metal sulphides and biomass slurry is re-used as concentrate in the roasting stage.

**Achieved environmental benefits**

The metal contents of the effluent of such a biological process are similar to those of the cleaned water of the best-performing waste water treatment based on inorganic sulphide addition (NaHS, $Na_2S$), mainly as the chemistry behind both processes is fundamentally the same (based on the low solubility of metal sulphides). The biological process has a positive effect because the sulphate content of the treated water is reduced but there are the significantly higher investment and operational costs .

**Cross-media effects**

No data has been reported.

**Operational data**

Operational data is described in the description.

**Applicability**

The technique is applicable to weak acid where there are no other recovery options and for waste waters from the RLE process in admixture with contaminated groundwater.

**Economics**

No data has been reported but one plant is operating viably.

**Driving force for implementation**

Clean up of historical environmental problems.

**Example plants**

NL.

**Reference literature**

[ 319, Biotechnology for Sustainable Hydrometallurgy 2003 ], [ 320, Biologically produced Sulphide 2004 ], [ 240, Nl Input on Zn production 2008 ].

#### 2.12.2.2.4 Sedimentation and flotation

**Description**

Sedimentation is a solid-liquid separation technique that utilises gravity to separate the insoluble metal complexes and solid particles from the liquid effluent. Sedimentation can take place in a variety of different settling vessels like sedimentation basins, lagoons or specialised sedimentation tanks (thickeners, clarifiers) with a sludge removal device on the bottom of the tank. Sedimentation basins, which are commonly used, are rectangular, square or circular. The sludge that is removed from the sedimentation step can be dewatered, by using, e.g. a vacuum filter press. The filtrate that is generated may be sent back to the beginning of the effluent treatment process or to the process step where it was generated, depending on the treatment process. Sedimentation can be used to separate solid particles from waste water that has been used for the granulation of slag or the production of metal shot.

An alternative to sedimentation may be flotation. Flotation techniques are used to separate large flocs or floating particles like plastic parts from the effluent by bringing them to the surface of the suspension. Flotation can be achieved by dissolved air flotation. Air is dissolved in the suspending medium under pressure and comes out of solution when the pressure is released as minute air bubbles attached to suspended particles. This causes the particles to float to the surface and the flocs can then easily be taken away from the surface of the liquid.

**Achieved environmental benefits**
The minimisation of waste water can also be supported by good housekeeping, which may advantageously be based on a water management plan.

**Cross-media effects**
None reported.

**Operational data**
See Section 2.12.1 and Table 2.39.

**Applicability**
See Section 2.12.1.

**Economics**
None reported.

**Driving force for implementation**
Reduction of waste water emissions.

**Example plants**
See Section 2.12.1.

**Reference literature**
See Section 2.12.1.

#### 2.12.2.2.5 Filtration

**Description**
Filtration techniques are normally used for solid/liquid separation and as a final clarification step in a waste water treatment process. The filtration unit is usually located between the sedimentation step and the final control to remove solids carried over from the previous cleaning step. Filtration can take place in a variety of different filter systems depending on the solid particles that have to be removed.

The normal filter unit consists of a bed of material or materials through which the liquid effluent flows. The fine particles that cannot pass through the filter medium form a filter cake that should be removed either continuously or from time to time for example by back washing in order to keep the pressure loss low. If the pressure loss is low, it enables the filtration to be fed with the waste water flow via gravity flow.

Sand filters are designed for the mechanical removal of suspended solids or semi-solid materials, e.g. sediments or metal hydroxides. The purification of waste water by using sand filtration is due to the combined effects of filtration, chemical sorption and assimilation. Sand filters are sometimes operated as a pressure vessel filled with layered sand, which increases in grade with depth. Initially the filter cake can lead to an enhancement of the filtration efficiency particularly for smaller particles. After a period of time, the sand bed should be back washed. Sand filters are often used for polishing a bleed from a closed water cycle or to allow the effluent to be used as process water.

The sand filter is shown in Figure 2.55.

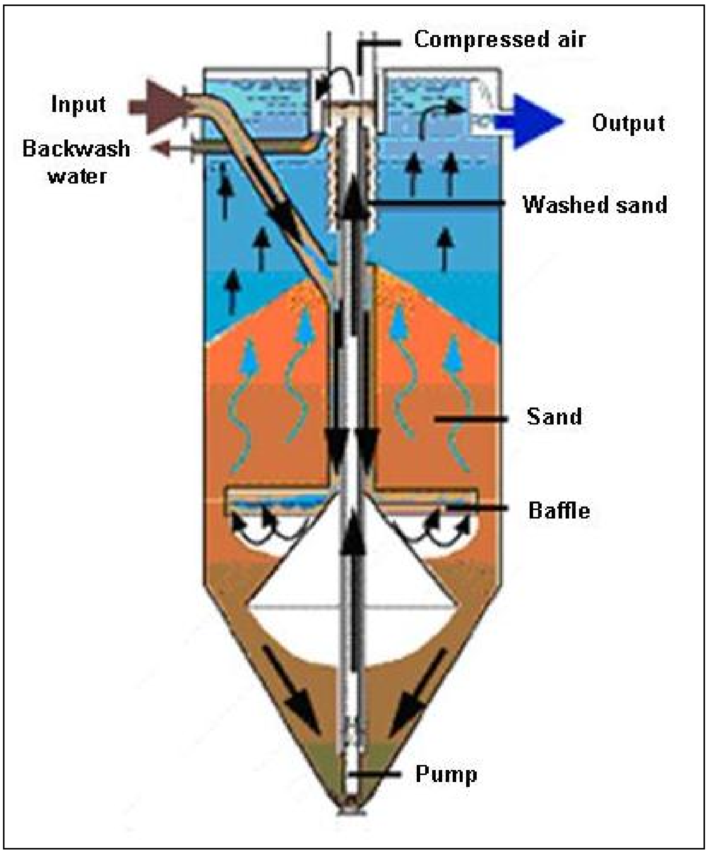

**Figure 2.55:** **Schematic of a sand filter**

Hyperfiltration or reverse osmosis is used to obtain the desired result with very fine particles. Hyperfiltration allows the passage of particles with a molecular mass of about 100 to 500, whereas ultrafiltration is used in the range of 500 up to 100000.

Ultrafiltration is a simple and effective method of waste water treatment but has a high energy requirement. The effluent is placed in contact with an ultrafiltration membrane. This membrane, which contains small pores allows the passage of molecular particles like water and hinders larger molecular particles. With a very fine membrane it is even possible to filter solutes as small as metals. The filtration processes based on membranes produce a clean permeate and a concentrate that may require further treatment.

### Achieved environmental benefits

The minimisation of waste water can also be supported by good housekeeping, which may advantageously be based on a water management plan.

### Cross-media effects

None reported.

### Operational data

See Section 2.12.1 and Table 2.39.

### Applicability

See Section 2.12.1.

### Economics

None reported.

### Driving force for implementation

Reduction of waste water emissions.

**Example plants**
See Section 2.12.1.

**Reference literature**
See Section 2.12.1.

#### 2.12.2.2.6 Electrolysis

**Description**
Electrolytic techniques are used to remove metals such as copper, precious metals, chromium, manganese, cadmium, etc. from process water streams. Because the metal concentrations are usually low, electrolysis is most effective for waste streams before they are diluted with other effluents. Special electrodes such as fluidised bed electrodes or three-dimensional electrodes can be used to improve efficiency. Maximum efficiency of the cell is achieved when the current density changes with solute concentration and the mass transfer takes place close to the limiting current density. In other words, the cathode must always have a fresh supply of ions to reduce.

An alternative, and very successful, use of electrochemical methods for metal clean up is to oxidise metals in effluents so that they can be recycled. One example is the treatment of effluents that contain chromium (III). The largest use of chromium is as an oxidising agent where chromium is in its (VI) oxidation state. The by-product from the oxidation is chromium (III), which is normally released with waste. Anodic oxidation of chromium (III) effluent has been used to regenerate chromium (VI), which can be re-used.

The difference in the relative position in the electrochemical series or the redox potential of the elements can also be exploited by controlling the current and voltage of an electrolytic cell to recover the more noble metals. These properties can also be exploited by using cementation where for example, copper can be precipitated by adding iron.

Another electrochemical treatment method is electrodialysis. The electrodialysis cell consists of two electrodes separated by an ion exchange membrane. The theory is fairly straightforward. Cations under the influence of an electrode potential migrate through a cationic exchange membrane where they are exchanged for less toxic cations (for example exchanging cadmium for sodium). This method aims to combine the advantages of ion exchange with the advantages of electrochemical treatment [ 145, Dairymple, I. 1999 ], [ 166, Clark, J.H. 1995 ].

**Achieved environmental benefits**
The minimisation of waste water can also be supported by good housekeeping, which may advantageously be based on a water management plan.

**Cross-media effects**
None reported.

**Operational data**
See Section 2.12.1 and Table 2.39.

**Applicability**
See Section 2.12.1.

**Economics**
None reported.

**Driving force for implementation**
Reduction of waste water emissions.

**Example plants**
See Section 2.12.1.

**Reference literature**
[ 145, Dairymple, I. 1999 ], [ 166, Clark, J.H. 1995 ].

#### 2.12.2.2.7 Reverse osmosis

**Description**
Reverse osmosis is extensively used for the removal of dissolved metals, especially in the electroplating industry. Osmosis is the natural diffusion of a solvent such as water caused by a difference in the concentration of two solutions separated by a membrane. The solvent flows in the direction that will reduce the concentration of the stronger solution. In reverse osmosis a driving force is applied to reverse the solvent flow. A pressure difference applied between the compartments separated by the membrane causes water to flow from the stronger solution to the weaker. The pressure required must exceed the osmotic pressure. Typical data of the passage of ions across the reverse osmosis membrane are presented in Table 2.35. Reverse osmosis is sometimes used for the recovery of precious metals in the metal plating industry.

| Ions | Passage (%) | Rejection (%) |
|---|---|---|
| Ammonium | 8 | 92 |
| Sodium | 5 | 95 |
| Potassium | 5 | 95 |
| Magnesium | 3 | 97 |
| Strontium | 3 | 97 |
| Calcium | 2 | 98 |
| Nitrate | 15 | 85 |
| Bisilicate | 10 | 90 |
| Chloride | 5 | 95 |
| Fluoride | 5 | 95 |
| Bicarbonate | 5 | 95 |
| Sulphate | 3 | 97 |
| Phosphate | 1 | 99 |

**Table 2.35: Typical passage of ions across the reverse osmosis membrane**
**[ 146, Kemmer, F.N. 1998 ]**

**Achieved environmental benefits**
The minimisation of waste water can also be supported by good housekeeping, which may advantageously be based on a water management plan.

**Cross-media effects**
None reported.

**Operational data**
See Section 2.12.1 and Table 2.39.

**Applicability**
See Section 2.12.1.

**Economics**
None reported.

**Driving force for implementation**
Reduction of waste water emissions.

**Example plants**
See Section 2.12.1.

**Reference literature**
[ 146, Kemmer, F.N. 1998 ].

#### 2.12.2.2.8 Ion exchange

**Description**
Ion exchange is sometimes used as a final cleaning step in the removal of metals from process waste water. By using ion exchange, unwanted metal ions can be removed from a waste water stream by transferring them to a solid matrix while giving back an equivalent number of other ions stored on the ion exchanger skeleton. The ion exchange process is usually used if the metal concentration is below 500 mg/l.

The ion exchange process normally takes place in a column that is packed with beads of the ion exchange resin. The exchange starts first at the top of the column and then passes through the column in order to keep the equilibrium exchange conditions. Depending on the amount of ions stored on the skeleton, the capacity of the ion exchanger is limited. The ion exchanger should therefore be regenerated with hydrochloric acid or caustic soda. In some cases, such as the removal of selenium and rhenium from the off-gas of a molybdenite roaster, the ion exchangers are replaced periodically so that the metal can be recovered by themselves or by specialised plants.

Some specified ion exchangers are able to remove specific metals from the waste water. This selective ion exchange process is much more efficient in removing toxic metals from the effluent. Furthermore, the column is capable of a very high level of clean up, which is also able to operate efficiently in mixed content effluents.

**Achieved environmental benefits**
The minimisation of waste water can also be supported by good housekeeping, which may advantageously be based on a water management plan.

**Cross-media effects**
None reported.

**Operational data**
See Section 2.12.1 and Table 2.39.

**Applicability**
See Section 2.12.1.

**Economics**
None reported.

**Driving force for implementation**
Reduction of waste water emissions.

**Example plants**
See Section 2.12.1.

**Reference literature**
See Section 2.12.1.

#### 2.12.2.2.9 Activated carbon

**Description**

Activated carbon, a highly porous carbonaceous substance, is usually used to remove organic materials from waste water but it also has applications in the removal of mercury and precious metals. These filters are normally used in the form of beds or cartridges operated in multiples so that the breakthrough from one filter is treated by a second one. The spent filter is then replaced and becomes the downstream filter. This operation depends on an adequate method to detect breakthrough from the filters.

**Achieved environmental benefits**

Reduction of organic materials, mercury and precious metals in waste water.

**Cross-media effects**

None reported.

**Operational data**

See Section 2.12.1 and Table 2.39.

**Applicability**

See Section 2.12.1.

**Economics**

None reported.

**Driving force for implementation**

Reduction of waste water emissions.

**Example plants**

See Section 2.12.1.

**Reference literature**

See Section 2.12.1.

### 2.12.2.3 Process control techniques for effluent treatment

**Description**

Process operation and control has developed in this sector. The following techniques are used [ 103, Farrell, F. 1998 ]:

- Reagent metering systems are used extensively.
- Microprocessor control of reagent feed and plant performance is used. On-line monitoring of temperature, turbidity, pH, conductivity, REDOX, TOC, individual metals and flow is used.
- Environmental management and quality systems are used (see also Section 2.2):
  - operators are trained and assessed in the use of operating instructions and the use of the modern control techniques described.
  - levels of supervision are optimised to take advantage of the above and to maintain operator responsibility.
  - robust maintenance systems are used. There is growing use of dedicated maintenance staff forming part of the operator teams.

**Achieved environmental benefits**

The prevention of emissions of metals, suspended solids and other compounds.

The composition of the liquid effluents from pyrometallurgical as well as from hydrometallurgical methods depends very much of the metal being produced, the production process and the raw material that is used. However, the liquid effluents from a non-ferrous metal production plant normally contain metals, e.g. copper, lead, zinc, tin, nickel, cadmium, chromium, arsenic, molybdenum, mercury, and suspended solids.

Table 2.36 gives some examples of the metal content in waste waters before and after treatment for three separately discharged water streams for a primary and secondary copper plant based on measured values from 2005~~relevant to a copper smelter/refinery complex~~ and Table 2.37 gives the effect of treating of some copper waste-streams. The consumption of water, the amount and composition of the liquid effluent and the achievable emission values will be discussed in more detail in the chapter for the individual non-ferrous metal chapters.

*The following table presents data for different waste waters before and after treatment. The techniques mentioned in the bullets in the first paragraph are not directly associated to the values in the table. Low emissions result from treatment techniques which are not described in this section.*

| **Source** | **Main Component (mg/l)** | | | | | |
|---|---|---|---|---|---|---|
| | **Cu** | **Pb** | **As** | **Ni** | **Cd** | **Zn** |
| Process water<br>(180000 $m^3$/yr)<br>- Before treatment<br>- After treatment | 2000<br>0.01 - 0.2 | 500<br>0.001 - 0.04 | 10000<br>0.01 - 0.1 | 1000<br>0.004 - 0.15 | 500<br>0.0001 - 0.1 | 1000<br>0.01 - 0.2 |
| Precipitation water<br>(700000 $m^3$/yr)<br>- Before treatment<br>- After treatment | 15 – 30<br>0.01 - 0.4 | <5<br>0.005 - 0.2 | <2<br>0.003 - 0.007 | <2<br>0.002 - 0.4 | <0.5<br>0.0002 - 0.1 | <2<br>0.03 - 0.4 |
| Direct cooling water(1)<br>(11300000 $m^3$/yr)<br>- Before treatment<br>- After treatment | <3<br>0.01 - 0.25 | <0.5<br>0.001 - 0.1 | <0.1<br>0.001 - 0.1 | <0.1<br>0.002 - 0.06 | <0.05<br>0.0001 - 0.003 | <0.5<br>0.02 - 0.5 |
| Overall pollutant rate (g/t of Cu produced) | 1 – 2.3 | 0.03 – 0.3 | 0.05 – 0.23 | 0.1 – 0.2 | 0.02 – 0.05 | 0.16 – 0.8 |

(1)The total volume of direct and indirect cooling water was 65000000 $m^3$/yr. Metal concentrations (mg/l) are annual averages.

**Table 2.36: Example of the metal content in waste waters before and after treatment relevant to a copper smelter/refinery complex**

[ 234, UBA Copper, lead, zinc and aluminium 2007 ]

**[ 121, Rentz, O. et al. 1999 ]**

*Try to find out which kind of treatment the separated waste waters undergo and complete relevant sections in Chapter 3.3. Relocate the data in table 2.37 to relevant specific section in chapter 3.3.*

| **Component** | **Source and treatment method** | | | | | | |
|---|---|---|---|---|---|---|---|
| | **Process water from primary and secondary Copper production. Lime and iron sulphate treatment, settlement** | **Secondary copper process and surface water after NaHS treatment, settlement and sand filtration** | **Direct cooling water after pH adjustment and settlement** | **Surface run-off water after pH adjustment and settlement** | **Copper wire-rod process water after treatment** | **Copper semis process water after treatment** | **Copper alloy semis process water after treatment** |
| pH | 6.5 - 9.5 | 6.5 - 9.5 | 8.5 - 9.5 | 6.5 - 8.5 | 6.5 – 9.5 | 6.5 - 9.5 | 6.5 - 9.5 |
| Cu mg/l | 0.2 - 0.5 | 0.04 | 0.01 - 0.25 | 0.01 - 0.4 | 0.2 - 0.3 | 0.3 - 0.4 | 0.2 - 0.4 |
| Pb mg/l | 0.2 | 0.04 | 0.001 - 0.1 | 0.005 - 0.2 | | 0.02 - 0.03 | 0.2 - 0.3 |
| Ni mg/l | 0.5 | 0.07 | 0.002 - 0.06 | 0.002 - 0.4 | | 0.09 - 0.1 | 0.3 - 0.4 |
| Zn mg/l | | 0.13 | 0.02 - 0.5 | 0.03 - 0.4 | | 0.7 - 0.8 | 0.8 - 1.0 |
| As mg/l | 0.1 | <0.01 | 0.001 - 0.1 | 0.003 - 0.07 | | 0.01 - 0.03 | <0.1 |
| Cd mg/l | 0.1 | 0.004 | 0.0001 - 0.003 | 0.0002 - 0.1 | | 0.001 | <0.2 |
| Hg mg/l | 0.05 | | | | | | <0.05 |
| Ba mg/l | | 0.10 | | | | | |
| Cr mg/l | | 0.01 | | | | | |
| Co mg/l | | 0.00 | | | | | |
| Fe mg/l | | 0.16 | | | | | |
| Ag mg/l | | 0.05 | | | | | |
| Oil or hydrocarbon mg/l | | | | | <10 | <10 | <10 |
| Suspended solids mg/l | | | | | <5 | <100 | <100 |
| Indications take variations in effluent composition into account. Metal concentrations are based on qualified random samples or 24 hour flow proportional samples. | | | | | | | |

**Table 2.37: The effect of treating of some copper waste-streams**

~~[ 234, UBA Copper, lead, zinc and aluminium 2007 ]~~ *Wrong reference. Unclear where the new information comes from. The rest is from the old BREF Document. If one compares the data in table 2.37 for precipitation water with the data for surface run-off water in table 2.38 and the data in both tables for cooling water it is obvious that these are the same data. Also the data for the secondary copper process are similar. Only the data for primary and secondary process water divagate quite much. Sometime in table 2.38 the upper range and sometimes the lower range of the corrwsponding data from table 2.37 are used. This is totally unclear considering that table 2.37 refers to annual averages and table 2.38 to 24 hourly averages.*

An overview of some sources of waste water and the minimisation and treatment methods is given below in Table 2.38.

| Source of waste water | Associated process | Minimisation methods | Treatment methods |
|---|---|---|---|
| Process water | Alumina production<br>Lead-acid battery breaking<br>Pickling | Return to process as far as possible | Neutralisation and precipitation<br>Electrolysis |
| Indirect cooling water | Furnace cooling for most metals<br>Electrolyte cooling for Zn | Use of sealed cooling system<br>System monitoring to detect leaks | Settlement |
| Direct cooling water | Cu and Al castings<br>Carbon electrodes<br>Ferro-alloys<br>Chromium metal | Settlement or other treatment<br>Closed cooling system | Settlement<br>Precipitation if needed |
| Slag granulation | Cu, Ni, Pb, precious metals, ferro-alloys | Re-use in a sealed system | Settlement<br>Precipitation if needed |
| Electrolysis | Cu, Ni, Zn, Mg | Sealed system<br>Electrowinning of electrolyte bleed | Neutralisation and precipitation |
| Hydro-metallurgy (blowdown) | Zn, Cd | Sealed system<br>Blowdown treatment | Settlement<br>Precipitation if needed |
| Abatement system (blow-down) | Wet scrubbers<br>Wet ESPs and scrubbers for acid plants | Blowdown treatment<br>Re-use of weak acid streams if possible | Settlement<br>Precipitation if needed |
| Surface water | All | Cleaning yards and roadways<br>Good raw materials storage | Settlement<br>Precipitation if needed<br>Filtration |

**Table 2.38: Overview of waste water streams and the treatment and minimisation techniques**
*Useful table!*

**Cross-media effects**
There is the potential to produce a waste for disposal.

**Operational data**
As already explained all the waste water treatment methods are all to be considered in the determination of BAT. The best available treatment technique or a combination of the different treatment methods can only be chosen on a site by site basis by taking into account the site-specific factors. The most important factors to decide, which in a specific case would be the best solution in order to minimise the amount of waste water and the concentration of the pollutants are:

- the process where the waste water is generated
- the amount of water
- the pollutants and their concentrations
- the level of clean up required, i.e. local or regional water quality standards
- the availability of water resources.

Table 2.39 presents the advantages and disadvantages of the most common treatment techniques.

**Applicability**
This techniques are generally applicable to most plants.

**Economics**
No economic data was provided but the processes are operating economically.

**Driving force for implementation**
Reduction of emissions and saving raw materials.

**Example plants**
Plants in DE, AT, FR, BE, PL.

**Reference literature**
[ 166, Clark, J.H. 1995 ].

| Treatment Technique | Advantages | Disadvantages |
|---|---|---|
| **Precipitation** | Cheap and simple technique<br>Long history of successful use<br>Does not require large expenditure in a new plant<br>Capable of treating a wide range of metal contaminants particularly if two-stage precipitation with hydroxide and then sulphide reagents is used<br>Under the correct conditions can give excellent removal of metals<br>Specified precipitants are commercially available<br>Allows absorptive precipitation<br>Precipitates can often be returned to the feed | Acid effluents can be difficult to treat<br>Non-selective: gives a high water content sludge that contains a cocktail of toxic and non toxic metals<br>The sludge may have to be disposed of at sometimes great cost<br>The presence of other salts, organic complexing agents and solvents can severely compromise the precipitation efficiency<br>Cannot always be used to treat low concentrations of metals<br>Some hydroxides inefficiently precipitated |
| **Sedimentation** | Cheap and simple technique<br>Long history of successful use | Can only remove solid particles<br>For particles with a small density difference to water, sedimentation takes a long time and large basins are required |
| **Filtration** | Cheap and simple technique<br>Long history of successful use<br>Filtration, e.g. sand filters are best used for a known solid matter | Can only remove solid particles<br>The filtration efficiency decreases if the particles are very small<br>Filtration efficiency decreases with increased velocity |
| **Flotation** | Cheap and simple technique<br>Long history of successful use | Can only remove solid particle complexes that are floatable<br>Air needs first to be dissolved in pressurised water to be dispersed |
| **Ultrafiltration** | Simple technique<br>Very fine particles, even molecules, can be removed from the waste water<br>Very fine membranes will also filter solutes as small as metals<br>Virtually zero solids emissions | Limited flowrate and filtration velocity<br>Membranes can quickly decompose in corrosive effluents<br>No separation of metals<br>Old membranes can leak<br>Membranes can be easily fouled |
| **Electrolysis** | Can be used to recover and recycle metals<br>Can be used to treat concentrated metal effluents (about 2 g/l) in a single step<br>Technology mostly available<br>Tried and tested with good track record in electroplating industries<br>Can be used to clean up organic contaminants simultaneously<br>Can be used in batch or continuous flow modes | Better than ppm level of clean up is difficult<br>Ineffective cells are expensive to maintain and operate<br>Electrolysis not selective<br>Needs constant monitoring<br>Poor at treating variable content, high volume effluents |
| **Electrodialysis** | Can be used to recover and recycle metals<br>Electrodialysis can be selective<br>Electrodialysis already used in desalination and electroplating industries<br>Electrodialysis capable of sub-ppm level of clean up | Electro-dialysis suffers from the same disadvantages as ion exchange methods (for example, membrane fouling)<br>Needs constant monitoring<br>Poor at treating variable content, high volume effluents |

| Treatment Technique | Advantages | Disadvantages |
|---|---|---|
| **Reverse osmosis** | Virtually zero emission<br>Technology exists and equipment is commercially available<br>Can be used for recycling metals<br>Can be operated in continuous flow or batch mode<br>Can deal with a large range of metal concentrations<br>Can be used to remove organics in effluent<br>Efficacy is not strongly dependent on the concentration of non-corrosive contaminants in effluent | Limited flowrate and filtration velocity<br>Membranes can quickly decompose in corrosive effluents<br>No separation of metals<br>Old membranes can leak<br>Membranes can be easily fouled<br>Membranes need frequent monitoring and replacement<br>Equipment is specialised and expensive<br>Uses high pressure<br>Restriction of a minimum flowrate of approximately 200 l/min<br>Concentrated bleed is produced that needs further treatment |
| **Ion exchange** | Relative inexpensive<br>Commercial products available<br>Tried and tested in industrial applications (e.g. Rhenium and selenium removal and recovery)<br>Capable of clean up to ppb level (selective ion exchange capable of ppt level)<br>Can be easily used in conjunction with other techniques (for example precipitation) as part of an integrated waste water treatment<br>Can be selective for metals<br>Can be applied to many flow types: intermittent, continuous, relatively large volume<br>Selective ion exchange has been used in isolated cases, such as the treatment of nuclear industry effluents | Cannot handle large concentrations of metal<br>Matrix easily fouled by solids and some organics<br>Traditional ion exchange is not selective<br>Exhausted exchanger must usually be disposed of as toxic waste<br>Matrices can decompose over time<br>Performance is sensitive to effluent pH<br>Large volume effluents require very large ion exchange columns<br>Selective ion exchange does not have extensive industrial use to date<br>Regeneration of selective ion exchange columns is time consuming<br>Long contact times with effluent may be needed |
| **Activated carbon** | Can be used for a wide range of applications (e.g. the removal of mercury or PCDD/F from effluent)<br>Can be added after coagulation and sedimentation as a layer in sand filters<br>Technology exists and equipment is commercially available | Activated carbon is expensive<br>Activated carbon can become a breeding ground for micro-organisms<br>High emissions of $SO_2$ generated from the heating process in manufacturing carbon from coal |

**Table 2.39: Summary of advantages and disadvantages of common waste water treatment techniques**

*This table is not connected to any section. It is unclear where this table should be included.*

# 2.13 Waste minimisation and handling

## 2.13.1 Residues and waste from non-ferrous metal production

The production of non-ferrous metals from primary and secondary raw material is related to the potential generation of a wide variety of by-products, intermediate products and residues. The focus should always be on the minimisation of waste by optimising the process and by utilising residues and wastes as far as possible, provided there are no negative cross-media effects. These residues arise from different stages of the production process such as from the metallurgical operations, the smelting process as well as from the off-gas and waste water treatment [ 83, NRW (D) 1997 ]. The content and value of the elements contained in the residue influence its potential for re-use, e.g. anode slime is a viable raw material for the recovery of precious metals. Any designation of a residue as waste for disposal should take this into account. Also some filter dust such as silica fumes that arise from the smelting process of ferro-silicon and silicon metal can be used as a by-product [ 226, Nordic Report 2008 ].

According to the current EU legislation (Decision 2000/532/EC), many of these residues are regarded as wastes. However the non-ferrous metals industry has for many decades used many residues as raw materials for other processes and an extensive network of metallurgical operators has been established for many years to increase the recovery of metals and reduce the quantities of waste for disposal. It has been reported that some legislative measures to control waste movements are inhibiting the recycling of residues from metallurgical operations [ 96, Bontoux, L. et al. 1997 ]. It is also well known that the metal-producing industries obtain one of the highest recycling rates in all industrial sections. This helps to reduce cross-media issues to a minimum. Nevertheless, the problem of residues from production facilities and the designation of some of these materials will also play an important role in future permits and the techniques tend to concentrate on this aspect.

Table 2.40 and Table 2.41 offer examples of the potential wastes according to the European Waste Catalogue (Council Decision 2000/532/EC)[1]. Waste in general terms is defined by the framework directive on waste Directive 2008/98/EC as 'any substances or objects in the categories set in Annex I which the holder discards or intends or is required to discard'. A second definition of waste coexists with the definition presented above. It is that from the Basel Convention, adopted by the European Union in 1993: 'Wastes are substances or objects which are disposed of or are intended to be disposed of or required to be disposed of by provisions of national law' [ 96, Bontoux, L. et al. 1997 ].

It must be stressed that mentioning the name of a material in the European Waste Catalogue is not a sufficient reason to define this material as a waste. In the first place, the material should fulfil the criteria of the definition of a waste. A lot of residues of metallurgical processes can be covered by the concept of by-product, which is in the new Directive 2008/98/EC on Waste. ~~and Repealing Certain Directives such as 2006/12/EC 75/042/EC.~~

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[1] The EWC is a harmonised, non-exhaustive list of wastes, that is to say, a list which will be periodically reviewed and if necessary revised in accordance with the committee procedure. However, the inclusion of a material in the EWC does not means that the material is a waste in all circumstances. The entry is only relevant when the definition of waste has been satisfied [ 96, Bontoux, L. et al. 1997].

| Waste from the production of non-ferrous metals | | | |
|---|---|---|---|
| **EWC Code** | **Description** | **Hazardous waste** | **Origin** |
| | Wastes from physical and chemical processing of metalliferous minerals | | |
| 01 03 04 | Acid-generating tailings from processing of sulphide ore | | |
| 01 03 05 | Other tailings that contain dangerous substances | ● | |
| 01 03 06 | Tailings other than those mentioned in 01 03 04 and 01 03 05 | | |
| 01 03 07 | Other wastes that contain dangerous substances from physical and chemical processing of metalliferous minerals | ● | |
| 01 03 08 | Dusty and powdery wastes other than those mentioned in 01 03 07 | | |
| 01 03 09 | Red mud from alumina production | | Bauxite process |
| 01 03 99 | Wastes not otherwise specified | | |
| | Wastes from the manufacture, formulation, supply and use (MFSU) of acids | | |
| 06 01 01 | Sulphuric acid and sulphurous acid | ● | Acid plant |
| 06 01 02 | Hydrochloric acid | ● | |
| 06 01 03 | Hydrofluoric acid | ● | |
| 06 01 04 | Phosphoric and phosphorous acid | ● | |
| 06 01 05 | Nitric acid and nitrous acid | ● | |
| 06 01 06 | Other acids | ● | |
| 06 01 99 | Wastes not otherwise specified | | |
| 06 04 03 | Waste containing arsenic | ● | |
| 10 03 00 | Wastes from aluminium thermal metallurgy | | |
| 10 03 02 | Anode scraps | | Pot room |
| 10 03 04 | Primary production slags | ● | Smelting |
| 10 03 05 | Waste alumina | | Smelting |
| 10 03 08 | Salt slag from secondary production | ● | Smelting |
| 10.03 09 | Black dross from secondary production | ● | Smelting |
| 10 03 13 | Solid waste from gas treatment | | Abatement system |
| 10 03 14 | Sludges from gas treatment | | Abatement system |
| 10 03 15 | Skimmings that are flammable or emit, upon contact with water, flammable gases in dangerous quantities | ● | Smelting |
| 10 03 16 | Skimmings other than those mentioned in 10 03 15 | | Smelting |
| 10 03 17 | Tar containing wastes from Anode manufacture | ● | Anode baking plant |
| 10 03 18 | Carbon containing wastes from anode manufacture | | |
| 10 03 19 | Flue-gas dust that contains dangerous substances | ● | Abatement system |
| 10 03 20 | Flue-gas dust other than those mentioned in 10 03 19 | | Abatement system |
| 10 03 21 | Other particulates and dust (including ball-mill dust) that contain dangerous substances | ● | Abatement system |
| 10 03 22 | Other particulates and dust (including ball-mill dust) other than those mentioned in 10 03 21 | | Abatement system |
| 10 03 23 | Solid wastes from gas treatment that contain dangerous substances | ● | Abatement system |
| 10 03 24 | Solid wastes from gas treatment other than those mentioned in 10 03 23 | | Abatement system |
| 10 03 25 | Sludges and filter cakes from gas treatment that contain dangerous substances | ● | Abatement system |
| 10 03 26 | Sludges and filter cakes from gas treatment other than those mentioned in 10 03 25 | | Abatement system |
| 10 03 27 | Wastes from cooling-water treatment that contain oil | ● | Abatement system |
| 10 03 28 | Wastes from cooling-water treatment other than those mentioned in 10 03 27 | | Abatement system |
| 10 03 29 | Wastes from treatment of salt slags and black drosses that contain dangerous substances | ● | Salt slag recovery |

| Waste from the production of non-ferrous metals | | | |
|---|---|---|---|
| **EWC Code** | **Description** | **Hazardous waste** | **Origin** |
| 10 03 30 | Wastes from treatment of salt slags and black drosses other than those mentioned in 10 03 29 | | Salt slag recovery |
| 10 03 99 | Wastes not otherwise specified | | |
| 10 04 00 | Wastes from lead thermal metallurgy | | |
| 10 04 01 | Slags from primary and secondary production | ● | Smelting |
| 10 04 02 | Dross and skimmings from primary and secondary production | ● | Smelting |
| 10 04 03 | Calcium arsenate | ● | Abatement system |
| 10 04 04 | Flue-gas dust | ● | Abatement system |
| 10 04 05 | Other particulates and dust | ● | Storage, handling |
| 10 04 06 | Solid wastes from gas treatment | ● | Abatement system |
| 10 04 07 | Sludges and filter cakes from gas treatment | ● | Abatement system |
| 10 04 09 | Wastes from cooling-water treatment that contain oil | ● | Cooling system |
| 10 04 10 | Wastes from cooling-water treatment other than those mentioned in 10 04 09 | | Cooling system |
| 10 04 99 | Wastes not otherwise specified | | |
| 10 05 00 | Wastes from zinc thermal metallurgy | | |
| 10 05 01 | Slags from primary and secondary production | ● | Smelting |
| 10 05 03 | Flue-gas dust | ● | Abatement system |
| 10 05 04 | Other particulates and dust | | Storage, handling |
| 10 05 05 | Solid waste from gas treatment | ● | Abatement system |
| 10 05 06 | Sludges and filter cake from gas treatment | ● | Abatement system |
| 10 07 08 | Wastes from cooling-water treatment that contain oil | ● | Cooling system |
| 10 05 09 | Wastes from cooling-water treatment other than those mentioned in 10 05 08 | | Cooling system |
| 10 05 10 | Dross and skimmings that are flammable or emit, upon contact with water, flammable gases in dangerous quantities | ● | |
| 10 05 11 | Dross and skimmings other than those mentioned in 10 05 10 | | |
| 10 05 99 | Wastes not otherwise specified | | |
| 10 06 00 | Wastes from copper thermal metallurgy | | |
| 10 06 01 | Slags from primary and secondary production) | | Smelting |
| 10 06 02 | Dross and skimmings from primary and secondary production | | Smelting |
| 10 06 03 | Flue-gas dust | ● | Abatement system |
| 10 06 04 | Other particulates and dust | | Storage, handling |
| 10 06 06 | Solid waste from gas treatment | ● | Abatement system |
| 10 06 07 | Sludges and filter cakes from gas treatment | ● | Abatement system |
| 10 06 09 | Wastes from cooling-water treatment that contain oil | ● | Cooling system |
| 10 06 10 | Wastes from cooling-water treatment other than those mentioned in 10 07 07 | | Cooling system |
| 10 06 99 | Wastes not otherwise Specified | | |
| 10 07 00 | Wastes from silver, gold and platinum thermal metallurgy | | |
| 10 07 01 | Slags from primary and secondary production | | Smelting |
| 10 07 02 | Dross and skimmings from primary and secondary production | | Smelting |
| 10 07 03 | Solid wastes from gas treatment | | Abatement system |
| 10 07 04 | Other particulates and dust | | Storage, handling |
| 10 07 05 | Sludges and filter cakes from gas treatment | | Abatement system |
| 10 07 07 | Wastes from cooling-water treatment that contain oil | ● | Cooling system |
| 10 05 08 | Wastes from cooling-water treatment other than those mentioned in 10 05 08 | | Cooling system |
| 10 07 99 | Wastes not otherwise specified | | |
| 10 08 00 | Wastes from other non-ferrous thermal metallurgy | | |

| Waste from the production of non-ferrous metals | | | |
|---|---|---|---|
| **EWC Code** | **Description** | **Hazardous waste** | **Origin** |
| 10 08 04 | Particulates and dust | | Storage, handling, powder metal process |
| 10 08 08 | Salt slag from primary and secondary production | ● | Smelting |
| 10 08 09 | Other slags | | Smelting |
| 10 08 10 | Dross and skimmings that are flammable or emit, upon contact with water, flammable gases in dangerous quantities | ● | Smelting |
| 10 08 11 | Dross and skimmings other than those mentioned above | | Smelting |
| 10 08 12 | Tar containing wastes from anode manufacture | ● | Anode plant |
| 10 08 13 | Carbon-containing wastes from anode manufacture other than those mentioned in 10 08 12 | | Anode plant |
| 10 08 14 | Anode scrap | | Anode plant |
| 10 08 15 | Flue-gas dust that contain dangerous substances | ● | Abatement system |
| 10 08 16 | Flue-gas dust other than those mentioned in 10 08 15 | | Abatement system |
| 10 08 17 | Sludges and filter cakes from flue-gas treatment that contain dangerous substances | ● | Abatement system |
| 10 08 18 | Sludges and filter cakes from flue-gas treatment other than those mentioned in 10 08 17 | | Abatement system |
| 10 08 19 | Wastes from cooling-water treatment that contain oil | ● | Cooling system |
| 10 08 20 | Wastes from cooling-water treatment other than those mentioned in 10 08 19 | | Cooling system |
| 10 08 99 | Wastes not otherwise specified | | |
| 11 02 00 | Wastes and sludges from non-ferrous hydrometallurgical processes | | |
| 06 05 02 | Sludges from on site effluent treatment containing hazardous substances | ● | Waste water treatment |
| 06 05 03 | Sludges from on site effluent treatment other than those mentioned in 06 05 02 | | |
| 11 02 02 | Sludges from zinc hydrometallurgy (including jarosite, goethite) | ● | Leaching process |
| 11 02 03 | Wastes from the production of anodes<br>For aqueous electrolytic processes | | Anode production plant |
| 11 02 05 | Wastes from copper hydrometallurgical processes that contain dangerous substances | ● | Leaching process |
| 11 02 06 | Wastes from copper hydrometallurgical processes other than those mentioned in 11 02 05 | | Leaching process |
| 11 02 07 | Other wastes that contain dangerous substances | ● | |
| 11 02 99 | Wastes not otherwise specified | | |
| 12 01 02 | Ferrous metal dust and particles | | |
| 12 01 09 | Machining emulsions and solutions free of halogens | ● | |

**Table 2.40: Waste from non-ferrous metal production**

| | | | |
|---|---|---|---|
| 13 01 00 | Waste hydraulic oils and break fluids | | |
| 13 01 01 | Waste hydraulic oils, that contain PCPs or PCTs | ● | Transformer |
| 13 01 09 | Other chlorinated hydraulic oils<br>(not emulsions) | ● | Transformer |
| 13 01 10 | non chlorinated hydraulic oils<br>(not emulsions) | ● | Transformer |
| 13 01 06 | Hydraulic oils that contain only mineral oil | ● | Transformer |
| 13 03 00 | Waste insulating and heat transmission oils and other liquids | | |
| 13 03 01 | Insulating or heat transmission oils<br>and other liquids | ● | Transformer |

| | | | |
|---|---|---|---|
| 13 03 02 | Other chlorinated insulating oils and other liquids that contain PCBs or PCTs | | Transformer |
| 13 03 04 | Synthetic insulating and heat transmission oils and liquids | ● | Transformer |
| 13 03 05 | Mineral based non chlorinated gear and lubricating oils | ● | Transformer |
| 13 03 06 | Mineral based chlorinated insulating and heat transmission oils other than those mentioned in 13 03 01 | ● | Transformer |
| 13 05 00 | | | |
| 13 05 01 | Solids from grit chambers and oil interceptors | ● | |
| 13-05 02 | Sludges from oil-water interceptors | ● | |
| 15 02 00 | Absorbents, filter materials, wiping cloths and protective clothing | | |
| 15 02 02 | Absorbents, filter materials,<br>wiping clothes, protective clothes | ● | Abatement system (dry dedusting) |
| 16.11.01 | Carbon from spent pot lining | | Cell room - Al |
| 16.11.03 | Refractory from spent pot lining | | Cell room - Al |
| 16 11 04 | Other linings other than those mentioned in 16 11 03 | | |

**Table 2.41: Other waste that might be encountered**

Most of the materials listed above are recycled or re-used within the non-ferrous metals industries themselves as well as in other industries, for example in the cement, abrasives manufacturing and construction industries. It is not the intention to discard or dispose of them. They are the result of the metal separation that is necessary for their recovery and the production of pure metals from complex sources. Some examples are given below.

## 2.13.2 Applied process and techniques

### 2.13.2.1 Residues from the smelting process

The main residues arising from the smelting of non-ferrous metals are slag, dross and skimmings removed during the pyrometallurgical processes. Slag is generated by the reaction of slag forming accompanying elements (e.g. Fe) with added fluxes. In the smelting process, the slag is liquid and has a different density to the melted metal and can therefore be tapped off separately.

Most of the slag generated by downstream or refining operations in the non-ferrous metal production processes can usually be recycled or used for further metal recovery. Figure 2.56 shows the electric furnace cleaning of copper slags to achieve the internal recycling of the slag. In this example, molten slag obtained from the converter, which has a high copper content, is returned to the smelter. The slag leaving the smelter is de-copperised in an electric slag-cleaning furnace. This furnace is operated continuously with an almost continuous flow of slag. Depending on local facilities, the resulting clean slag is either granulated to produce abrasives or cooled slowly and broken into lumps for filling or construction material.

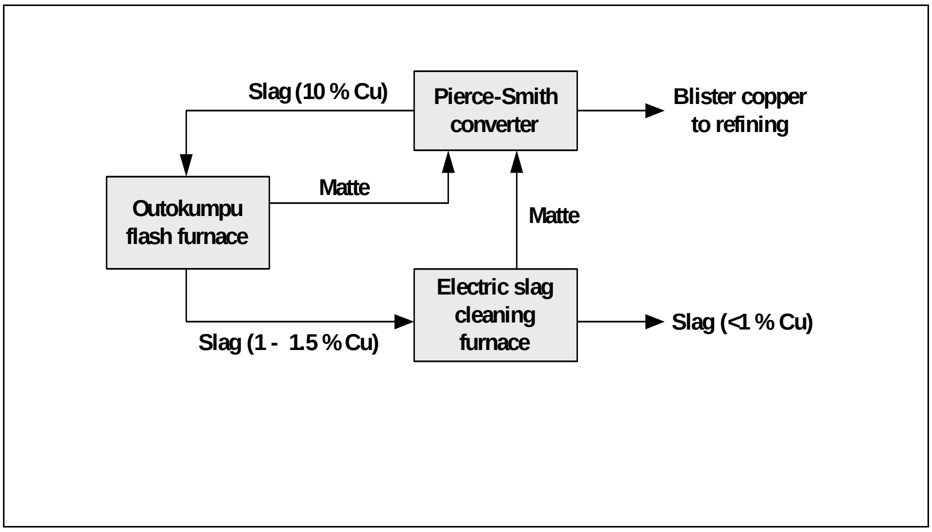


**Figure 2.56: Electric furnace cleaning of copper slags**

There is a distinction between slag with a high metal content, which is recycled within the process, and final slag with a low metal content.

Several facilities in the non-ferrous metals industries have demonstrated that there is a market in which they are able to sell slag for further beneficial use. The use of slag as a construction material to replace aggregates is only possible if the amount of the leachable metal compounds is low. There are various tests to demonstrate this such as [ 268, Belgium Input 2008 ], [ 289, USEPA Method 1311 and 1312 2008 ]. Slag that cannot be used as an abrasive or in civil engineering and construction is used for recycling or used as construction material in special cases (e.g. construction of disposal areas) or sent for disposal.

Salt slag is generated by melting light metals (aluminium, magnesium). The use of a salt flux prevents the melted metal from oxidation and binds the impurities from the process. There are different ways to minimise the amount of salt flux used as well as different treatment techniques for salt and metal recovery that are available and they are discussed in more detail in Chapter 4 of this document.

Dross and skimmings are generated by the oxidation of metals at the bath surface or by reactions with fireproof material used as furnace linings. The metal content of skimmings or dross is relatively high (between 20 and 80 %), therefore they can normally be recycled to the main process or supplied as secondary raw material to other non-ferrous metal plants.

Another source of residues is spent linings and refractories. These arise when refractory material falls out of the furnace linings or when the furnace lining should be renewed completely. The durability of a furnace lining lies between a few weeks and several years depending on the process and metal (e.g. for the Outotec flash furnace in the primary copper production, 6 to 10 years are possible). The amount of furnace lining material could rise up to 5 kg/t of metal produced according to the melted metal [ 83, NRW (D) 1997 ]. The following practices are used for furnace linings: treatment in a smelter to form an inert slag, e.g. linings from a brass melting process are sent directly to a local secondary copper smelter; use as a component in the tap-hole mass; disposal of inert linings. Table 2.42 gives an overview of the amount of recycled, re-used and discharged residues from some non-ferrous metal smelting furnaces in Germany. In this sense, recycling means that the residue is returned to the process from where it was produced. Re-use means that the residue is used for another purpose, e.g. slag may be re-used as a construction material.

| Residue | Amount of residue reported in tonnes for 1996 | | |
|---|---|---|---|
| | Recycled or re-used | Disposed of | Total amount |
| Refractory waste (silicon dioxide) | 21 | 188 | 209 |
| Refractory waste | 1655 | 1145 | 2800 |
| Refractory waste with harmful components | 637 | 728 | 1365 |
| Slag | 16869 | 3 | 16872 |
| Dross from lead smelting | 1903 | 0 | 1903 |
| Aluminium-containing skimmings or dross | 45904 | 927 | 46831 |
| Magnesium-containing dross | 615 | 81 | 696 |
| Salt slag from aluminium smelting | 112438 | 0 | 112438 |
| Other residues | 348 | 0 | 348 |

**Table 2.42: Amount of recycled, re-used and discharged residues that were reported in 1996 for some non-ferrous metal plants in North Rhine-Westphalia**
[ 81, Ministerium in NRW (D) 1997 ]

### 2.13.2.2 Residues from abatement systems

Abatement systems are another major source of solid materials. These are flue-gas dust and sludge recovered from the air pollution control equipment as well as other solid waste like spent filter material such as filter bags.

Dust from the storage and handling of raw material or from preprocessing unit operations is collected by the dedusting system (usually a fabric filter) and sent back to the main process or another smelter. In some cases, the dust should be agglomerated before it can be recycled to the raw material storage and handling station.

Dust-laden off-gas from the smelting and refining facilities can be cleaned (as described in Section 2.9) by using different abatement techniques. The material collected as dust by the off-gas-cleaning can be agglomerated and sent back to the smelter or supplied as a raw material for further metal recovery in other facilities. An example is the zinc-rich dust from a converter or an electric slag cleaning furnace in the primary copper smelting process which can be treated as a by-product and re-used as a raw material in a zinc recovery plant [ 90, Traulsen, H. 1998 ]. Another example is the use of silica fumes (micro-silica), which are collected in the fabric filter by smelting silicon metal or ferro-silicon and sold as a valuable by-product to the construction industry.

The sludge from a scrubber that contains metal is normally drained for instance in a chamber filter press, and sent back to the smelter.

When off-gas-cleaning takes place in a dry dedusting system, the filter material occasionally should be replaced. The filters contain metal compounds and particles from the process. There are a number of examples where filter material is used in the pyrometallurgical process. If this is not possible, they are sent for ultimate disposal to an incinerator or other disposal site. Table 2.43 gives some information about the amount of recycled, re-used and discharged residues from abatement systems in some non-ferrous metal plants in Germany.

| Residue | Amount of residue reported in tonnes for 1996 | | |
|---|---|---|---|
| | Recycled or re-used | Disposed of | Total amount |

| | | | |
|---|---|---|---|
| Dust that contains metals | 6550 | 1886 | 8436 |
| Dust | 201 | 13 | 214 |
| Mineral residues from the abatement system | 2638 | 1752 | 4390 |
| Sludge | 508 | 4 | 512 |
| Dust that contains aluminium | 1477 | 66 | 1543 |

**Table 2.43: Amount of recycled, re-used and discharged residues that have been reported in 1996 for some non-ferrous metal plants in North Rhine-Westphalia**
[ 82, Ministerium NRW (D) 1997 ]

### 2.13.2.3 Residues from liquid effluent treatment

Pyrometallurgical processes for the production of non-ferrous metals do not normally produce harmful waste water. The water is used for the direct or indirect cooling of furnaces, blowing lances and casting machines, e.g. for copper anode or continuous casting. This water is warmed up by cooling the equipment but is normally not polluted with chemical impurities or metal particles. Therefore cooling water is usually discharged directly after settlement or another treatment step back into the receiving source. Solid material that is removed is returned to the smelter.

If a wet scrubber is used for cleaning the process off-gas, waste water is generated. This stream of waste water should be treated to reduce the amount of metal compounds. From this treatment, sludge is produced that may be rich in metal and can sometimes be recycled to the process if the metal content is high enough.

Process water arises from hydrometallurgical operations and presents a high risk of water pollution. It should therefore be cleaned in a waste water treatment plant. The cleaning takes place by the neutralisation or precipitation of specific ions. The main residue from these effluent treatment systems is gypsum ($CaSO_4$), metal hydroxides and sulphides. The sludge sometimes is recycled back to the main production process.

### 2.13.2.4 Residues from the non-ferrous metal hydrometallurgical processes

The production of non-ferrous metals by hydrometallurgical processes is another significant sources of solid residues. The leaching process can generate relatively large quantities of sludge (e.g. approximately 0.3 to 0.5 tonnes iron-based solids per tonne of zinc depending on the quality of the concentrate). These residues are normally disposed of in specially-sealed lagoons or underground deposits, e.g. blasted mountain caverns. Some residues are also being compacted or treated in the Jarofix process before disposal.

The leaching and purification process and the electrolysis processes also generate other metal-rich solids. They are usually rich in a specific metal and can sometimes be recycled to the production process or sent for metal recovery to other non-ferrous metals facilities (e.g. for the production of precious metals, lead, copper and cadmium). The anode slime from the copper tankhouse for instance is one of the most important raw materials of the recovery of precious metals and is therefore considered a valuable by-product of copper production. These issues are discussed in the chapters dealing with the individual metal groups.

### 2.13.2.5 Other residues from the production of non-ferrous metals

There are several other kinds of residues like hydraulic and heat transmission oils that result from regular maintenance of the equipment, for example the transformer for the electric furnaces. This is usually supplied to a used oil refinery (or in some countries, e.g. Italy, to a compulsory consortium or agency). In some circumstances, they can be used as a source of energy on site but since this technique involves the incineration of waste, the installation should comply with the Waste incineration Directive (2000/76/EC).

### 2.13.3 Techniques to consider in the determination of BAT

*Here is a subheading missing.*

The sections of this document entitled 'Techniques to consider in the determination of BAT' set out techniques considered generally to have potential for achieving a high level of environmental protection in the industries within the scope of the document. The background to the way the techniques are described is given in Section 2.1.2 and Table 2.2.

This section presents a number of techniques for the prevention or reduction of emissions and residues as well as techniques reducing the overall energy consumption. They are all commercially available. Examples are given in order to demonstrate techniques, which illustrate a high environmental performance. The techniques that are given as examples depend on information provided by the industry, European Member States and the valuation of the European IPPC Bureau.

**Description**

During 2005, a plant for the reduction of hexavalent chromium in filter dust was put into operation. It consists of equipment for the collection of filter dust and an installation where the filter dust is mixed with ferrous sulphate ($FeSO_4.7H_2O$) [ 226, Nordic Report 2008 ].

The collected dust is mixed with ferrous sulphate in a mobile concrete mixer truck for the reduction of $Cr^{VI}$. The volume of the tank on the truck is 7.5 $m^3$ which makes it possible to treat 6.5 tonnes of dust.

Water and ferrous sulphate and dust are metered into the truck to obtain the optimum mixture. The HC FeCr filter dust is finer than the charge filter dust and therefore needs more water to get the same consistency in the slurry. The resulting slurry is spread out in cells on the disposal site, where it cures into solid cake. By the end of the day the truck is cleaned by tumbling slag (16 - 32 mm) and water in the mixer. The slag and water is put on an assigned place on the deposit.

**Achieved environmental benefits**

The method has almost eliminated the environmental impact regarding the handling of fine ferro-chrome dust including:

- the spreading of dust from the depository has in principle ceased
- the number of transports back and forth from the depository has been halved
- the dusting from the handling of containers has been minimised
- the content of water-soluble chromium has decreased with more than 99 % since the hexavalent chromium was reduced to trivalent chromium precipitating as chromium hydroxide
- the treated dust is no longer classified as hazardous waste and is re-used.

**Cross-media effects**

Use of reagents.

**Operational data**

The treatment of filter dust has successively resulted in lower levels of Cr(VI) in the leaching water. When the pilot plant project started, the water from the leaching ditch contained about 3 - 4 mg Cr(VI) per litre. One year later, the chromium level dropped to around 0.5 - 0.1 mg CrVI per litre. Deposit of slurry in cells formed by concrete support produced a solid surface in just a few days. Under ideal conditions, the slurry hardens quickly into a homogenous material. The dry strength of the material is high and its hydraulic conductivity, e.g. permeability of water, is low. The fluidity of the slurry gives it a sealing quality. The slurry fills up the cracks in the underlying layer in the cells.

**Applicability**
This technique is applicable to filter dust containing Cr(VI).

**Economics**
No data has been reported.

**Driving force for implementation**
Cost of disposal and environmental regulation.

**Example plants**
SW.

**Reference literature**
[ 233, Farrell Nordic Mission 2008 ], [ 226, Nordic Report 2008 ].

#### 2.13.3.1 Minimisation of residues from the metallurgical process

**Description**
As mentioned in Section 2.13.2.1, the amount of slag and skimmings or dross that is produced by smelting metals is mainly influenced by the impurities of the raw material, so that cleaner materials lead to a reduced generation of these solids. In some cases, this can be ensured by the selection of the raw material that will be used. For example, some zinc concentrates can contain lower quantities of iron [ 98, Lijftogt, J.A. et al 1998 ], and the processes developed to used these concentrates can minimise the production of iron-based residues. The limited availability and higher costs of these concentrates means that this is not a global solution. For secondary aluminium, the pretreatment of scrap or the use of cleaner materials results in the reduction or elimination of salt flux used depending on the furnace used. The economics of pretreatment need to be balanced.

On the other hand, inappropriate storage and handling may lead to the wetting of materials. For example, in a remelting process for aluminium, the water is vaporised with the potential of an explosion.

The generation of skimmings or dross can be minimised by optimising operation of the furnace, e.g. decreasing the burn-up by avoidance of overheating of the melt. Modern process control techniques are used to ensure optimised operation conditions.

To avoid oxidising the bath surface of a melt, a closed furnace operation could be used. For example, by melting aluminium under a reducing atmosphere (rinsing the furnace with inert gas), the amount of skimmings or dross that is generated is reduced. Similarly, the use of a pumping system and a side-well is another measure which can reduce oxidation.

It has been demonstrated that lead ashes and a large amount of the slag that is generated by the smelting process can be recycled or re-used to a large extent.

Spent linings and refractories cannot be completely avoided, but a decrease of the quantity can be obtained by the following measures:

- careful construction of the brick lining of the furnace;
- continuous use of the furnace and thus minimisation of the variations in temperature;
- thermal monitoring to detect temperatures outside the operating range;
- cooling blocks to remove heat from the linings;
- short impact time of the fluxing agents;

- avoidance of aggressive fluxing agents;
- careful cleaning of furnaces and crucibles;
- reduction of furnace agitation (rotation).

Under certain conditions, depending on the composition of the spent linings and refractories, re-use is possible.

Refractories can be re-used in primary and secondary copper smelting after grinding to produce a castable or tapping mass or as a flux to adjust slag composition. Alternatively the metal content can be separated from the material by milling and grinding and the spent linings and refractories can be re-used for construction purposes or to produce refractory linings or refractory cement. The metal content can be recycled to the smelter or supplied to other non-ferrous metal facilities.

In a secondary copper plant, bricks from the shaft furnace, converter and anode furnace can be completely recycled. Converter brick contains up to 1.5 % copper and the shaft furnace brick contains up to 4 % copper. Bricks are milled and the copper is recovered, the remaining material is used to make refractory cement and refractory linings for the casting wheel. White bricks are re-used in the anode furnace and as cement in the shaft furnace and black brick is used for ladle insulation. Furnace linings are crushed, copper is removed and returned for processing and the refractory parts are reformulated to make moulds for the anode casting wheel [ 249, Austria Brixlegge Report 2007 ].

Controlling the quality of slag to allow further use is also an important technique to consider. Several slags are relatively inert and can be used as construction materials to replace aggregates, and as abrasives. Good quality control of the material is needed to ensure that it is acceptable for use as construction or other uses and leaching tests are available to demonstrate acceptability [ 289, USEPA Method 1311 and 1312 2008 ], [ 268, Belgium Input 2008 ]. The Landfill Directive specifies CEN standard leaching tests for granular waste EN 14405 and EN12457/1-4.

**Achieved environmental benefits**
Reduced amount of waste for disposal and the replacement of virgin material to use inert slags, to reduce residues or produce refractory cement, etc. and the re-use of material.

**Cross-media effects**
None reported.

**Operational data**
Several techniques exist to reduce the amount of residues that are formed in the production processes. Important techniques are to reduce the amount of slag, to recover metals in the slag and to reduce the amount of metals in the residue slag. For example, a ferro-chrome works in Finland has managed to reduce the amount of residue with a ferro-chrome slag extraction process [ 226, Nordic Report 2008 ]. A machine working with a spiral screw is used to separate chromium from processed fine slag. Chromium is heavier than slag so it is concentrated in the centre of the spiral. The recovered chromium can be re-used in the melting shop and the slag is used as a material for new filler products. Filler products are used, for example, in cement and asphalt. This technique has reduced the amount of residue going to disposal by about 10000 tonnes.

**Applicability**
These techniques are applicable to the use of materials that are suitable for the duty envisaged. Spent refractories can be made into lower grade refractory cement or ladle linings and metallurgical slags can be used for construction provided that they meet leachability standards.

**Economics**
No data has been reported.

**Driving force for implementation**
The cost of disposal and purchase of virgin refractory.

**Example plants**
AT, BE, DE.

**Reference literature**
[ 233, Farrell Nordic Mission 2008 ], [ 249, Austria Brixlegge Report 2007 ].

### 2.13.3.2 Minimisation of residues arising from the abatement system

**Description**
As described above, the main source of residue generated by abatement systems is flue-gas dust and sludge depending on the abatement technology. The volume of process gases that should be cleaned is largely dependent on the furnace type. For example, a totally sealed furnace develops far less flue dust than a semi-closed or an open furnace.

As already mentioned, the metal-laden dust can normally be recycled to the smelter or sold for further beneficial use to other non-ferrous metal facilities. The direct re-use of dust as a raw material often requires an agglomeration step as a pretreatment process. Flue dust and sludge may be processed in a variety of pyrometallurgical or hydrometallurgical processes.

Drying of the smelter feed can lead to a release of $SO_2$, especially when sulphidic ores or concentrates are used as raw material (the other source is the sulphur content of the fuel). The gypsum ($CaSO_4\,2H_20$) produced in the $SO_2$ scrubber can sometimes be recycled to the dryer as part of the furnace flux feed depending on the process used.

The quantity of spent filter bags may be decreased be using modern filter materials that are more robust. Fabric filters are characterised as an abatement technique that does not need very much maintenance. In the case of bag damage, the appropriate filter compartment can be isolated with cover plates until repairs can be carried out safely. A filter change is normally only necessary if 10 to 20 % of the filter compartments have been taken out of service.

The replacement of filter bags with modern, reliable fabrics is often easy but the technical requirements and the related investment costs of individual cases should be considered. Used filter bags can be recycled into the smelter but since this technique involves the incineration of waste, the installation should comply with the Waste Incineration Directive (2000/76/EC). In the case of a conversion or renewal of the filter system, the service life and the filter susceptibility can generate fewer bags. If this results in additional installation costs, they usually can be compensated for by the decrease in the number of bag failures.

**Achieved environmental benefits**
The minimisation of material destined for disposal and the re-use of resources.

**Cross-media effects**
None reported.

**Operational data**
None provided

**Applicability**
These techniques are applicable to most processes.

**Economics**
No data has been reported but the techniques are operating viably.

**Driving force for implementation**
Compliance with environmental permits

**Example plants**
AT, DE, ES, FR.

**Reference literature**
[ 234, UBA Copper, lead, zinc and aluminium 2007 ].

### 2.13.3.3 Reduction of residue generated by the effluent treatment

**Description**
The avoidance of thermally loaded cooling water to the environment can be reduced by using different kinds of cooling systems, such as closed cooling systems, quasi-closed systems and open cycle cooling techniques (cooling towers). If a closed cooling cycle (e.g. air-coolers) is used the release of cooling water can be minimised, some blow down may be required to avoid salt buildup . It should be noted that the choice of the best cooling system depends on a variety of site-specific parameters. In order to minimise the impact of cooling on the environment as a whole the BAT Reference Document for Cooling Systems should be consulted.

The amount of waste water that is generated by a wet scrubber can be reduced if the treated water is recycled back to the scrubber. To avoid an increasing content of salts in the washing water cycle, a small quantity of water should be bled continuously from the system and replaced by fresh water.

All machinery that is operated in an industrial installation uses oil as a lubricant. This should be changed, due to metal pick-up and chemical reactions in the oil. Regular maintenance, repairs and preventive maintenance can minimise oil loss by leakage and increases the intervals between the oil change. A reduction of the quantity of used oil is reached also by using filtration, which gives an extension of the service life. For example by-pass filters may be installed to continuously clean a small part of the oil. These measures cause result in an extension of the service life by up to a factor of 10 depending on the specific filter system. If used oil filters are collected separately, they can be crushed in a shredder. The metal can be re-used in a smelter as secondary raw material, the oil can be centrifuged and then sent to a used oil refinery.

**Achieved environmental benefits**
Minimisation of material destined for disposal and re-use of resources.

**Cross-media effects**
There is the increased use of energy.

**Operational data**
None provided

**Applicability**
These techniques are applicable to most processes.

**Economics**
No data has been reported but the techniques are operating viably.

**Driving force for implementation**
Compliance with environmental permits

**Example plants**
AT, DE, ES, FR.

**Reference literature**

[ 234, UBA Copper, lead, zinc and aluminium 2007 ].

### 2.13.3.4 Recycling and re-use of residues from non-ferrous metal smelting processes

**Description**

As already shown in this section, residues from the production of non-ferrous metals can be recycled and re-used to a large extent. Table 2.44 summarises the different possibilities of recycling and re-use of these residues.

| Source of the residues | Associated metals | Intermediate product or residue | Options for recycling or re-use |
|---|---|---|---|
| Raw materials handling, etc. | All metals | Dust, sweepings | Feed for the main process |
| Smelting furnace | All metals | Slag | Return to smelting;<br>Construction material;<br>Abrasive industry;<br>Parts of slag may be used as refractory material, e.g. slag from the production of chromium metal |
| | Ferro-alloys | Rich slag | Raw material for other ferro-alloy processes |
| Converting furnace | Cu | Slag | Recycle to smelter |
| Refining furnaces | Cu | Slag | Recycle to smelter |
| | Pb | Skimmings or dross | Recovery of other valuable metals |
| | Precious metals | Skimmings or dross and slag | Internal recycle |
| Slag treatment | Cu and Ni | Cleaned slag | Construction material, abrasives, drainage filling material, filler in cement production |
| | | Matte | Metal recovery |
| Melting furnace | All metals<br>Secondary Al | Skimmings or dross | Return to process after treatment |
| | | Slag | Metal recovery |
| | | Salt slag | Metal, salt and oxide recovery |
| Electrorefining | Cu | Electrolyte bleed | Recovery of Ni |
| | | Anode remnants | Return to converter |
| | | Anode slime | Recovery of precious metals |
| Electrowinning | Zn, Ni, Co, PMs | Spent electrolyte | Re-use in leaching process |
| Fused salt electrolysis | Al<br>Na and Li | SPL | Carburant or disposal |
| | | Excess bath | Sale as electrolyte |
| | | Anode stubs | Recovery |
| | | Cell material | Scrap iron after cleaning |
| Distillation | Hg | Residues | Re-use as process feed |
| | Zn, Cd | Residues | Return to ISF |
| Leaching | Zn | Ferrite residues | Disposal, re-use of liquor |
| | Cu | Residues | Disposal |

| Source of the residues | Associated metals | Intermediate product or residue | Options for recycling or re-use |
|---|---|---|---|
| | Ni | Cu/Fe residues | Recovery, disposal |
| Sulphuric acid plant | | Catalyst | Regeneration |
| | | Acid sludges | Disposal |
| | | Weak acid | Leaching, decomposition, neutralisation |
| Furnace linings | All metals | Refractory | Use as slagging agent, disposal<br>Re-use as a refractory |
| Milling, grinding | Carbon | Carbon and graphite dusts | Use as raw material in other processes |
| Pickling | Cu, Ti | Spent acid | Recovery |
| Dry abatement systems | Most metals (using fabric filters or ESPs) | Filter dust | Return to process<br>Recovery of other metals |
| Wet abatement systems | Most metals (using scrubbers or wet ESPs) | Filter sludge | Return to process or recovery of other metals. Disposal (e.g. Hg). |
| Waste water treatment sludge | Most metals | Hydroxide or sulphide sludges. | Disposal, re-use |
| Digestion | Alumina | Red mud | Disposal, re-use of liquor |

**Table 2.44:** **Residues and potential uses**

According to a research project on the avoidance and recycling of waste from a large number of non-ferrous metal smelting plants in North Rhine-Westphalia the following breakdown shown in Figure 2.57 can be presented to demonstrates the importance of the different recycling routes [ 81, Ministerium in NRW (D) 1997 ], [ 165, Neuhaus, W. 1999 ].

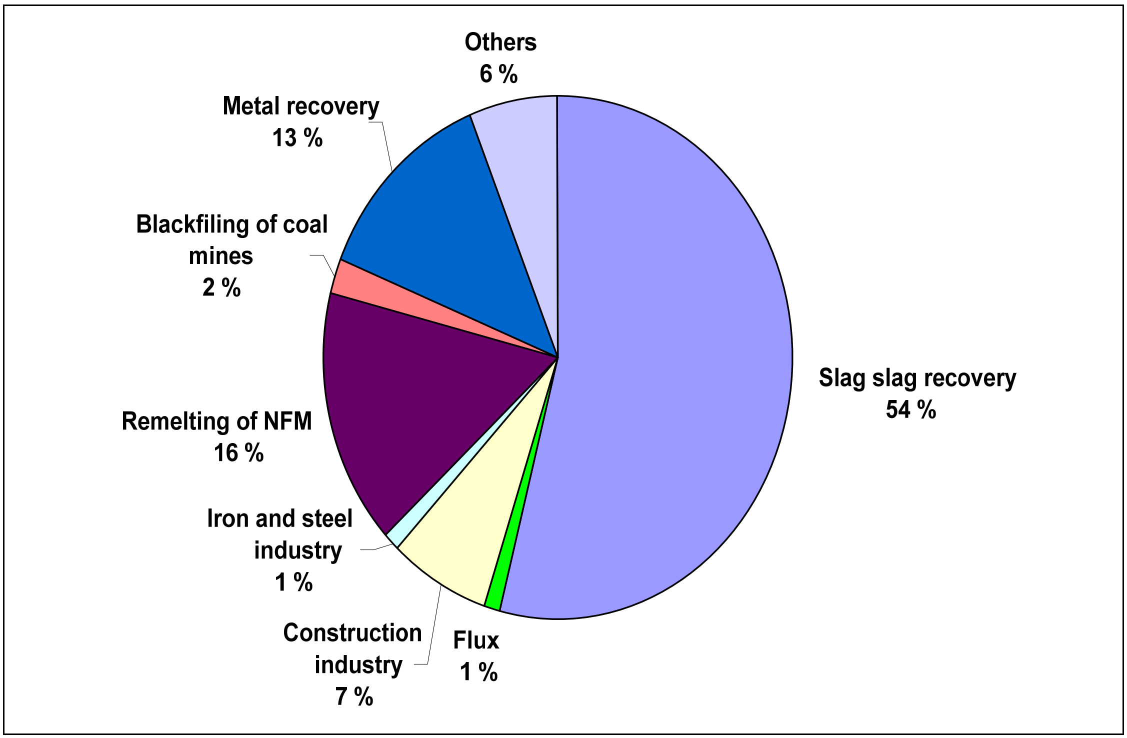


**Figure 2.57:** **Different recycling routes according to the amount of residues generated by some non-ferrous metals plants in North Rhine-Westpfalia**

## Achieved environmental benefits

The minimisation of material destined for disposal and re-use of resources.

**Cross-media effects**
None reported.

**Operational data**
To achieve effective waste minimisation and recycling, the following should be considered:

- Waste minimisation audits can be conducted periodically according to a programme.
- The active participation of staff can be encouraged in these initiatives.
- Active monitoring of materials throughput, and appropriate mass balances should be available. Monitoring should include water, power, and heat.
- There should be a good understanding of the costs associated with waste production within the process. This can be achieved by using accounting practices that ensure that waste disposal and other significant environmental costs are attributed to the processes involved and are not treated simply as a site overhead.

**Applicability**
These techniques are applicable to most processes.

**Economics**
No data has been reported but the techniques are operating viably.

**Driving force for implementation**
Compliance with environmental permits.

**Example plants**
AT, DE, ES, FR.

**Reference literature**
[ 234, UBA Copper, lead, zinc and aluminium 2007 ], [ 81, Ministerium in NRW (D) 1997 ], [ 165, Neuhaus, W. 1999 ].

### 2.13.3.5 Pyrometallurgical slags and residues

**Description**
Controlling the quality of slag to allow further use is also an important technique to consider. Several slags are relatively inert and can be used as construction materials to replace aggregates, and as abrasives. Good quality control of the material is needed to ensure that it is acceptable for use as construction or other uses and leaching tests are available to demonstrate acceptability [ 289, USEPA Method 1311 and 1312 2008 ], [ 268, Belgium Input 2008 ]. The Landfill Directive specifies CEN standard leaching tests for granular waste EN 14405 and EN12457/1-4.

Several techniques exist to reduce the amount of residues that are formed in the production processes. Important techniques are to reduce the amount of slag, to recover metals in the slag and to reduce the amount of metals in the residue slag. For example, a ferro-chrome works in Finland has managed to reduce the amount of residue with a ferro-chrome slag extraction process [ 226, Nordic Report 2008 ]. A machine working with a spiral screw is used to separate chromium from processed fine slag. Chromium is heavier than slag so it is concentrated in the centre of the spiral. The recovered chromium can be re-used in the melting shop and the slag is used as a material for new filler products. Filler products are used, for example, in cement and asphalt. This technique has reduced the amount of residue going to disposal by about 10000 tonnes.

Slags from the blast furnace, ISF, direct smelting and Waelz kiln processes usually contain very low concentrations of leachable metals. They are therefore generally suitable for use in construction [ 99, Hähre, S. 1998 ]. The slag output is between 10 and 70 % of the weight of the metal produced depending on the raw materials used.

Slags from the battery processing plants account for 13 to 25 % of the weight of lead produced. They may be suitable for construction uses depending on the leachability of the metals they contain. The leachability is influenced by the fluxes used and the operating conditions [ 99, Hähre, S. 1998 ]. The use of sodium-based fluxes ($Na_2CO_3$) to fix sulphur in the slag causes an increase in the quantity of leachable metals. These slags and dross from battery recovery processes can contain antimony. This is normally recovered but storage in damp conditions can cause emissions of stibine.

The dross and solids, removed during the zinc and lead melting and refining stages, contain metals that are suitable for recovery. Table 2.45 shows the solid material from the refining of lead bullion.

| Refining step | Solid output | Use/treatment options |
|---|---|---|
| Drossing/de-copperising | Copper dross | Further processing to recover copper and lead |
| Softening (Harris process/oxygen softening) | Harris slags<br>Antimony slag | Hydrometallurgical treatment for metal recovery<br>Pyrometallurgical treatment for metal recovery |
| De-silvering | Zinc-silver crust | Recovery of noble metals |
| De-zincing | Zinc metal | Re-use for de-silvering |
| De-bismuthising | Bismuth crust | Recovery of bismuth |
| Removal of alkali metals and alkaline-earth metals | Mg-Ca oxide dross | Internal recycling as flux |
| Finishing | Caustic dross | Internal recycling |

**Table 2.45: Solid material from the refining of lead bullion**

**Achieved environmental benefits**
Reduced amounts of waste for disposal and replacement of virgin refractory material to produce refractory cement, etc.

**Cross-media effects**
None reported.

**Operational data**
A number of standard leachability tests and criteria for leachable metals are used by Member States and these are specific to the country in question [ 289, USEPA Method 1311 and 1312 2008 ], [ 268, Belgium Input 2008 ]. The Landfill Directive specifies CEN Standard leaching tests for granular waste EN 14405 and EN12457/1-4.

Some results of leaching tests are given in Table 2.46, Table 2.47 and Table 2.48.

| Component | Eluate (according to DEVS4) (mg/l) |
|---|---|
| As | 0.001 - 0.02 |
| Cu | <0.001 - 0.05 |
| Fe | 0.05 - 0.2 |
| Pb | 0.005 - 0.1 |
| pH | 7 - 11 |
| Zn | 0.02 - 0.1 |

**Table 2.46: Eluate values of granulated IS furnace slag**
**[ 99, Hähre, S. 1998 ]**

| Component | Eluate (according to DEVS4) Waelz slag (mg/l) |
|---|---|
| As | 0.008 |
| Cl | 5 |
| Crtot | 0.002 |
| Cu | 0.05 |
| F | 1 |
| Fe | 0.5 |
| Ni | 0.005 |
| Pb | 0.02 |
| pH | 9.9 |
| Zn | 0.05 |

**Table 2.47: Eluate values for acidic Waelz slag**
**[ 99, Hähre, S. 1998 ]**

| Component | Eluate (according to DEVS4) (mg/l) |
|---|---|
| As | 0.05 |
| Cd | 0.001 |
| Cu | 0.005 |
| Pb | 0.02 - 0.2 |
| FeO | <0.05 |

**Table 2.48: Eluate values for slag from QSL process**
**[ 99, Hähre, S. 1998 ]**

**Applicability**
These techniques are applicable to the use of materials that are suitable for the end use envisaged. Metallurgical slags can be used for construction provided that they meet leachability standards.

**Economics**
No data has been reported.

**Driving force for implementation**
Cost of disposal.

**Examples**
AT, BE, DE.

**Reference literature**
[ 249, Austria Brixlegge Report 2007 ], [ 99, Hähre, S. 1998 ], [ 268, Belgium Input 2008 ].

## 2.14 Energy Recovery

Article 3(d) of the IPPC Directive requires that energy is used efficiently and this note includes a comment on energy use and its place in the assessment of BAT under each of the metal production chapters. Energy use in the non-ferrous metal industry is covered by a series of reports prepared by the Centre for the Analysis and Dissemination of Demonstration Energy Technologies (CADDET). These reports have been used extensively in comparing techniques. The BREF document on Energy Efficiency [ 333, EC 2008 ] should also be referred to.

In Europe, ore deposits that contain metals in viable concentrations have been progressively depleted and few indigenous sources remain. Most concentrates are thus imported into Europe from a variety of sources worldwide and therefore use energy for transport. The importance of using indigenous secondary raw materials such as scrap metal and other residues cannot be emphasised enough due to the benefits of reduced energy consumption.

In the copper sector secondary raw materials account for the production of about 45 % of EU copper, but in some cases, such as brass rods, the product is made entirely from recycled copper and brass, with only a small input of primary zinc. When copper cathodes are produced from recycled materials, there is a saving of approximately 650000 t of $CO_2$ because specific direct emissions of secondary smelters are four times lower than those from primary smelters.

In the aluminium sector the production and refining of secondary aluminium is also much less energy demanding, accounting for a consumption per kg of about 5 % of the energy needed to produce primary aluminium.
*The yellow highlighted part contains almost no information about energy recovery and the informationincluded it so general that it should be deleted.*

### 2.14.1 Applied techniques

Energy and heat recovery is practised extensively during the production and casting of non-ferrous metals. A technique reported in the Energy Efficiency BREF [ 333, EC 2008 ] is the use of an energy efficiency management system E2MS.

Pyrometallurgical processes are highly heat intensive and the process gases contain a lot of heat energy. As a consequence, regenerative burners, recuperative burners, heat exchangers and boilers are used to recover this heat. Steam or electricity can be generated for use on or off site, for example in district heating schemes and process, or fuel gases can be preheated [ 115, ETSU (UK) 1996 ]. The technique used to recover heat varies from site to site. It is governed by a number of factors such as the potential uses for heat and energy on or near the site, the scale of operation and the potential for gases or their constituents to foul or coat heat exchangers.

The following examples are typical and constitute techniques to consider for use in the processes to produce non-ferrous metals [ 115, ETSU (UK) 1996 ]. The techniques described can be incorporated into many existing processes.

The hot gases produced during the smelting or roasting of sulphide ores are almost always passed through steam raising boilers. The steam produced can be used to produce electricity and/or for heating requirements. An example of this is where a copper smelter produces 25 % of its electrical requirements (10.5 $MW_e$) from the steam produced by the waste heat boiler of a flash furnace. In addition to electricity generation, steam is used as process steam in the concentrate dryer, and residual waste heat is used to preheat the combustion air. *This is not an examples for a technique to consider. This is much to general.*

Other pyrometallurgical processes are also strongly exothermic, particularly when oxygen enrichment of combustion air is used. Many processes use the excess heat that is produced during the smelting or conversion stages to melt secondary materials without the use of additional fuel. For example the heat given off in the Peirce-Smith converter is used to melt anode scrap. In this case, the scrap material is used for process cooling and the additions are carefully controlled. This avoids the need for cooling the converter by other means at various times of the cycle. Many other converters can use scrap additions for cooling and those that cannot are subject to process developments to allow it.

The use of oxygen-enriched air or oxygen in the burners reduces energy consumption by allowing autogenic smelting or the complete combustion of carbonaceous material. Waste gas volumes are significantly reduced allowing smaller fans, etc. to be used.

Furnace lining material can also influence the energy balance of a melting operation. In this case, low mass refractories are reported to have a beneficial effect by reducing the thermal conductivity and storage in an installation [ 103, Farrell, F. 1998 ]. This factor must be balanced with the durability of the furnace lining and metal infiltration into the lining and may not be applicable in all cases.

Separate drying of concentrates at low temperatures reduces the energy requirements. This is due to the energy required to superheat the steam within a smelter and the significant increase in the overall gas volume due to the steam produced. The larger gas volume increases the heat removed from the furnace and consequently the fan that is needed to deal with the increased gas volume must be increased in size.

The production of sulphuric acid from the sulphur dioxide emitted from roasting and smelting stages is an exothermic process and involves a number of gas cooling stages. The heat generated in the gases during conversion and the heat contained in the acid produced can be used to generate steam and/or hot water.

Heat is recovered by using the hot gases from melting stages to preheat the furnace charge. In a similar way, the fuel gas and combustion air can be preheated or a recuperative burner used in the furnace. Thermal efficiency is improved in these cases. For example, nearly all cathode/copper scrap melting shaft furnaces are natural gas-fired, the design offers an thermal efficiency (fuel utilisation) of 58 % to 60 %, depending on diameter and height of the furnace. Gas consumption is approximately 330 kWh/tonne of metal. The efficiency of a shaft furnace is high, principally because of charge preheating within the furnace. There can be sufficient residual heat in the off-gas to be recovered and re-used to heat combustion air and gas. The heat recovery arrangement requires the diversion of the furnace stack gases through a suitably sized heat exchanger, transfer fan and ductwork. The heat recovered is approximately 4 % to 6 % of the furnace fuel consumption.

Cooling prior to a fabric filter installation is an important technique as it provides temperature protection for the filter and allows a wider choice of fabric. It is sometimes possible to recover heat at this stage. For example, in a typical arrangement used by a shaft furnace to melt metal, gases from the top of the furnace are ducted to the first of two heat exchangers that produces preheated furnace combustion air. The temperature of the gases after this heat exchanger can be between 200 and 450 ºC. The second heat exchanger reduces the gas temperature to 130 ºC before the fabric filter. The heat exchangers are normally followed by a cyclone, which removes larger particles and acts as a spark arrestor.

Carbon monoxide produced in an electric or blast furnace is collected and burnt as a fuel for several different processes or to produce steam, e.g. for district heating or other energy. Significant quantities of the gas can be produced and examples exist where a major proportion of the energy used by an installation is produced from the CO collected from an electric arc furnace installation. In other cases, the CO formed in an electric furnace burns in the furnace and provides part of the heat required for the melting process.

The recirculation of contaminated waste gas back through an oxy-fuel burner has resulted in significant energy savings. The burner recovers the waste heat in the gas, uses the energy content of the contaminants and removes it [ 113, ALFED 1998 ]. Such a process can also reduce nitrogen oxides.

The use of the heat content of process gases or steam to raise the temperature of leaching liquors is practised frequently. In some cases, a portion of the gas flow can be diverted to a scrubber to recover heat into the water, which is then used for leaching purposes. The cooled gas is then returned to the main flow for further abatement.

During the smelting of electronic scrap or battery scrap, the combustible plastic content contributes to the energy that is used in the smelting process and reduces the amount of fossil fuel that is needed.

The advantage of preheating the combustion air used in burners is well documented. If an air preheat of 400 °C is used, there is an increase in flame temperature of 200 °C, while if the preheat is 500 °C, the flame temperature increases by 300 °C. This increase in flame temperature results in a higher melting efficiency and a reduction in energy consumption. It has been reported that regenerative burners can be used to preheat the combustion air to 900 °C which reduces the energy consumption by 70 %. This is well established and payback times of less than one year are achieved.

The alternative to preheating the combustion air is to preheat the material charged to the furnace. Theory shows that 8 % energy savings can be obtained for every 100 °C preheat and in practice it is claimed that preheating to 400 °C leads to 25 % energy savings while a preheat of 500 °C leads to a 30 % energy savings. Preheating is practised in a variety of processes, for example the preheating of the furnace charge using the hot furnace off-gases during the production of ferro-chrome and secondary aluminium. In the latter case, the use of a charge preheating chamber is very effective. Hydrocarbons are emitted during charge preheating as the contents are pyrolised from the scrap. The gases that are produced are directed to the furnace burner system which destroys the hydrocarbons and utilises the energy content for melting.

Under many circumstances, pre-drying of raw materials offers energy savings because the latent heat added to the steam produced is not wasted and also the gas volumes are lower and so fans and abatement plants need not be too large and need not have higher energy consumption [ 258, Finland input 2007 ].

Gases from anode furnaces should be considered for use in drying or other process stages. Hot gases extracted from launders can be used as preheated combustion air.

Figure 2.58 illustrates the energy balance of the Contimelt process, which uses the rising, hot gases in a shaft furnace to preheat the charge.

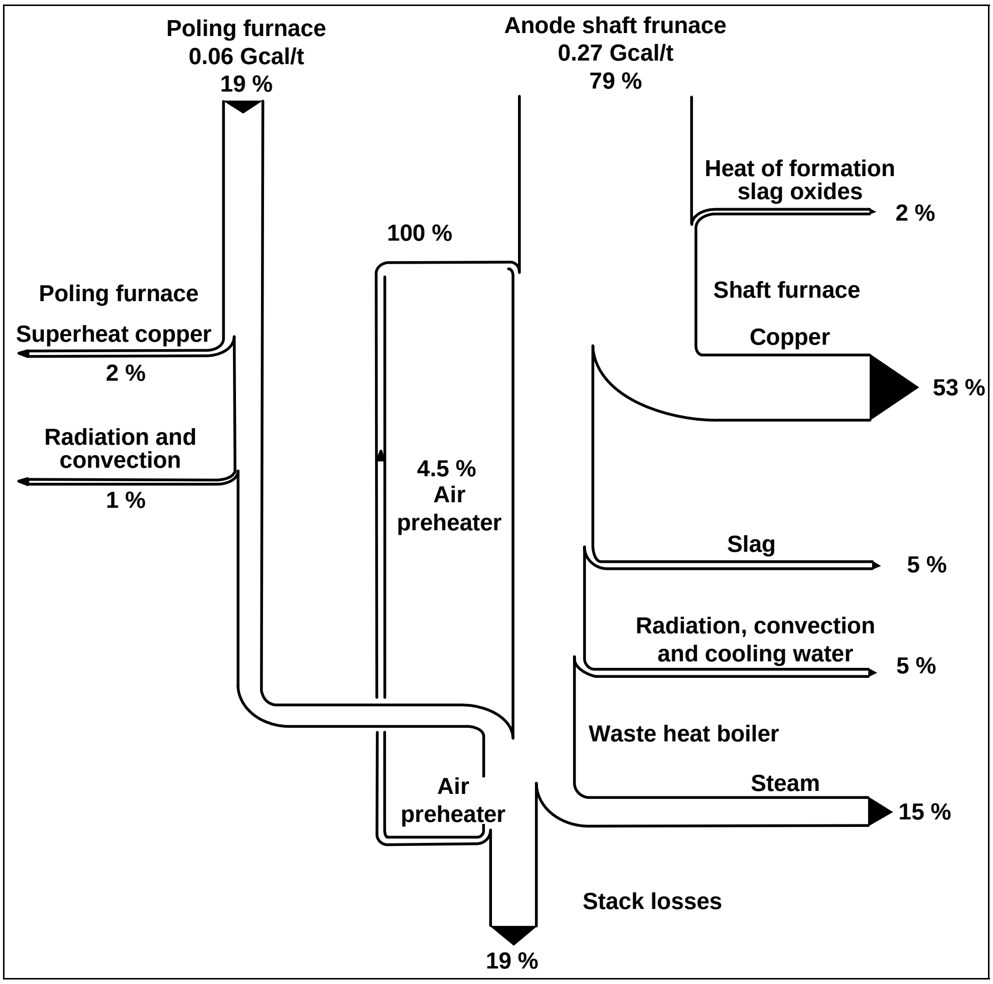


**Figure 2.58:** **Energy balance of the Contimelt process**
[ 121, Rentz, O. et al. 1999 ]

Heat and energy recovery is therefore an important factor in the non-ferrous metals industries and reflects the high proportion of costs that energy represents. Many techniques for energy recovery are relatively easy to retrofit [ 115, ETSU (UK) 1996 ] but there are occasionally some problems of deposition of metal compounds in heat exchangers. Good design is based on a sound knowledge of the compounds released and their behaviour at various temperatures. Heat exchanger cleaning mechanisms are also used to maintain thermal efficiency.

Whilst these savings are examples of individual components of installations, they are critically dependent upon the site and process-specific conditions including economics.

## 2.14.2 Techniques to consider in the determination of BAT

The sections of this document entitled 'Techniques to consider in the determination of BAT' set out techniques considered generally to have potential for achieving a high level of environmental protection in the industries within the scope of the document. The background to the way the techniques are described is given in Section 2.1.2 and Table 2.2.

### 2.14.2.1 Use of a regenerative burner

**Description**

In a regenerator, exhaust gas and combustion air alternately flow through a chamber filled with a heat storage medium, charging with waste gas flow and discharging with air flow. Regenerators, if constructed from materials which will accept the full exhaust gas temperature from the fired chamber and resist any corrosive elements contained therein, display none of the difficulties usually seen for recuperators.

A twin bed regenerative burner consists of an all ceramic high temperature burner close coupled to a compact, fast cycle, ceramic regenerator. The burner serves double duty, acting as the inlet or the exhaust from the fired chamber depending on the cycle. One complete twin bed regenerative burner set comprises two burners, two regenerators, reversing valves, and the control system.

While one of the burners fires using cool air fed to the base of its regenerator, exhaust gas is drawn through the other burner and down into its associated regenerator to preheat the packing, then discharged to the gas-cleaning plant. When the regenerator being heated is sufficiently charged, the airflow is reversed so that cool air flows to the newly heated regenerator and is preheated, the previously cooled regenerator being reheated by the exhaust gas generated by the other burner firing. The first and second half of the cycle are shown in Figure 2.59 and Figure 2.60.

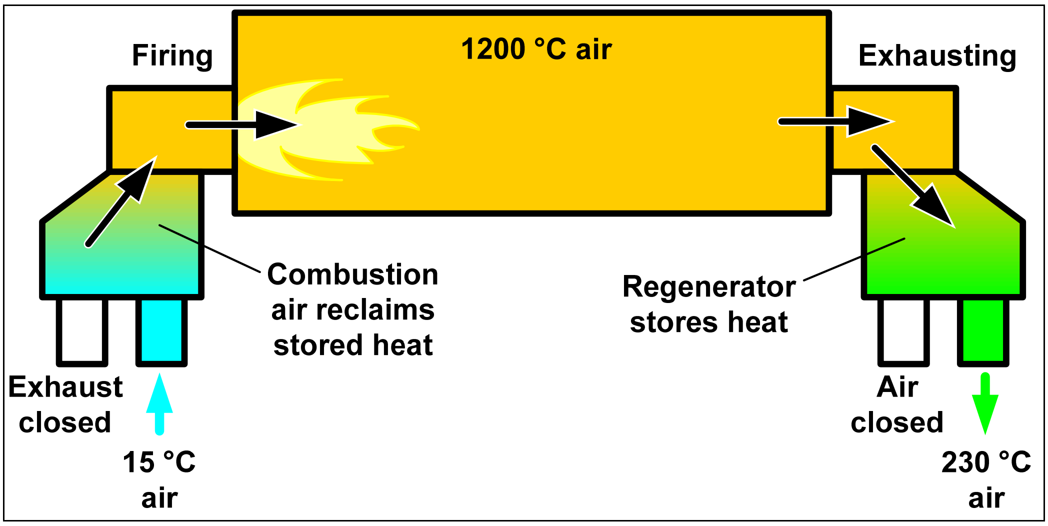


Figure 2.59: First half of the cycle

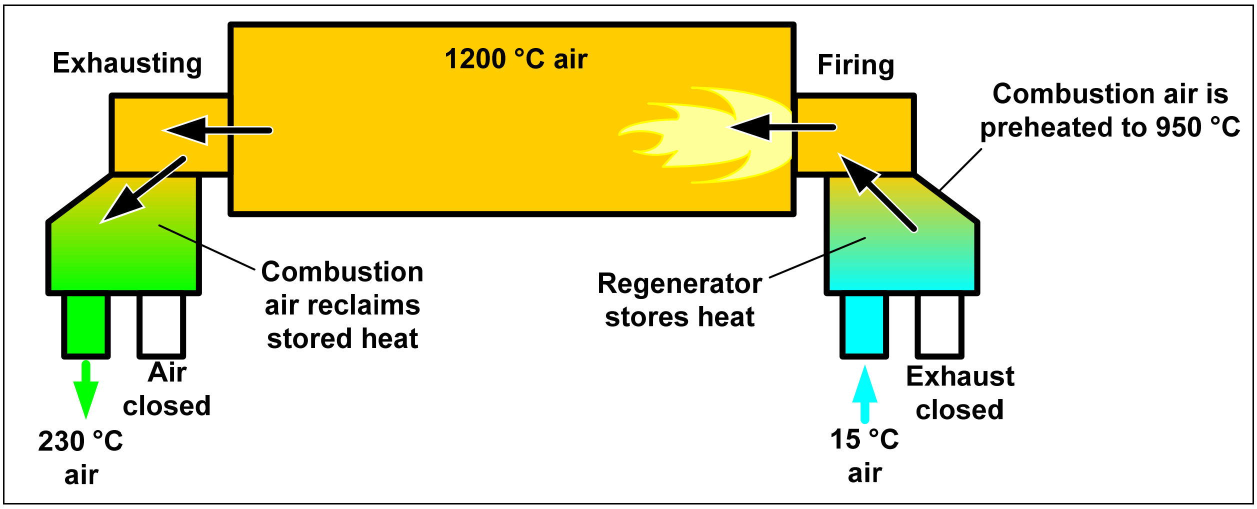


**Figure 2.60:** Second half of the RTO cycle
[ 256, Plant visit report AMAG 20071114.doc 2007 ]
*(Is this really a RTO?)*

**Achieved environmental benefits**
The energy content of the hot gases is used to heat the support materials and can reduce the energy consumption by 70 % compared to that of a normal burner. Regenerative burners are reported to use 30 % less energy than recuperative burners.

**Cross-media effects**
None reported.

**Operational data**
Regenerative burners are used in a number of applications. The process depends on an alternating cycling of gases through a series of support zones using ceramic balls where heating and cooling cycles take place. Combustion air can be preheated to approximately 900 °C.

**Applicability**
This technique is applicable to a variety of new and existing processes. Additional post treatment of the gases might be required depending on input material.

**Economics**
Pay back time for regenerative burners in the secondary aluminium sector is reported to be less than one year.

**Driving force for implementation**
Improved energy efficiency.

**Example plants**
AT.

**Reference literature**
[ 103, Farrell, F. 1998 ], [ 256, Plant visit report AMAG 20071114.doc 2007 ].

### 2.14.2.2 Use of a regenerative afterburner

**Description**
Regenerative afterburners have been used in a number of applications. The process depends on an alternating cycling of gases through a series of support zones where heating, cooling and cleaning cycles take place. The combustible fraction is heated in the heating zone and passes to a common residence chamber where combustion is completed. The hot gases then pass into a

cooling section which is heated to become the next heating zone. The zones are changed using a manifold system to allow cleaning.

A regenerative afterburner is shown in Figure 2.61.

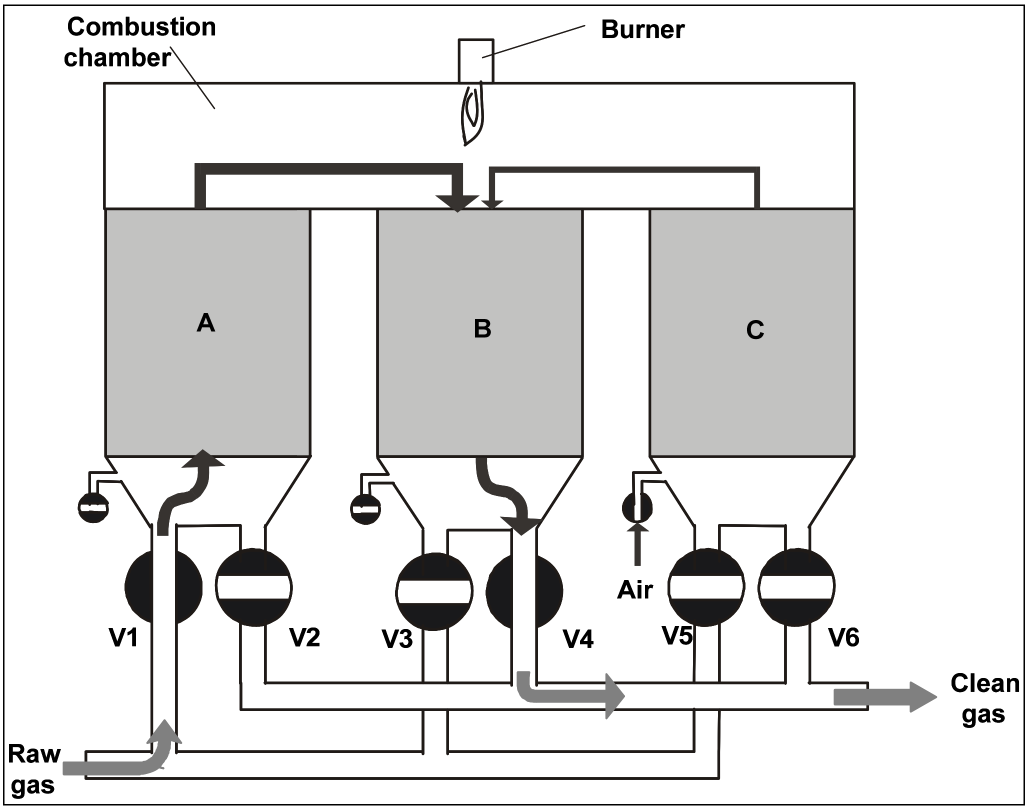


**Figure 2.61:** **Regenerative afterburner**
[ 157, Winter, B. et al. 1999 ]

### Achieved environmental benefits

The energy content of the hot gases and of the contaminants (hydrocarbon and PAH) is used to heat the support materials and can reduce the energy consumption by 70 % compared to that of a normal afterburner.

### Cross-media effects

Increases in PCDD/F concentrations have been reported for a regenerative afterburner installation serving a blast furnace. This is thought to be due to the longer residence time of gases in the de novo synthesis temperature range.

### Operational data

Regenerative burners or afterburners are used in a number of applications. The process depends on an alternating cycling of gases through a series of support zones using ceramic chips where heating and cooling cycles take place. Combustion air can be preheated to approximately 900 °C.

### Applicability

This technique is applicable to a variety of processes. The basic principle is good but the change-over to the cleaning phase and longer residence time of gases in the de novo synthesis temperature range may cause the emission of un-combusted material if the design is poor. Additional pre and post treatment of the gases might be required for the regenerative afterburner.

### Economics

None available but several installations are operating economically.

**Driving force for implementation**
Reduction of emissions of PAH, PCDD/F and improved energy efficiency.

**Example plants**
AT, DE, UK, NL.

**Reference literature**
[ 103, Farrell, F. 1998 ], [ 157, Winter, B. et al. 1999 ], [ 242, Nl Anode Input 2008 ].

### 2.14.2.3 Use of low grade heat

**Description**
All metallurgical processes produce heat either as hot gases or hot water. The options to recover low grade heat has always been a difficult issue as the options for recovery are limited. It is possible to recover heat from liquids at a temperature of about 55 °C and two examples have been reported.

The first example is the use of water from the spray cooling of metallurgical slag which is collected in a sump and passed through a heat exchanger to heat a circuit that uses ethylene glycol. The users of low grade heat extract heat from the circuit through another heat exchanger [ 233, Farrell Nordic Mission 2008 ].

The second example is where low grade heat is used to generate electrical power. and this provides the opportunity to produce electricity from heated waste water with head temperatures from 85 °C and higher.

**Achieved environmental benefits**
Recovery of heat and the prevention of emission of heat.

**Cross-media effects**
No data has been reported.

**Operational data**
The heat is exchanged and transferred into a closed loop comprising a carrier fluid that expands and drives a turbine which in turn drives a generator, see Figure 2.62. The generator normally provides electrical power.

Small capacity power plants use two container mounted units. They are (12.2 m in length, 2.3 m in width, 3.0 m in height) with a gross weight of 25 tonnes.

The containers are equipped for connections to heat waste water flow lines as well as connections for the inlet of required cooling water. The containers furthermore house the required appliances for hook up to existing power distribution grids. Larger plants can be constructed on site or alternatively be established through the required number of container units connected in parallel.

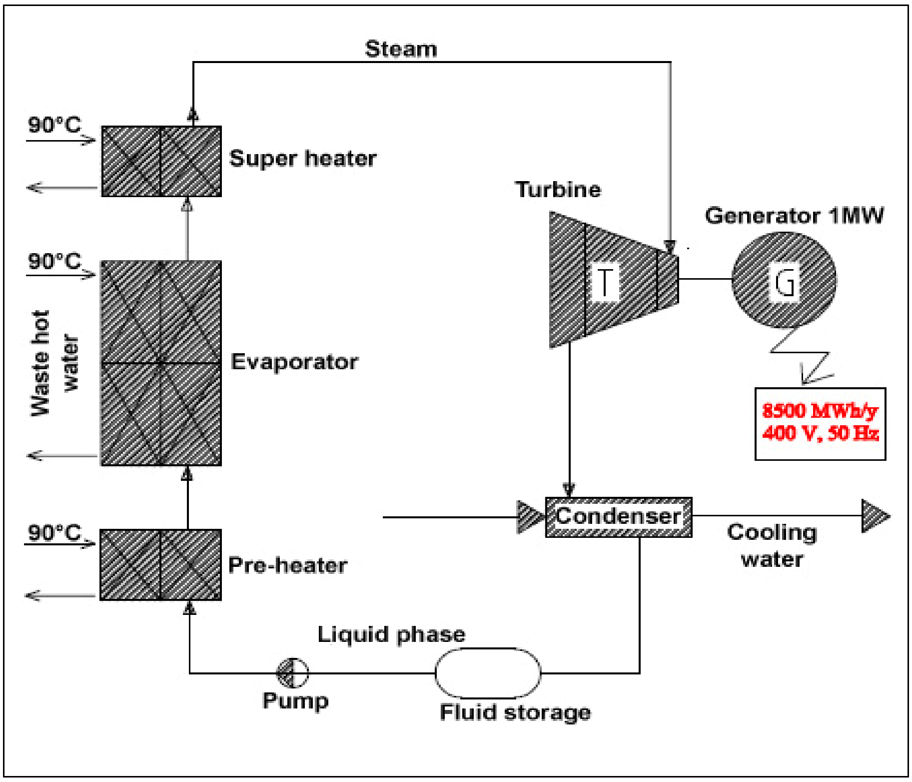


**Figure 2.62: Electrical generation from low grade heat**

**Applicability**
This technique is applicable to a variety of processes.

**Economics**
None available but several installations are operating economically.

**Driving force for implementation**
Improved energy efficiency.

**Example plants**
NO.

**Reference literature**
[ 233, Farrell Nordic Mission 2008 ].

### 2.14.2.4 Use of waste as a fuel or reducing agent

Conventional fuels or reducing agents can be replaced by waste materials. Different types of waste are used as fuels or reducing agents in the non-ferrous metals industries. Since this technique involves the incineration of waste, the installation should comply with the Waste Incineration Directive (2000/76/EC).

Waste can often only be used after certain pretreatment stages to provide tailor-made fuels for the burning process. Since waste treatment operations are not covered by this document, more useful information can be found in the Waste Treatment Industries BREF [ 341, EC 2006 ].

**Description**
Selected wastes with recoverable net calorific values such as waste oil, solvents and plastics can be used as fuels, replacing conventional fossil fuels provided that they meet certain

specifications and characteristics. Different criteria play a decisive role in the selection of waste fuels as they can have an impact on kiln operation and on emissions.

To guarantee the characteristics of the waste fuel a quality assurance system is required. In particular this should include provisions for sampling, sample preparation, analysis and external monitoring. More useful information can be found in the technical specifications of the European Committee for Standardisation, such as CEN/TC 343 "Solid recovered fuels."

**Achieved environmental benefits**
The selection of waste fuels is driven by a number of interrelated considerations, including the following main points:

- the reduction of emissions, e.g. $CO_2$ derived from fossil fuels;
- the reduction in the use of natural resources, e.g. fossil fuels;
- reduced transportation distances;
- avoidance to landfill;
- a safe recovery route for waste;
- reduced $CO_2$ emissions.

**Cross-media effects**
Depending on their characteristics, e.g. high metal concentrations, waste fuels may have an effect on emissions.

**Operational data**
The study 'Assessment of the application and possible development of community legislation for the control of waste incineration and co-incineration' identified 6 plants in the non-ferrous metals industry that use waste as a fuel. The study was conducted on behalf of the European Commission by ÖKOPOL in 2007 [ 315, Okopol Report 2007 ].

Wastes that are used as fuel in the non-ferrous metals industry have a high net calorific value, e.g. waste oil with a net calorific value of 37 MJ/kg and solvents with a net calorific value of 26 MJ/kg.

In a rotary kiln of a nickel roasting plant in Austria, conventional fuels are replaced by waste oil an solvents.

**Applicability**
These fuels can, in principle, be used where complete combustion of organic matter is assured and waste input control as well as emissions control guarantees a low level of emissions, e.g. metals and dioxins.

**Economics**
In comparison to the use of fossil fuels, the use of waste fuels can reduce operational costs.

**Driving force for implementation**
Reduction of fuel costs and availability of resources.

**Example plants**
AT.

**Reference literature**
[ 311, Mauschitz 2007 ], [ 315, Okopol Report 2007 ].

## 2.15 Cross-media issues

Delete all this.

Cross-media issues result from the abatement of emissions from one environmental medium producing emissions to another environmental medium. IPPC encourages the prevention of emissions by process design and good operation and maintenance. This factor will minimise the overall environmental impact on all environmental media. Few processes can be operated with zero emissions but some "clean technologies" are suggested as techniques to consider when determining BAT. The principles of the minimisation and re-use of residues and water and the energy recovery techniques discussed above are prime examples of this.

In a similar way, the use of oxygen, the minimisation of the transfer of molten material in ladles and the collection and recirculation or conversion of gases are also significant factors in minimising cross-media issues. Common examples are the collection of chlorine from electrolysis with re-use in a leaching stage and the recovery of sulphur dioxide.

The choice of abatement process is also a significant factor and a prime example is a comparison of a wet scrubber with a fabric filter. The wet scrubber will generate an effluent from the liquor bleed and will also generate a wet sludge. Wet sludges may be more difficult to re-use and may cause problems at a disposal site but they will not form dust during storage. On this basis a wet scrubber is less attractive than a fabric filter and also suffers from inferior particle removal in most installations. The wet scrubber, however, does have an application where the dust to be removed is very abrasive and dense or is very hygroscopic. In these cases rapid wear or bag blinding can make a fabric filter very difficult to operate and can result in significant emissions during breakdown. pH-controlled wet scrubbing is very efficient in $SO_2$ absorption from gases with low $SO_2$ concentrations. These factors need to be considered and balanced on a site-specific basis.

The environmental cost of producing the energy required for processes and abatement is another important cross-media effect. This factor is taken into account in the examples used in this document. There are difficulties however in making direct comparisons and issues such as the source of the energy for a particular site can make this a complicated assessment.

The assessment of cross-media issues is a significant factor and is identified under the metal-specific chapters where site and technique-specific aspects are illustrated.

## 2.16 Noise and vibration

Noise and vibration are common issues in the sector and the sources are encountered in all sections of the industry. Process noise emitted from an installation into the surrounding environment is a factor that has caused many complaints in the past and some information about causes and approaches to prevent and minimise noise and vibration have been received. The effect of noise on operators within an installation is not within the scope of this document.

The significant sources of noise and vibration are transport and handling of raw materials and products; production processes involving pyrometallurgy, grinding and milling operations; the use of pumps and fans; the venting of steam and the existence of unattended alarm systems. Noise and vibration can be measured in a number of ways but generally the detail is site-specific and takes account of the frequency of the sound and the location of population centres.

New plants can be specified with low noise and vibration levels. Good maintenance can prevent equipment such as fans and pumps from becoming unbalanced. The interconnections between equipment can be designed to prevent or minimise the transmission of noise. Common noise abatement techniques are:

- the use of embankments to screen the source of noise;
- the enclosure of noisy plants or components in sound-absorbing structures;
- the use of anti-vibration supports and interconnections for equipment;
- the orientation of noise-emitting machinery;
- the change of the frequency of the sound.

## 2.17 Odour

There are several potential sources of odour in the non-ferrous metals industries. The most significant are metal fumes, organic oils and solvents, sulphides from slag cooling and waste water treatment, chemical reagents used in hydrometallurgical and effluent treatment processes (e.g. ammonia) and acid gases. Odours can be prevented by careful design, choice of reagents and by correct material handling. For example, the production of ammonia from aluminium skimmings or dross can be prevented by keeping the material dry.

The abatement techniques described earlier in this chapter will all contribute to the prevention and elimination of odours. The general principles of good housekeeping and good maintenance practice also play a major role in prevention and control.

The basic hierarchy of the principles of odour control are:

- to prevent or minimise the use of malodorous materials
- to contain and extract odorous materials and gases before they are dispersed and diluted
- to treat them possibly by afterburning or filtration (see also Section 2.14.2.1 and 4.1.1.5.1).

The use of biological media such peat or similar material that acts as a substrate for suitable biological species have been successful in removing odours [ 156, VDI (D) 1976 ]. The removal of odours can be a very complex and expensive process if strongly odorous materials are diluted. The treatment of very large gas volumes with low concentrations of odorous materials requires major process plant.

A biofilter is shown in Figure 2.63.

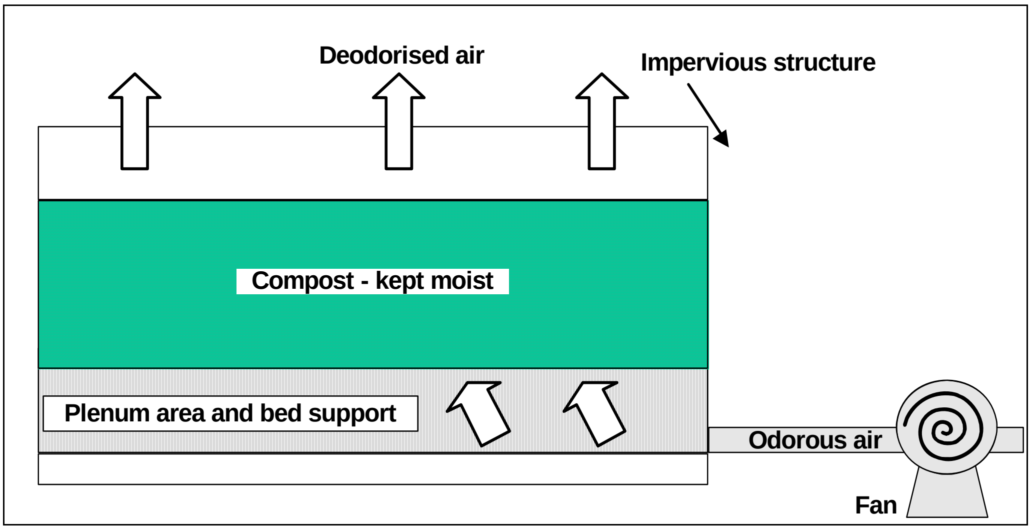


**Figure 2.63: Arrangement of a simple biofilter**

## 2.18 Safety Aspects

Safety issues can be covered in a management system based on OHSAS 18001. The general policy for the prevention of, the preparation for and the response to industrial accidents is based on the principles described below.

### 2.18.1 Prevention principle

The construction and operation of a plant should be carried out:

- in such a way as to prevent the uncontrolled development of abnormal operation;
- in such a way that the consequences of accidents are reduced;
- according to the best available safety techniques (state-of-the-art safety technology).

### 2.18.2 Consideration of complex systems in process industries

Complex systems can only be examined sufficiently by means of systematic, logical methods. This is taken into account by applying:

- systematic analytical investigation methods such as hazard and operability studies (HAZOP);
- a detailed safety analysis considering the conditions of the individual case.

### 2.18.3 Appropriateness of means

Safety requirements are graded according to 'type and scope of hazards to be expected'. To this end, rules within Member States are usually set up for:

- substances relevant to accidents (substance criteria, list of substances)
- industrial activities relevant to accidents (list of plants).

The objective dependence of the disaster potential upon the quantity of hazardous substances is considered by a quantity threshold concept that defines staged safety requirements as a function of quantity.

## 2.19 Decommissioning

Article 3(f) of the IPPC Directive requires that the necessary measures be taken upon definitive cessation of activities to avoid any pollution risk and to return the site of operation to a satisfactory state. Soil and water protection are of major importance and the resuspension of soil and dust to air should be prevented so that they do not form diffuse emissions once an installation or part of an installation is closed [ 237, Austria M168 2004 ]. An integrated approach means that the following measures are taken at least:

- Minimise the amount of soil that should be excavated or replaced due to construction and to make sure that excavated soil material is treated carefully (in order to avoid harmful changes of soil properties).
- Minimise the input of substances into the soil by leakage, aerial deposition and inappropriate storage of raw materials, products or process residues during the operational phase of a facility.
- Assess historical contamination to take account of conditions prior to regulation to ensure a clean closure when a facility is shut down, e.g. clean up and rehabilitation with regard to the future use of the area. Natural soil functions should be safeguarded, if feasible.

Site reports can be made at the earliest opportunity to establish a baseline from which further site contamination can be assessed. This baseline report can then be compared to latter reports when the installation is sold, closed or redeveloped. The baseline report can also be used to prioritise action to be taken at the installation.

The remediation measures that could be taken are specific to individual sites but can include intermediate cover, leachate collection, surface cover, removal of contaminated earth and the provision of geological barriers [ 237, Austria M168 2004 ], [ 248, M168 UBA Austria report, 2008 ].

For new plants decommissioning should be considered at the design stage to prevent contamination. The UK Environment Agency has published a guide that describes the techniques to be used at the design stage so that decommissioning forms part of the total concept. The guide was prepared by the University of Bath [ 288, UKEA and Uni of Bath 2007 2002 ]. The UK Environment Agency also requires operators to submit a decommissioning plan to supplement their IPPC permits. For existing installations, the operator is asked to produce the plan as part of an Improvement programme.

### 2.19.1 Techniques to consider in the determination of BAT

The sections of this document entitled 'Techniques to consider in the determination of BAT' set out techniques considered generally to have potential for achieving a high level of environmental protection in the industries within the scope of the document. The background to the way the techniques are described is given in Section 2.1.2 and Table 2.2.

**Description**
Assessment of the initial state of a site, before building a new plant.

Prevention of chronic risks during the whole life of the plant, to prevent soil pollution, e.g:

- identify areas that can contribute to diffuse emissions so that action can be taken to prevent windblown dust causing environmental damage or impact on health in the surrounding areas;
- take action to prevent further contamination of groundwaters;
- establish a spill management programme and other soil protection measures;
- extend the containment of other sources that have been identified.

Using an environmental monitoring programme, especially relative to groundwaters, during the whole life of the plant, in order to detect would-be impacts outside the plant, in its neighbourhood.

**Achieved environmental benefits**
Prevents environmental issues during decommissioning and the prevention of soil pollution.

**Cross-media effects**
None reported.

**Operational data**

- Considering decommissioning at the design stage, thereby minimising risks and excessive costs during later decommissioning.
- For existing installations, where potential problems have been identified, put in place a programme of improvements. These improvement designs need to ensure that:
    - underground tanks and pipework are avoided where possible (unless protected by secondary containment or a suitable monitoring programme);
    - ensure that there is a provision for the draining and cleaning-out of vessels and pipework prior to dismantling;
    - lagoons and disposal sites are designed with a view to their eventual clean-up or surrender;
    - insulation is used which can be readily dismantled without dust or hazards arising;
    - any materials used are recyclable (although bearing in mind they still meet operational or other environmental objectives).
- Develop a site closure plan to demonstrate that, in its current state, the installation can be decommissioned to avoid any pollution risk and to return the site of operation to a satisfactory state. The plan should be kept updated as material changes occur. However, even at an early stage, the closure plan can include:
    - either the removal or the flushing out of pipelines and vessels where appropriate and their complete emptying of any potentially harmful contents;
    - plans of all underground pipes and vessels;
    - the method and resource necessary for the clearing of lagoons;
    - the method of ensuring that any on-site landfills can meet the equivalent of surrender conditions;
    - the removal of asbestos or other potentially harmful materials unless agreed that it is reasonable to leave such liabilities to future owners;
    - methods of dismantling buildings and other structures, for the protection of surface;
    - groundwater at construction and demolition-sites;
    - testing of the soil to ascertain the degree of any pollution caused by the activities and the need for any remediation to return the site to a satisfactory state as defined by the initial site report.

**Applicability**
Techniques mentioned here are applicable throughout the installation's operational lifetime, during the design and building stage of the site and activities and immediately after the site closure.

**Economics**
None reported but it is possible to minimise excessive costs during later decommissioning

**Driving force for implementation**
Reduction of future costs and liabilities.

**Example plants**
None reported directly.

**Reference literature**
[ 245, French Report on De-commissioning 2008 ], [ 288, UKEA and Uni of Bath 2007 2002 ], [ 237, Austria M168 2004 ].

## 2.20 Best Available Techniques

In understanding this section and its contents, the attention of the reader is drawn back to the Preface of this document and in particular the fifth section of the Preface: 'How to understand and use this document'. The techniques and associated emission and/or consumption levels, or ranges of levels, presented in this chapter have been assessed through an iterative process involving the following steps:

- identification of the key environmental issues for the non-ferrous metals sector
- examination of the techniques most relevant to address these key issues
- identification of the best environmental performance levels, on the basis of the available data in the European Union and worldwide
- examination of the conditions under which these performance levels were achieved; such as costs, cross-media effects, and the main driving forces involved in implementation of the techniques
- selection of the best available techniques (BAT) and the associated emission and/or consumption levels for this sector in a general sense, all according to Article 2(12) and Annex IV to the Directive.

Expert judgement by the European IPPC Bureau and the relevant Technical Working Group (TWG) has played a key role in each of these steps and in the way in which the information is presented here.

On the basis of this assessment, best available techniques, and as far as possible emission and consumption levels associated with their use, are presented in this section that are considered to be appropriate to the sector as a whole and in many cases reflect the current performance of some installations within the sector. Where emission and consumption levels "associated with best available techniques" are presented, this is to be understood as meaning that those levels represent the environmental performance that could be anticipated as a result of the application, in this sector, of the techniques described, bearing in mind the balance of costs and advantages inherent within the definition of BAT. However, they are neither emission nor consumption limit values and should not be understood as such. In some cases, it may be technically possible to achieve better emission or consumption levels but due to the costs involved or cross-media considerations, they are not considered to be appropriate as BAT for the sector as a whole. However, such levels may be considered to be justified in more specific cases where there are special driving forces.

The emission and consumption levels associated with the use of BAT have to be seen together with any specified reference conditions (e.g. averaging periods).

The concept of 'levels associated with BAT' described above is to be distinguished from the term 'achievable level' used elsewhere in this document. Where a level is described as 'achievable' using a particular technique or combination of techniques, this should be understood to mean that the level may be expected to be achieved over a substantial period of time in a well maintained and operated installation or process using those techniques.

Where available, data concerning costs have been given together with the description of the techniques presented in the previous sections that describe the Techniques to Consider in the Determination of BAT. These give a rough indication about the magnitude of the costs involved. However, the actual cost of applying a technique will depend strongly on the specific situation regarding, for example, taxes, fees, subsidies, and the technical characteristics of the installation concerned. It is not possible to evaluate such site-specific factors fully in this document. In the absence of data concerning costs, conclusions on economic viability of techniques are drawn from observations on existing installations.

The BAT (including the associated emission and consumption levels) given in this section are 'BAT <u>in a general sense</u>' (i.e. considered to be appropriate to the sector as a whole). It is intended that they are a reference point against which to judge the current performance of an existing installation or to judge a proposal for a new installation. In this way, they will assist in the determination of appropriate 'BAT-based' conditions for the installation or in the establishment of general binding rules under Article 9([8]) of the IPPC Directive. It is foreseen that new installations can be designed to perform at or even better than the BAT levels presented in this section. It is also considered that existing installations could move towards the BAT levels presented in this section or do better, subject to the technical and economic applicability of the techniques in each case.

While the BAT reference documents do not set legally binding standards, they are meant to give information for the guidance of industry, Member States and the public on achievable emission and consumption levels when using specified techniques. The appropriate permit conditions for any specific case will need to be determined taking into account the objectives of the IPPC Directive and the local considerations.

This section reports on best available techniques for some of the common process stages but there are other influences depending on the specific metal group, for example the selection of the production process can only be done on a metal by metal basis after taking account of the various influences of raw materials that are available. BAT for the specific metals are reported in the those sections and include BAT reported here. Where applicable, additional BAT is reported in these sections depending on the metals and the raw materials used.

**Recommendation to help users/readers of this document:**

It is strongly recommended that this section on BAT be read in conjunction with the sections of this document that describe the techniques to consider in the determination of BAT. The applicability of the techniques and measures are reported in these sections and should be taken into account at a local level. To help the reader, references to the appropriate sections are included in the description of BAT.

If not otherwise mentioned, BAT-associated emission and consumption levels given in this section are expressed as follows:

- For pollutants emitted to air (except dioxins): expressed on a daily average basis with standard conditions of 273 K, 101.3 kPa, measured oxygen content and dry gas with the plant operating normally under steady-state conditions and no dilution of the gases.
- For dioxins: expressed as the average over the sampling period which should preferably be a minimum of 6 hours.
- For waste water: based on qualified random samples or 24 hour flow proportional composite samples.

As described in the Preface, this document does not propose emission limit values. The best available techniques and the ranges of emission or consumption levels associated with best available techniques (BAT-AEL ranges) are related to installations with different sizes, different kinds of operation and different raw materials. In this document, special local considerations cannot be taken fully into account. The determination of appropriate permit conditions will involve taking account of local, site-specific factors such as the technical characteristics of the installation concerned, its geographical location and the local environmental conditions. In the case of existing installations, the economic and technical viability of upgrading them also should be taken into account. Even the single objective of ensuring a high level of protection for the environment as a whole will often involve making tradeoff judgements between different types of environmental impact, and these judgements will often be influenced by local considerations.

Although an attempt is made to address some of these issues, it is not possible for them to be considered fully in this document. The techniques and levels presented here will therefore not necessarily be appropriate for all installations. On the other hand, the obligation to ensure a high level of environmental protection including the minimisation of long-distance or transboundary pollution implies that permit conditions cannot be set on the basis of purely local considerations. It is therefore of the utmost importance that the information contained in this document be fully taken into account.

The best available techniques included in this section for the common processes are:

- environmental management systems (EMS)
- material handling and storage
- process control
- fume and gas collection
- the prevention and the destruction of PCDD/F
- sulphur dioxide removal
- the removal of mercury
- effluent treatment and water re-use
- energy efficiency
- intermediate products, process residues and wastes
- emission monitoring
- prevention of the formation of $NO_X$
- dust and particle removal

In addition to this section, the sector-specific BAT sections should be read to provide a complete understanding.

### 2.20.1 Environmental management systems (EMS)

A number of environmental management techniques are determined as BAT. The scope (e.g. level of detail) and nature of the EMS (e.g. standardised or non-standardised) will generally be related to the nature, scale and complexity of the installation, and the range of environmental impacts it may have.

**BAT is to implement and adhere to an environmental management system (EMS) that incorporates, as appropriate to the local circumstances, the following features, (the letters (a), (b), etc. below correspond to those in Section 2.2.4):**

(a) commitment of top management (commitment of the top management is regarded as a precondition for a successful application of other features of the EMS)

(b) definition of an environmental policy that include continuous improvement for the installation by top management

(c) planning and establishing the necessary procedures, objectives and targets, in conjunction with financial planning and investment

(d) implementation of the procedures, paying particular attention to:

- structure and responsibility
- training, awareness and competence
- communication
- employee involvement
- documentation
- efficient process control

- maintenance programme
- emergency preparedness and response
- safeguarding compliance with environmental legislation.

(e) checking performance and taking corrective action, paying particular attention to:

- monitoring and measurement *(see also the Reference Document on the General Principles of Monitoring [ 293, EC 2003 ]* .
- corrective and preventive action
- maintenance of records
- independent (where practicable) internal auditing in order to determine whether or not the environmental management system conforms to planned arrangements and has been properly implemented and maintained.

(f) review of the EMS and its continuing suitability, adequacy and effectiveness by top management.

Three further features are listed below, and while these features have advantages, EMS without them can be BAT:

- Having the management system and audit procedure examined and validated by an accredited certification body or an external EMS verifier.

- Preparation and publication (and possibly external validation) of a regular environmental statement describing all the significant environmental aspects of the installation, allowing for year-by-year comparison against environmental objectives and targets as well as with sector benchmarks as appropriate.

- Implementation of and adherence to an internationally accepted voluntary system such as EMAS and EN ISO 14001:2004. This voluntary step could give higher credibility to the EMS. In particular EMAS, which embodies all the above-mentioned features, gives higher credibility. However, non-standardised systems can in principle be equally effective provided that they are properly designed and implemented.

Specifically for the non-ferrous metals industries, it is also important to consider the following potential features of the EMS:

- the environmental impact from the eventual decommissioning of the unit at the stage of designing a new plant;
- the development of cleaner technologies, and to follow developments;
- where practicable, the application of sectoral benchmarking on a regular basis, including energy efficiency and energy conservation activities, choice of input materials, emissions to air, discharges to water, consumption of water and generation of waste.

### 2.20.2 Material handling and storage

The techniques depend to a large extent on the type of material that is being used. For example large, heavy items are treated by a completely different range of techniques than fine, dusty material. In general the storage of dusty material in the open space should be avoided. Conveying systems should be equipped with enclosures. Fabric filters need to be examined and maintained regularly. There are several techniques to prevent emissions from material storage and handling processes that are considered more effective in preventing emissions (see Sections 2.6.1 and Section 2.6.3 and the BREF on Emissions from Storage [ 290, EC 2006 ]).

**a) BAT is to prevent emissions from material handling and storage by using the techniques given in Table 2.49 (see Section 2.6.3 and the BREF on Emissions from Storage [ 290, EC 2006 ]):**

| Material | Metal group | Technique for handling | Technique for storage | Additional measures |
|---|---|---|---|---|
| *Solid materials* | | | | |
| Concentrates:<br>- dust-forming<br>- non-dust-forming | All | Enclosed conveyors or pneumatic systems<br>Covered conveyors | Enclosed building<br>Covered storage | Prevention of water contamination and diffuse air emissions |
| Fine grained material, e.g. metal powder | Refractory metals | Enclosed conveyors or pneumatic<br>Covered conveyors | Closed drum,<br>Bins and hoppers | Prevention of water contamination and diffuse air emissions |
| Secondary raw materials:<br>- large items<br>- small items<br>- fines<br>- swarf | All | Mechanical loader<br>Charge skips<br>Enclosed or agglomerated<br>Charge skips | Open storage<br>Covered bays<br>Enclosed if dust-forming<br>Covered | Prevention of water contamination<br>Reactions with water<br>Oily drainage |
| Fluxes:<br>- Dust forming<br>- Non-dust-forming | All | Enclosed conveyors or pneumatic system<br>Covered conveyors | Enclosed building<br>Covered store | Prevention of water contamination |
| Solid fuel and coke (If not dust-forming) | All | Covered conveyors | Covered store | |
| Products: cathodes, wire-rod, billets, ingots, cakes, etc. | All | Depends on conditions | Open concrete area or covered storage | Appropriate drainage system |
| Process residues for recovery | All | Depends on conditions | Open, covered or enclosed depending on dust formation and reaction with water | Appropriate drainage system |
| Wastes for disposal (e.g. furnace linings) | All | Depends on conditions | Open covered or enclosed bays or sealed (drums) depending on the material | Appropriate drainage system |
| *Liquids* | | | | |
| Liquid fuels and LPG | All | Overhead pipeline | Certified storage, bunded areas | Back venting of delivery lines |
| Solvents | Cu, Ni, Zn group, precious metals and carbon | Overhead pipeline<br>Manual handling | Drums, tanks | Back venting of delivery lines |
| *Gases* | | | | |
| Process gases:<br>- oxygen<br>- chlorine, CO | All<br>Al, precious metals, Ni | Overhead pipeline<br>Reduced pressure pipeline | Certified storage | Pressure loss monitoring,<br>alarms for toxic gases |

**Table 2.49: Summary of BAT for material handling and storage**

**b) BAT is to prevent emissions from material handling and storage by using the following techniques (see Section 2.6.3):**

- Use of materials of construction for storage tanks that are resistant to the material stored. In some cases, double walled tanks are appropriate.

- Use of reliable leak detection systems and the display of tank contents and associated alarms that indicate leaks.
- Use of inventory control, inspection systems, planned deliveries and use of automatic control systems to prevent the overfilling of storage tanks.
- Storage of sulphuric acid and other reactive materials in double walled tanks or tanks placed in chemically-resistant bunds of the same capacity. The storage area should be impermeable and resistant to the material stored.
- Designing storage areas so that leaks from tanks and delivery systems are intercepted and contained in bunds that have a capacity capable of containing at least the volume of the largest storage tank within the bund. Delivery points should be within the bund to collect spilled material.
- Placement of transfer conveyors and pipelines in safe, open areas above ground so that leaks can be detected quickly and damage from vehicles and other equipment can be prevented. If buried pipelines are used for non-hazardous materials, their course should be documented and marked and safe excavation systems adopted.
- Automatic resealing of delivery connections.
- Segregation of incompatible materials (e.g. oxidising agents and organic materials).
- Back venting of displaced gases to the delivery vehicle to reduce emissions of VOCs.
- Use of inert gases for storage tanks holding materials that react with air.
- Use of well designed, robust pressure vessels for gases (including LPG) with pressure monitoring of the tanks and delivery pipework to indicate rupture and leakage. Gas monitors should be used in confined areas and close to storage tanks.
- Collection and treatment of rainwater that washes dust away before discharge.
- Use of oil and solid interceptors for the drainage from open storage areas. The storage of material that can release oil such as swarf should be on concreted areas that have curbs or other containment devices.
- Use of effluent treatment methods for the chemical species that are stored.
- Use of sealed delivery, storage and reclamation systems for dusty materials.
- Use of sealing agents such as molasses and polyvinyl acetate on fine materials stored in the open to reduce the tendency for material to form dust.
- Use of rationalised transport systems to minimise the generation and transport of dust within a site.
- Use of wheel and body washes or other cleaning systems to clean vehicles used to deliver or handle dusty material taking account of, e.g. ice formation.
- Use of planned campaigns for road sweeping.
- Monitoring of storage areas that contain fuels or reducing agents such as coal, coke or woodchips to detect fires caused by self-ignition.
- Integration of material sampling and assay systems into the material handling and storage system to identify raw material quality and plan the processing method.

### 2.20.3 Process control

Best available techniques include how a process is designed, operated, controlled, staffed and maintained. These factors allow good performance to be achieved in terms of emissions prevention and minimisation, process efficiency and cost savings (see Section 2.5). Good process control is used to achieve these gains and also to maintain safe conditions and to analyse past events and process responses.

**a) BAT is to achieve a smooth and stable process operation by implementing a process control system for all non-ferrous smelting and operating processes.**

**b) BAT is to achieve a smooth and stable process operation by using a combination of the following techniques, (see Sections 2.5.1 and 2.5.2):**

- Sampling and analysis of raw materials to control plant conditions.
- Good mixing of different feed materials to achieve optimum conversion efficiency and reduce emissions and rejects.
- Use of feed weighing and metering systems.
- Use of microprocessors to control material feed rate, critical process and combustion conditions and gas additions. Several parameters can be measured to allow processes to be controlled, alarms are provided for critical parameters.
- On-line monitoring of temperature, furnace pressure (or depression) and gas volume or flow.
- Monitoring of gaseous components ($O_2$, $SO_2$, CO).
- On-line monitoring of vibration to detect blockages and possible equipment failure.
- On-line monitoring of the current and voltage of electrolytic processes.
- On-line monitoring of the electrical contact temperatures of electrolytic processes.
- On-line monitoring of gases to control critical process parameters.
- Monitoring and control of the temperature of melting furnaces to prevent the production of metal and metal oxide fumes by overheating.
- Continuous training and assessment of operators, engineers and others in the use of operating instructions, the use of modern control techniques and the significance of and the actions to be taken when alarms are given.
- Optimised levels of supervision to take advantage of the above techniques and to maintain operator responsibility.

### 2.20.4 Fume and gas collection

Emissions to air arise from the storage, handling, pretreatment and pyrometallurgical and hydrometallurgical stages. The transfer of materials is particularly important. Data provided have confirmed that the significance of diffuse emissions in many processes is very high and that diffuse emissions can be much greater than those that are captured and abated. In these cases, it is possible to reduce the environmental impact by following the hierarchy of gas collection techniques from material handling and storage, reactors or furnaces and from material transfer points. Potential diffuse emissions must be considered at all stages of process design and development.

**a) BAT is to reduce variations in gas volumes and to optimise the efficiency of off-gas collection by using a combination of the following techniques (see Section 2.4.4):**

- Thermal or mechanical pretreatment of secondary raw materials to minimise organic contamination of the feed to furnaces.
- Sealing of furnaces or other process units to prevent diffuse emissions, to allow heat recovery and to allow the collection of process gases for other uses (e.g. CO as a fuel and $SO_2$ as sulphuric acid) or to be abated.
- Use of semi-sealed furnaces where sealed furnaces are not available.
- Minimisation of material transfers between processes.
- Use of secondary or tertiary fume collection where material transfers take place.
- Optimisation of the design and operation of hooding and ductwork to capture fumes arising from hot metal, matte or slag transfers and tapping. The heat content of the captured gases should be recovered if possible by using the captured gases as heated combustion air.
- Use of furnace or reactor enclosures such as 'House in House' or 'Dog House' to prevent the emission of fume into the air.
- Use of control systems to automatically switch on dust or fume extraction only when it is required to minimise energy use.
- Use of computerised fluid dynamics studies and tracers to model the flow of furnace gases.
- Modification of furnace charging systems to give small, even additions of raw materials.

### 2.20.5 Prevention and destruction of PCDD/F

The presence of PCDD/F or their formation during a process should be considered for many of the pyrometallurgical processes used to produce non-ferrous metals. Particular instances are reported in the metal-specific chapters and in these cases the following factors are considered to be BAT for the prevention of the formation of PCDD/F and the destruction of any that are present. These techniques may be used in combination. Some non-ferrous metals are reported to catalyse de novo synthesis and it is sometimes necessary to remove dust and metals prior to further abatement.

**a) BAT is to prevent the formation of PCDD/F and, if this is not possible, to destroy or remove PCDD/F by using a combination of the following techniques (see Section 2.10.2.1):**

- Control selection and sorting of raw materials and scrap inputs to ensure that the appropriate feed material for the particular furnace or process is used.
- Making small, even additions of raw materials to furnaces.
- Use of optimum combustion conditions. Oxygen injection in the upper part of a furnace can ensure complete combustion.
- Correct design and operation of afterburners with rapid quenching of the hot gases to <250 °C in order to prevent de novo synthesis.
- Absorption of PCDD/F onto activated carbon in a fixed bed or moving bed reactor or by injection of activated carbon into the gas stream with subsequent removal as filter dust.
- Use of very high efficiency dust removal to achieve <1 mg/Nm$^3$ of dust. Examples are ceramic filters, high efficiency fabric filters or the gas-cleaning train that is used prior to a sulphuric acid plant.
- Use of a catalytic oxidation stage or fabric filters that incorporate a catalytic coating (see Section 2.10.2.1).
- Treatment of collected dusts in a high temperature furnace to destroy PCDD/F and to recover metals.

**The following emission level is the BAT-AEL: <0.1 ng I-TEQ/Nm$^3$** – expressed as the average over the sampling period which should preferably be a minimum of six hours.

### 2.20.6 Sulphur dioxide removal

The appropriate technique for the removal of sulphur dioxide depends on the strength of the gas that is produced.

#### 2.20.6.1 Low strength gases (<1 % $SO_2$)

**BAT and the BAT-AELs for the treatment of low strength gases (<1 %) are reported in the individual metal chapters.**

#### 2.20.6.2 High strength gases (>1 % $SO_2$)

**a) BAT is to prevent and control the emissions of sulphur dioxide from sources that have a high input strength of the gas by using one of the following techniques:**

**i) recovering sulphur dioxide using a cryogenic process or by absorption in cold water followed by stripping and the production of liquid sulphur dioxide from the absorbed**

**liquor and using this process in conjunction with a sulphuric acid plant (see Section 2.11.3.1)**

The cold water absorption technique is applicable where local markets exist for the sulphur dioxide that is produced in conjunction with a sulphuric acid plant to treat the tail gases or the gases when absorption plant is not used.

**The following emission level is the BAT-AEL: <50 to 200 mg/Nm$^3$ $SO_2$** expressed as a daily averages for plants operating under stable conditions and based on continuous monitoring during the operating period.

**ii) concerning the prevention and control of emissions of $SO_2$ and $SO_3/H_2SO_4$ mist, BAT is to apply BAT from Section 4.5 of the LVIC-AAF BREF on Large Volume Inorganic Chemicals – Ammonia, Acids and Fertilisers Industries (LVIC-AAF).**

**The BAT-AELs for double contact/double absorption plants have been revised to take account of the reduction in volume after the first absorption stage (see Section 2.11.1). The correction of the related BAT-AEL is shown in Table 2.50.**

For processes with increased $SO_2$ inlet concentrations, see also Section 2.21.2 of this BREF.

| **Conversion process type** | | **Daily averages** | |
|---|---|---|---|
| | | **Conversion rate (1)** | **$SO_2$ in mg/Nm$^3$ (2)** |
| Other double contact/double absorption processes | | 99.7 – 99.92 | 200 – **770** (3) |
| Single contact/single absorption | | | 100 – 450 |

(1) these conversion rates relate to the conversion including the absorption tower, they do not include the effect of tail gas scrubbing
(2) these levels might include the effect of tail gas scrubbing
(3) The corrected BAT-AEL is highlighted.

**Table 2.50: BAT-AELs for the production of sulphuric acid as laid down in the LVIC-AAF BREF.**

**Table 2.50 contains only the parts relevant to installations of the NFM sector**

## 2.20.7 Removal of mercury

Mercury removal is necessary when using some raw materials that contain the metal.

**a) BAT is to prevent and control the emissions of mercury by using the following techniques (see Section 2.9.2.8):**

- the Boliden-Norzink process with the recovery of the scrubbing solution and production of mercury metal;
- the Bolchem process and filtering off mercury sulphide to allow the acid to be returned to the absorption stage;
- the Outotec process;
- the sodium thiocyanate process;
- use of an activated carbon filter to remove mercury vapour and PCDD/F from the gas stream;
- the Tynfos-Miltec application;
- the Lurgi process;
- the Boliden/Contec process;
- the DOWA adsorption process.

**The BAT-AEL for emissions of mercury to air is less than 0.02 mg/Nm$^3$ as a daily average.**

In any case, the provisions of regulation EC 1102/2008 on the banning of exports of metallic mercury and certain mercury compounds and mixtures and the safe storage of metallic mercury shall be complied with.

### 2.20.8 Effluent treatment and water re-use

**a) BAT is to minimise the amount of waste water and the mass of pollutants by using a combination of the following techniques (see Section 2.12.2):**

- measuring the amount of water used and discharged;
- measuring the pollutants and their concentrations;
- determining and applying the most effective chemical, physical or biological treatment for the waste water for the metals that are present in the effluent.

**b) BAT is to prevent and control the emissions to waste water by using techniques shown in Table 2.51 or a combination of them.**

The data given may not be transposable to all installations and this will depend on the source of waste water and the metals that are present in the untreated waste water. *(this is a good argument to include the waste water issues to the specific sections.)* The ecotoxicology of metals in water is discussed in Section 2.3.2.2 and a methodology for determining impact is given in the MERAG report [ 301, MERAG Guidance 2007 ] (see Section 2.12.2).

| Source of waste water | Associated processes | Minimisation Techniques(1) | Treatment Techniques(1) |
|---|---|---|---|
| Process water | Alumina production<br>Lead-acid battery breaking<br>Pickling *(What about copper, zinc and ferroalloys, see table 2.32)?* | Return to process | Neutralisation<br>Precipitation by $S^{2-}$ or $OH^-$<br>Settlement or filtration<br>Electrolysis |
| | Mo or W production | Return to process | Accumulation in an anion exchange membrane and acidification to precipitate as the oxihydrate. |
| Indirect cooling water | Furnace cooling for most metals<br>Electrolyte cooling for Zn | Use of closed circuit cooling system<br>System monitoring to detect leaks | Settlement |
| Direct cooling water | Cu castings<br>Carbon electrodes | Settlement or other treatment<br>Closed cooling system | Settlement<br>Precipitation if needed. |
| Slag granulation | Cu, Ni, Pb, precious metals, ferro-alloys production | | Settlement<br>Precipitation |
| Electrolysis | Cu, Ni, Zn production | Sealed system<br>Electrowinning of electrolyte bleed | Neutralisation<br>Precipitation by $S^{2-}$ and or $OH^-$<br>Settlement or filtration |
| Hydrometallurgy (blowdown) | Zn, Cd production | Sealed system<br>Blowdown treatment | Settlement<br>Precipitation if needed |
| Abatement system | Wet scrubbers | Blowdown treatment | Settlement |

| | | | |
|---|---|---|---|
| (blowdown) | Wet ESPs and scrubbers for acid plants | (re-use of weak acid streams if possible) | Precipitation if needed |
| Surface water | All processes | Good raw materials storage<br>Historical pollution of the site surface has a major influence on water contamination | Settlement<br>Precipitation if needed |
| NB: Waste water volumes will be reduced by using the techniques for minimisation and this may result in higher concentrations of metals after treatment. | | | |

**Table 2.51:** **BAT to prevent and control the emissions to waste water**

*Extract the relevant onformation and relocate it to the specific section.*

**c) Where precipitation is used to remove metals, BAT is to optimise the addition of treatment chemicals to precipitate metals as hydroxides and/or sulphides in one or more stages followed by the removal of the precipitate by sedimentation and/or filtration. The method and order of the precipitation reactions will vary depending on the combination of the metals present in the waste water (see Section 2.12.2).**

**The BAT-AELs are given in the individual metal chapters.**
*(What is the sense of having here in this section a sentence about a generic treatment technique/measure when the associated BAT-AEL is in cluded in the specific section. Most likely this creates double inclusion. This is a good argument to include the waste water issues to the specific sections.)*

## 2.20.9 Energy efficiency

**a) BAT is to control energy consumption by using a combination of the following techniques (see Section 2.14.1):**

- Use of an energy efficiency management system (E2MS) and application of other BAT from the BREF for Energy Efficiency [ 333, EC 2008 ].
- Use of regenerative burners, regenerative afterburners, recuperative burners, heat-exchangers or boilers to recover process heat.
- Use of hot gases produced during the smelting or roasting of sulphide ores and other heat generating processes to raise steam or produce heat for other process stages, e.g. in the concentrate dryer or to preheat the combustion air.
- Use of the hot gases from melting stages to preheat the furnace charge, in the drying or other process stages, to generate steam and/or hot water or to raise the temperature of leaching liquors. Hot gases extracted from launders can be used as preheated combustion air.
- Use of the heat given off in converters or similar furnaces to melt metal scrap.
- Use of oxygen-enriched air or pure oxygen in the burners to reduce energy consumption by allowing autogenic smelting or the complete combustion of carbonaceous material. Waste gas volumes are significantly reduced allowing smaller fans, abatement plant, etc. to be used.
- Use of low mass refractories. The use of this technique must be balanced with the durability of the furnace lining and metal infiltration into the lining.
- Drying of concentrates at low temperatures before smelting to reduce the energy requirements compared to smelting wet concentrates. The energy required to superheat the steam that is produced combined with the significant increase in the overall gas volume has a greater energy debit.
- Use of carbon monoxide produced in an electric or blast furnace as a fuel after the removal of metals, in the production processes or to produce steam or other energy.
- Recirculation of contaminated waste gas back through an oxy-fuel burner to recover the energy of the total organic carbon present. Such a process can also reduce nitrogen oxides.

- Use of the combustible plastic content of raw materials to contribute to the energy that is used in the smelting process or as a reducing agent (see Section 2.14.2.3).

### 2.20.10 By-products, process residues and wastes

**a) BAT is to recycle or re-use intermediate products and process residues (slags, slimes and filter dusts) as far as possible in the processes; or, after meeting the requirements of leaching standards, as construction material; or after meeting the specific legal requirements, as sand blasting material by using the techniques listed in Table 2.52 (see Section 2.13.3). If recycling or re-use is not economically possible, secure disposal should be carried out.**

| Source of the residues | Associated metals | Intermediate product or process residue | Techniques for recycling or re-use |
|---|---|---|---|
| Raw material handling, etc. | All metals | Dust, sweepings | Use as feed for the main process |
| Smelting furnace | All metals | Slag | Return to smelting, use as construction material, use in the abrasive industry. Parts of slag may be used as refractory material |
| | Ferro-alloys | Rich slag | Raw material for other ferro-alloy processes |
| Converter | Cu | Slag | Recycle to smelter |
| Refining furnaces | Cu | Slag | Recycle to smelter |
| | Pb | Dross and slag | Recovery of other valuable metals |
| | Precious metals | Dross and slag | Internal recycling |
| Slag treatment | Cu and Ni | Cleaned slag | Use as construction material, abrasives, drainage filling material, filler in cement production |
| | | Matte | Metal recovery |
| Melting furnace | All metals | Skimmings or dross | Return to process after treatment |
| | | Slag | Metal recovery |
| | Secondary Al | Salt slag | Metal, salt and oxide recovery |
| Electrorefining | Cu | Electrolyte bleed | Recovery of Ni. |
| | | Anode remnants | Return to converter |
| | | Anode slime | Recovery of precious metals |
| Electrowinning | Zn, Ni, Co, precious metals | Spent electrolyte | Re-use in leaching process |
| Fused salt electrolysis | Al | Spent pot lining | Use as a carburant |
| | | Excess bath | Use as electrolyte |
| | | Anode stubs | Recovery as anode material |
| | Na and Li | Cell material | Scrap iron after cleaning |
| Distillation | Hg | Residues | Re-use as process feed |
| | Zn, Cd | Residues | Return to ISF |
| Leaching | Zn | Iron and iron/sulphur residues | Use of Waelz kiln, compaction, Jarofix process |
| | Cu | Residues | Use as raw material in other processes |
| | Ni | Cu/Fe residues | Use as raw material in other processes |
| Sulphuric acid plant | | Catalyst | Regeneration |
| | | Acid sludges | Recovery of the acid |
| | | Weak acid | Leaching, decomposition, neutralisation |
| Furnace linings | All metals | Refractory | Use as slagging agent, re-use as a refractory |
| Milling, grinding | Carbon and graphite | Dusts | Use as raw material in other processes |
| Pickling | Cu, Ti | Spent acid | Recovery by electrowinning |
| Dry abatement systems (fabric filters or ESPs) | Most metals | Filter dust | Return to process<br>Recovery of other metals |
| Wet abatement systems (scrubbers or wet | Most metals | Filter sludge | Return to process<br>Recovery of other metals. |

| Source of the residues | Associated metals | Intermediate product or process residue | Techniques for recycling or re-use |
|---|---|---|---|
| ESPs) | | | |
| Waste water treatment sludge | Most metals | Hydroxide or sulphide sludges. | Re-use as source of calcium in the smelter.<br>Use as clean gypsum |
| Digestion | Alumina | Red mud | Re-use of liquor, use of the alkalinity to absorb $CO_2$, high-pressure filtration to produce low moisture residue for use in cement and ceramic industries, road construction, etc. |

**Table 2.52: BAT for the recycling or re-use of intermediate products or process residues**

## 2.20.11 Emission monitoring

**a) BAT is to assess captured emissions by continuously monitoring emissions of dust from the main sources that have a significant environmental impact (see Section 2.3.1.4 and the Reference Document on Monitoring).**

*The main sources have to be identified and named as in the IS BREF. Ask the TWG.*

**b) BAT is to assess diffuse emissions by measuring the off-gas capture efficiency or by estimation using environmental monitoring (see Section 2.4.3).**

## 2.20.12 Prevention of the formation of $NO_X$

*I think this should be relocated to the specific metal sections and for each single case examples for the application of these techniques should be given with sufficient data. This should be assigned to specific processes (i.e. converting, smelting, firerefining, holding, anode ofen). Currently this info here is also included in the specific section. Avoid repetition.*

**a) BAT is to prevent and control the emissions to air of $NO_X$ using the techniques given in Table 2.53 (see also Section 2.9.2.4.3) or a combination of them.**

- For $NO_X$ formed during the treatment of materials with nitric acid, absorption of $NO_X$ in water or, hydrogen peroxide to produce nitric acid for reuse
- Use of a low-$NO_X$ burner
- Use of an oxy-fuel burner

**The emission levels given in Table 2.53 are the BAT-AELs.**

| Pollutant | Techniques | BAT-AELs | Comments |
|---|---|---|---|
| $NO_X$ | Low-$NO_X$ burner<br>Oxy-fuel burner | <100 to 300 mg/Nm$^3$ | Higher values are associated with oxygen enrichment to reduce energy use. In these cases gas volume and mass emissions are reduced |

**Table 2.53: BAT and BAT-AELs for nitrogen oxides**

## 2.20.13 Removal of dust and particles

*I think this should be relocated to the specific metal sections and for each single case examples for the application of these techniques should be given with sufficient data. This should be assigned to specific processes (i.e. converting, smelting, firerefining, holding, anode ofen). Currently this info here is also included in the specific section. Avoid repetition.*

**a) BAT is to prevent and control emissions of dust by using one of the techniques given in Table 2.54 (see Section 2.9.2.2).**

**The emission levels given in Table 2.54 are the BAT-AELs.**

| Pollutant | Techniques | BAT-AELs | Comments |
|---|---|---|---|
| Dust | Fabric filter or ceramic filter | <1 to 5 mg/Nm$^3$ | A filter failure detection system is needed (see Section 2.9.2.2.4) |
| | Wet electrostatic precipitator | | For gases from slag granulation or wet gas quenching (see Section 2.9.2.2.2) |
| NB: Collected emissions only. BAT-AELs are given as daily averages based on steady-state operation or, in cases where continuous monitoring is not practicable as the average over the sampling period. | | | |

**Table 2.54:** **BAT and BAT-AELs to prevent and control emissions of dust to air**

# 2.21 Emerging techniques

Emerging techniques are reported here only for the common processes described above in section 2.20. Emerging techniques for other processes are reported on in the subsequent chapters.

## 2.21.1 Sulphur removal

The following emerging techniques have been identified for the conversion of high strength sulphur dioxide into sulphuric acid:

### 2.21.1.1 The LUREC® and BAYQIK® processes

**Description**

The addition of an extra pass that is external to an existing contact plant can be used to uprate an existing sulphuric acid plant and use higher inlet concentrations of sulphur dioxide. The LUREC® process uses an additional contact chamber with one or two beds depending on the inlet gas concentration [ 326, High Concentrated SO2 2005 ]. This acts as a pre-converter and a heat exchanger and a pre-absorption stage can then be used before the existing plant. Inlet sulphur dioxide concentrations between 15 and 25 % have been tested.

The BAYQIK® process uses a series of concentric tubes where the catalyst and support are contained in the inner tube and the outer ring acts as the heat exchanger. The process is shown in Figure 2.64.

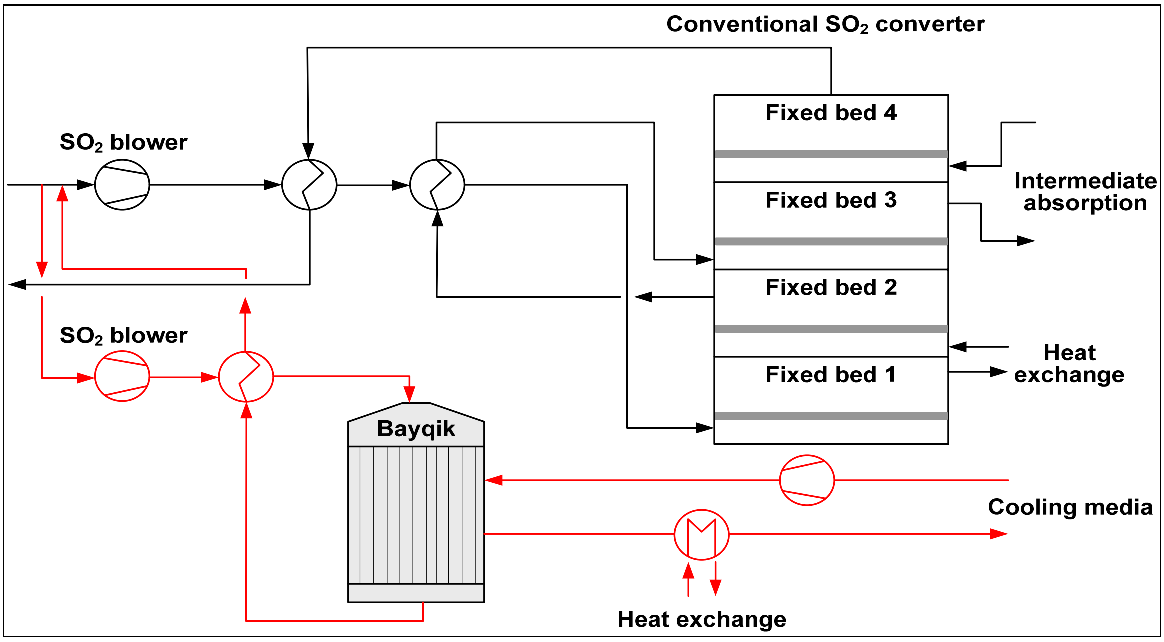


**Figure 2.64:** BAYQIK® process

**Achieved environmental benefits**

Reduction in emissions of $SO_2$, overall efficiency of an existing sulphuric acid plant can increased and higher inlet gas concentrations used to keep the overall gas flow low.

**Cross-media effects**

None reported for the additional process.

**Operational data**

The LUREC® process has been in operation since the summer of 2007 at a Chinese smelter Yanggu Xiangguang Copper, Shangdong Province, China (nominal capacity 2340 t/d) where an additional pre-contact pre-absorber unit precedes a five pass double contact sulphuric acid plant to give overall a seven pass triple contact plant. This is a greenfield plant operating with an inlet concentration of 16-18 % $SO_2$.

The BAYQIK® process adds an extra external stage to an existing sulphuric acid plant that comprises a catalyst bed with an integrated heat exchanger. The plant was commissioned in 2009 in Stolberg, Germany but no performance data was available in January 2010.

**Applicability**
The LUREC® process is available and can be used as an additional bed for all existing plants to give six or seven passes and triple absorption if the inlet gas concentration requires.

**Economics**
LUREC® costs are given as EUR 8 million for an addition to a 121000 $Nm^3$/hr gas flow at 20 % $SO_2$ inlet concentration. The capital cost comparison of the Lurec add on module and conventional plant is given in Table 2.55.

| Item | Unit | Amount | |
|---|---|---|---|
| | | Conventional plant | Add-on LUREC plant |
| Existing capacity | (Tonne/day) | 2000 | |
| Existing smelter gas flow | ($Nm^3$/h) | 51700 | |
| Existing gas flow to inlet of plant | ($Nm^3$/h) | 143000 | |
| Inlet $SO_2$ concentration | (vol-%~~ v/v~~) | 13.0 | |
| Additional capacity required | (Tonne/day) | 600 | |
| Future gas flow required at 13 % inlet $SO_2$ concentration | ($Nm^3$/h) | 185600 | |
| Estimated cost for 600 tonne per day plant | | 11 | |
| Future capacity required | (Tonne/day) | 1240 | 1360 |
| Gas flow from smelter at 36 % inlet $SO_2$ concentration | ($Nm^3$/h) | 67200 | |
| Gas flow to inlet of plant | ($Nm^3$/h) | 120000 | 121000 |
| Inlet $SO_2$ concentration | (vol-%~~ v/v~~) | 9.5 | 20 |
| Estimated capital cost for 1360 tonne per day LUREC module | | | 8 |

**Table 2.55: The capital cost comparison of the Lurec add on module and conventional plant**

BAYQIK® costs are given as EUR 7.5 million for a plant to take 50 % side-stream from 25000$m^3$/hr process.

**Driving force for implementation**
An increase in plant throughput without replacement.

**Example plants**
Yanggu Xiangguang Copper, Shangdong Province China; Stolberg, Germany.

**Reference literature**
[ 274, Farrell Mission in DE 2008 ], [ 326, High Concentrated SO2 2005 ].

# 3 PROCESSES TO PRODUCE COPPER AND ITS ALLOYS (INCLUDING TIN AND BERYLLIUM) FROM PRIMARY AND SECONDARY RAW MATERIALS

## 3.1 Applied processes and techniques

### 3.1.1 Primary copper

Primary copper can be produced by pyrometallurgical or hydrometallurgical processes. Approximately 10 % of the primary copper is produced by the direct leaching of ores (hydrometallurgical route). Nowadays sulphidic concentrates (15 - 45 % Cu) are the most important raw materials for the pyrometallurgical primary copper route with a share of more than 85 %. To a small extent, oxidic/sulphidic mixed ores and, more seldom, bituminous ores are processed. The sulphidic concentrates consist of complex copper/iron sulphides; they are derived from ores that contain 0.5 - 2 % copper by flotation. Further inputs used for primary copper production are fluxes (silicate, lime, sands, etc.), additives/reactants (iron, carbon, etc.) and recycled materials (scrap, dross, lime sludges, used abrasive materials, slags, dusts, etc.) [ 234, UBA Copper, lead, zinc and aluminium 2007 ]. The generic processes are discussed below.

#### 3.1.1.1 The pyrometallurgical route

The pyrometallurgical route entails a number of steps depending on the concentrate used. The majority of concentrates are sulphidic and the stages involved are roasting, smelting, converting, refining and electrorefining. Overviews of all of the furnaces mentioned in this section are given in Section 2.8 and more detail is provided here where needed [ 90, Traulsen, H. 1998 ].

##### 3.1.1.1.1 Concentrate to matte smelting

Roasting and smelting are usually carried out simultaneously in a single furnace at high temperatures to produce a melt that can be separated into a matte (copper sulphide with some iron sulphide) and a slag rich in iron and silica. A fluxing agent that contains silica and if required, lime (CaO) is usually added to the melt to aid the formation of the slag. The sulphur-based gases generated by this process are directed to on-site acid plants to be used as a raw material in the production of sulphuric acid or rarely, the production of liquid $SO_2$. The smelting stage is then used to separate the copper sulphide from the other solids present in ores by the formation of silicates, particularly iron silicates. This reaction depends on the high affinity of copper to sulphur compared to other metallic impurities.

In the case of very impure copper concentrates, partial roasting converts the complex sulphides of iron and copper in the concentrate into the simple sulphides by heating the ore or concentrate under oxidising conditions. The sulphur-based gases generated by this process are directed to an on-site acid plant. The smelting stage is then used to separate the copper sulphide from the other species, i.e. oxides present in ores by the formation of silicates, particularly iron silicates.

There are two basic smelting processes in use: bath smelting and flash smelting. The flash smelting process uses oxygen enrichment to produce autothermal (autogenic) or nearly autothermal operation. Bath smelting processes generally use a lower degree of oxygen enrichment. The use of oxygen also gives higher sulphur dioxide concentrations that make the collection of the gas more effective using one of the sulphur recovery systems (usually the production of sulphuric acid or the production of liquid sulphur dioxide). Table 3.1 shows the smelting processes that are used for primary copper production.

| **Smelting Process** | **Status of Development** | | **Remarks** | |
|---|---|---|---|---|
| | **Industrial scale operation status** | **Environmental performance: potential or constraints** | **Production level: potential and/or limitations** | **Comment** |
| Shaft or blast furnace | Established | Needs to be combined with processes that can recover the heat and sulphur content of the gases | Used specifically for low grade concentrates with a low sulphur content and a high carbon content | High carbon content makes processing with other technology difficult because of the heat release |
| Partial roasting and electric furnace smelting | Established | Good | Limitation for production rate | Possible roaster size may be a limiting factor |
| Outotec flash smelting and Peirce-Smith converting | Established | Good | Very high smelting rate possible in one unit, depending on the furnace design and the type of concentrates, 400000 t/yr blister copper is possible | Worldwide the standard primary copper smelting concept still has potential for improvement |
| Outotec direct blister flash smelting | Established | Good | Three plants in operation, >200000 t/yr reached | Applicable to concentrates with low iron/low slag fall |
| Ausmelt/ISA Smelt | Established | Good | Upper production rate per unit not tested | Potential for further improvement |
| INCO flash smelting | Established | Good | Limitation of proven smelting rate per unit | Size of furnaces installed. Still further potential |
| Teniente converter, Noranda process | Established | Good | Limitation of smelting rate by reactor size and $O_2$ enrichment limits | Related to other processes relatively higher ingress air ratio requiring increased effort for process gas capture |
| Vanyukov process | Six industrial scale furnaces in Russia and Kazakhstan | Potentially good | No definite analysis available | Information for a substantiated judgement is not available; in general, technology may have considerable potential |
| Baiyin process | Exact number not known.<br>At least two industrial units in operation. | Potentially good | No definite analysis available; information available suggests production rates up to 75000 t/yr Cu achieved | Information is not available to substantiate. May have considerable potential |
| Mitsubishi process for continuous copper smelting | Established | Good | So far >200000 t/yr production level reached | Potential for further development |
| Kennecott/Outotec® continuous flash converter | Operating in one plant.<br>Second plant ordered | Good | Higher production rate in a single converter and low gas volume | Potential for substantial further development |
| Reverberatory furnace smelting | Established | Limited to a certain extent | Limitation for smelting rate of one unit | |
| Noranda continuous converter | Commissioned on industrial scale | Good | No data for final analysis available | Effectively available, potential still to be evaluated when data from operation available |

**Table 3.1: Primary copper smelting technologies**
[ 135, Gershel, T. 1998 ]

Bath smelting is carried out in a number of proprietary furnaces such as the reverberatory, shaft (or blast), electric, Ausmelt/ISA Smelt, Noranda, Mitsubishi, El Teniente, Baiyin, Vanyukov furnaces [ 21, European Commission, DG XI 1991 ], [ 25, OSPARCOM 1996 ], [ 134, Metallurgical Consulting Traulsen GmbH 1998 ]. All of the processes rely on the oxidation and smelting processes taking place in a molten bath with slag and matte separation and tapping taking place in various ways. Some furnaces can operate without the predrying of the concentrate but the superheated water vapour increases the gas volume and decreases the energy efficiency of the process. The differences between these processes can be significant, for example in the position of air/oxygen or fuel addition points and some processes operate on a batch basis. Bath smelters are generally operated with a holding furnace or a separate settler. The general descriptions are covered in Chapter 2 and are summarised in Table 3.1 [ 134, Metallurgical Consulting Traulsen GmbH 1998 ].

Flash smelting is carried out in either the Outotec or INCO flash smelters [ 21, European Commission, DG XI 1991 ], [ 25, OSPARCOM 1996 ] or in a cyclone furnace (Contop). The Outotec and cyclone processes use oxygen enrichment and the INCO process uses pure oxygen. Flash smelting relies on the oxidation and smelting of dry concentrates in airborne particles. The reacted particles fall into a settling chamber where the separation of the matte and slag takes place, sometimes additional fuel is used in the settler to maintain the temperature. Matte and slag are subsequently tapped and processed further and gases pass from the furnace through a vertical chamber or uptake shaft to a heat exchanger. Oxygen can be fed into the uptake shaft to afterburn combustible dusts and sulphatise metal oxides. The flash furnace is also used to produce blister copper directly.

In addition to the techniques reported above, other techniques may be encountered worldwide as bath or flash smelting processes [ 134, Metallurgical Consulting Traulsen GmbH 1998 ].

Top blown rotary converters (TBRCs) have also been used in the past in primary copper smelting. They are no longer used for primary smelting mainly due to the high operating costs but this type of furnace is used for secondary smelting. The worldwide use of the smelting technologies is shown in Table 3.2.

| Process | Number of smelters using that technology | Number of furnaces | Blister production 1998 (1000 t/yr) |
|---|---|---|---|
| Outotec flash smelting | 26 | 26 | 3801 |
| Outotec flash smelting, direct blister | 3 | 3 | 238 |
| Reverberatory furnace | 27 | 37 | 1604 |
| El Teniente reactor | 7 | 12 | 1344 |
| Electric furnace | 6 | 8 | 560 |
| Blast furnace | 14 | 29 | 548 |
| Mitsubishi process | 4 | 4 | 497 |
| INCO flash smelting | 3 | 3 | 448 |
| Vanyukov process | 3 | 5 | 448 |
| Ausmelt/ISA Smelt | 11 | 13 | 1000 |
| Noranda reactor | 2 | 2 | 197 |
| Bayin process | 1 | 1 | 57 |
| Kivcet | 1 | 1 | 15 |

**Table 3.2: Worldwide use of the smelting technologies**

*(What is the difference between semlters and furnaces?)*

The reverberatory furnace is also used for matte smelting but not within EU-27. It does not use the energy content of the sulphur and the iron in the concentrates and relies on the use of fossil fuel to melt the concentrates by the hot combustion gases sweeping over the hearth. The process is therefore not as efficient as the other processes described. The combustion gases add to the overall gas volume and result in a very low sulphur dioxide content, which is very difficult to remove effectively. The use of reverberatory furnaces has declined significantly since the 1970s. The $SO_2$ content of the off-gases is normally very low so that they cannot be treated in an acid plant.

The overall process to produce copper from primary raw materials is shown in Figure 3.1.

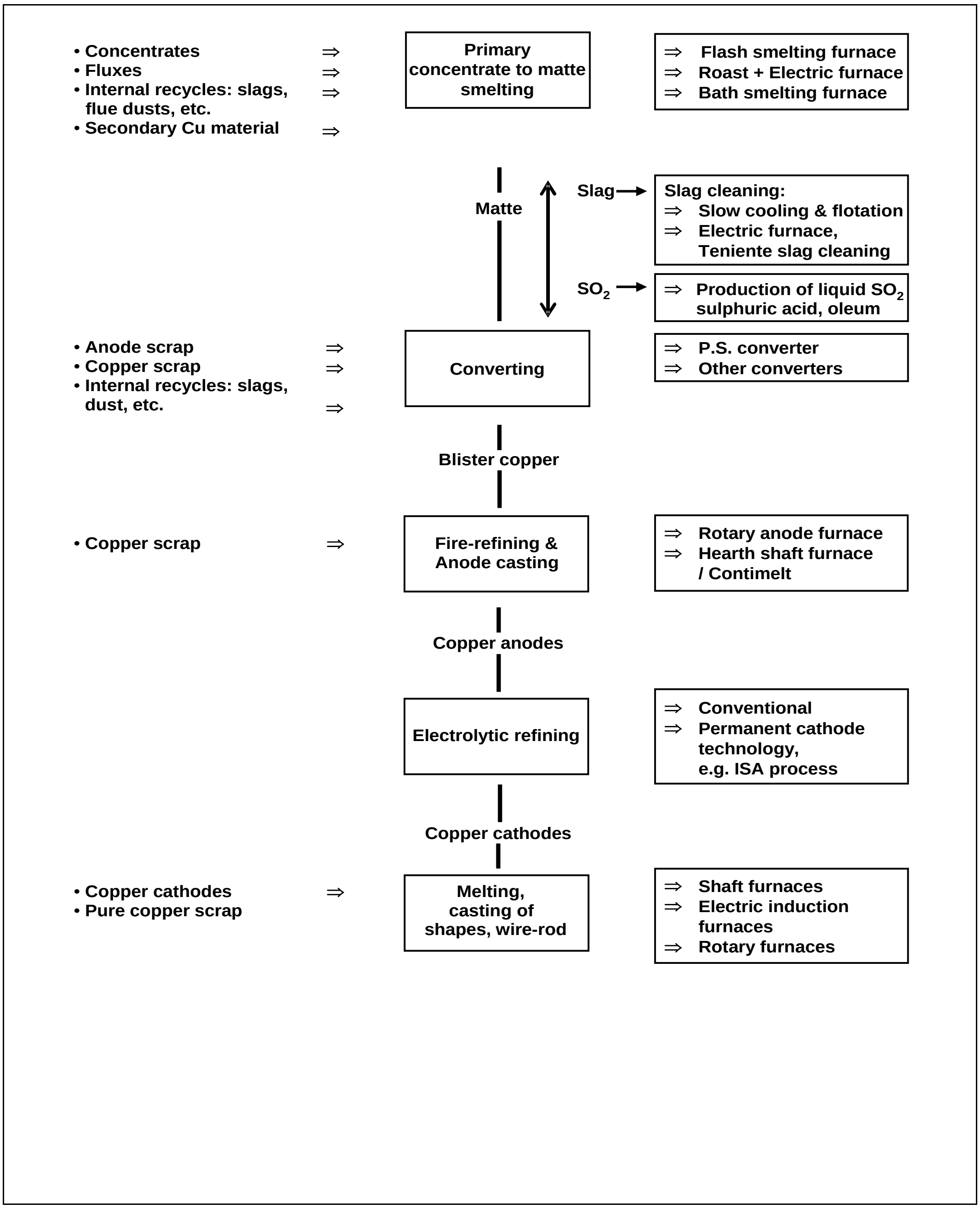


**Figure 3.1:** **Primary copper production route**

#### 3.1.1.1.2 Converting

Three types of converter processes are used during primary process, two are matte conversion processes and one is alloy conversion. The matte conversion processes are the conventional batch processes, which are most commonly used, and the continuous converting process [ 135, Gershel, T. 1998 ].

**Batch matte converting process**

The batch converting process comprises two-stages. It is carried out by blowing an air/oxygen mixture through the matte recovered from the smelting operation. A cylindrical bath furnace is most commonly used [ 21, European Commission, DG XI 1991 ], [ 25, OSPARCOM 1996 ] and flux additions are made. In the first stage iron and part of the sulphur are oxidised and slag and sulphur dioxide gas are formed; the slag is skimmed off periodically and is further processed to recover copper. Normally the first stage blow is carried out in several steps with incremental matte additions. In the second stage, the copper blow, the copper sulphide is oxidised to blister copper (98.5 % Cu) and more sulphur dioxide gas is formed. The blister copper is tapped at the end of the copper blow. The process is operated to control the residual sulphur and oxygen in the blister copper. The sulphur dioxide that is formed is further treated for sulphur recovery, normally in a sulphuric acid plant.

The reaction is strongly exothermic and also volatilises metallic impurities such as lead and zinc that are then captured in an abatement plant and recovered. The process heat can also be used to melt anode scrap and other copper scrap without the addition of primary heat. There can be variations in sulphur dioxide concentrations during the various stages of conversion depending on the type of furnace used.

The Peirce-Smith and the Hoboken type converters are operated batch wise, (they are referred to as Peirce-Smith or similar converters in this chapter). They are cylindrical bath furnaces with laterally arranged tuyères for air/oxygen blowing. [ 21, European Commission, DG XI 1991 ], [ 25, OSPARCOM 1996 ]. The Ausmelt/ISA Smelt furnace has also been used for the batch wise conversion of matte into blister copper. Top blown rotary converters (TBRC) have been used in the past for batch wise conversion of primary copper material to blister copper but are not in use anymore.

**Continuous matte converting process**
The continuous converting processes that are in industrial use are the Kennecott/Outotec flash converting furnace [ 52, Newman, C.J. et al. 1998 ], [ 66, George, D.B. et al. 1995 ], [ 62, Helle, L. et al. 1994 ], the Mitsubishi furnace *(converter?)* (which forms part of the integrated Mitsubishi process) and the Noranda converter [ 135, Gershel, T. 1998 ].

The Mitsubishi and the Noranda converters receive molten feed for conversion. In contrast the Kennecott/Outotec process has the following features: matte from a smelting furnace is first granulated in water, crushed and dried. The material is then blended with slagging agents and fed into the concentrate burner of a specific flash furnace using an oxygen-rich atmosphere; conversion takes place in the airborne particles. The process produces a high and constant concentration of sulphur dioxide that is recovered. Slag and blister copper are tapped for further processing. The use of ground matte allows the matte quality to be balanced with feed rate and degree of oxygen enrichment to produce the optimum conversion efficiency and also allows the matte production and conversion stages to be decoupled.

There are significant differences between batch wise and continuous converter concepts in operation and sulphur dioxide output variations throughout the converting cycles. There are also variations in the ease of collecting fumes during charging and in the ability to melt scrap anodes. Most processes rely on ladles for the transfer of matte, slag and blister copper and diffuse emissions may result. In one case, the ventilation gases from the converter aisle are collected and treated, in another case, an intelligent secondary fume collection system is used [ 198, Velten 1999 ].

**Alloy converting process**
Alloy converting is a batch process in which alloy from the electric furnace serving a direct to blister flash furnace is treated. One converter cycle lasts about 8 hours. About 5 - 6 t of limestone per batch is added to help the slagging of the oxidised iron and lead in the first converting stage. To prevent the over-oxidation of copper, a small amount of coke (0.1 to 1 t) is added per batch. When the lead content drops below 2 %, the second blow starts and silica is added to the converter to bind PbO. The process ends when the Pb content drops below 0.3 %. The converter off-gas is handled in a dedicated wet-cleaning system and the slurry that contains 55 - 65 % Pb is utilised in a lead recovery plant.

#### 3.1.1.1.3 Fire refining

Fire refining is a further purification step applied to the crude metal (blister copper) produced by the conversion stage. The refining step involves the addition of air and then a reducing agent (e.g. hydrocarbons) to reduce any oxide present [ 21, European Commission, DG XI 1991 ], [ 25, OSPARCOM 1996 ] [ 90, Traulsen, H. 1998 ].

Fire refining is achieved by first blowing air through the molten metal to oxidise impurities and to remove final traces of sulphur producing a small amount of slag. A source of reducing agent, such as natural gas or propane, is then added to reduce any copper oxide formed. Ammonia may also be used as a reducing agent but has been reported to increase $NO_X$ levels [ 292, Kojo et al. 2006 ]. Historically, wooden poles or logs were used as the source of reducing agent (and are still used in a small number of cases) and the process is therefore termed poling. Several installations use an afterburner to treat the gases during the poling stage.

In primary and some secondary smelters, cylindrical rotary furnaces (anode furnaces) are used for fire-refining. These furnaces are similar to the Peirce-Smith converter and use tuyères for gas additions. They are charged with molten copper. Some secondary processes use a reverberatory furnace with lances for air additions, they are fed with converter copper and copper scrap. Some reverberatory furnaces are tiltable and are fitted with tuyères. Hot gases from anode furnaces are often used for drying, oxygen evaporation or other uses. Stirring of the molten copper is sometimes achieved by blowing nitrogen through porous plugs in the furnace. This improves homogeneity and increases efficiency [ 265, AJ Rigby et alles 1999 ].

The Contimelt system is also used for fire-refining when the feed is solid and should be melted first. During semis production, fire-refining is also sometimes performed. Combinations of hearth shaft furnaces (for batch wise melting) and rotary furnaces (for batch wise reduction) are also used. These systems can be applied for primary (blister) and secondary (scrap) materials.

The metal from the anode furnace is then cast into anodes. The most commonly used technique is a casting wheel that comprises a series of anode-shaped moulds on the circumference of a rotating table. Molten metal is metered into the moulds to obtain a consistent anode thickness and the wheel rotates taking the anodes through a series of water jets to cool them.

As an alternative to the stop-to-cast mould on a wheel system, copper anodes are also produced continuously using a Hazelett twin belt caster. A copper strip with the desired anode thickness is produced. From the strip, anodes can be obtained by shearing into the traditional anode shape or, according to the Contilanod® system, by casting anode lugs in special side dam blocks spaced in defined intervals in the caster. The preformed anode plates are cut off using a plasma torch or special shears. The advantage of the method is the uniformity of the anodes produced; however, the system requires careful maintenance and the operating costs are comparatively higher.

#### 3.1.1.1.4 Electrolytic refining

An electrolytic cell is used consisting of a cast copper anode and a cathode, placed in an electrolyte that contains copper sulphate and sulphuric acid. The cathode is either a thin blank of pure copper (starter sheet) or a stainless steel former sheet as the permanent cathode plate (Mount ISA process, Outotec permanent cathode system and Noranda/Kidd Creek system) [ 21, European Commission, DG XI 1991 ], [ 25, OSPARCOM 1996 ], [ 90, Traulsen, H. 1998 ]. At high current density and low voltage, copper ions are dissolved from the impure anode and pass into solution from where they are deposited onto the cathode. Copper is removed from the anode to the extent that the remaining anode is still mechanically strong enough to prevent a collapse. The remaining anode is then recycled to the production process, usually the converter, to cool the reaction and recover the copper. When using permanent cathode plates, the pure copper deposits can be stripped and then, in the same way as solid copper cathode plates, melted and cast into the required shape.

During electrorefining other metals contained in the anodes are separated, less noble metals like Ni are dissolved in the electrolyte and more noble metals like the precious metals, selenium and tellurium form an anode slime that settles in the electrolytic cells. Anode slimes are periodically removed from the cells and the valuable metals recovered (see Chapter 6; precious metals).

A portion of the electrolyte is bled from the system. Copper is eliminated by electrowinning or in some plants, a portion is recovered as copper sulphate. Evaporation, crystallisation and further refining recover nickel as nickel sulphate. The following techniques are used for the treatment and elimination of arsenic: solvent extraction; precipitation during the final copper electrowinning; precipitation from the black acid. In some cases, copper arsenate is produced and is converted to copper chrome arsenate for use as a wood preservative.

The removal of impurities during electrorefining is targeted to produce a cathode copper with a quality at least equal or better than the grade A quality standard of the London Metal Exchange. In Table 3.3 an example is shown of the anode composition and the cathode quality achieved. It should be noted that the level of impurities in the anode affects the cathode quality; the impurity level in anodes also depends on the source of the concentrate or secondary material.

| Element | Content in anode(1) (g/t) | Content in cathode (g/t) |
|---|---|---|
| Silver | 600 - 720 | 9 - 10 |
| Selenium | 50 - 510 | <0.5 |
| Tellurium | 20 - 130 | <0.5 |
| Arsenic | 700 - 760 | <1 |
| Antimony | 330 - 700 | <1 |
| Bismuth | 60 | <0.5 |
| Lead | 990 - 500 | <1 |
| Nickel | 1000 - 5000 | <3 |
| (1)Anode quality depends on raw material contents | | |

**Table 3.3: Example of impurity removal during electrorefining**
[ 121, Rentz, O. et al. 1999 ]

The current trend is for larger cells with a greater number of electrodes to be used in the tankhouse and for stainless steel cathode formers to be used [ 90, Traulsen, H. 1998 ]. A gain in efficiency is seen when these factors are coupled with good quality control of anodes. Quality control is needed to ensure that anodes are straight, flat, have good electrical contact and have been adequately fire refined. Similarly there is also an improvement in cathode quality using stainless steel blanks as fewer impurities are mechanically carried over and subsequently incorporated into the cathode. These cathode blanks give an increase in current efficiency to 97 % or even more. Modern tankhouses use a high degree of automation for cathode and anode changes and the stripping cathode deposits from permanent cathode plates [ 21, European Commission, DG XI 1991 ], [ 25, OSPARCOM 1996 ]. Mechanically prepared copper starter sheets can also be used instead of stainless steel blanks.

### 3.1.1.1.5 Slag treatment

The slags produced from primary smelting with high matte grades and converting stages are rich in copper and are subjected to a number of slag treatment processes [ 90, Traulsen, H. 1998 ]. One process is the use of an electric furnace for the reaction of slag with carbon in the form of coke breeze or the electrodes themselves and for the settling of copper matte that is formed to produce an inert slag. The electric furnaces can be operated continuously or on a batch basis.

Converter slag can also be returned directly to the electric slag-cleaning furnace or to the smelting furnace. Alternatively, flotation processes are also used after the slag has been slow cooled, crushed and milled and the flotation concentrate obtained is a copper-rich portion and is returned to the smelter. This method is only used where sufficient space is available and where the tailings can be adequately treated and disposed of.

Electric furnace treatment of smelting furnace slag and separate handling of converter slag by slow cooling and flotation is also practised *(This sentence seems to explain the same option as the one mentioned in the previous paragraph. Probably delete this sentence).*

Slags from the slag treatment processes are used for civil engineering projects, road construction, river embankment and similar applications as well as shot blasting as they often have properties that are superior to alternative materials. Fine material is used as a filler in cement production.

Other slags rich in copper like refining slags are normally recirculated to a prior process stage, mostly converting, or, in secondary smelters, to the smelting stage.

### 3.1.1.2 The hydrometallurgical route

This process is usually applied to oxide or mixed oxide/sulphide ores at the mine site where there is sufficient space to form the leaching and treatment areas. The process is particularly useful for ores that are difficult to concentrate by conventional means and which do not contain precious metals [ 54, Biswas, A.K. et al. 1976 ], [ 55, Kojo, I.V. et al. 1994 ], [ 134, Metallurgical Consulting Traulsen GmbH 1998 ]. Some proprietary processes have been developed such as the Outotec L-SX-EW® and Hydro Copper processes® [ 261, Outokumpu ref 2002 ], [ 308, Hydrocopper 2007 ], [ 309, A MODERN VSF™ SX PLANT 2007 ].

A generic hydrometallurgical flow sheet is shown in Figure 3.2.

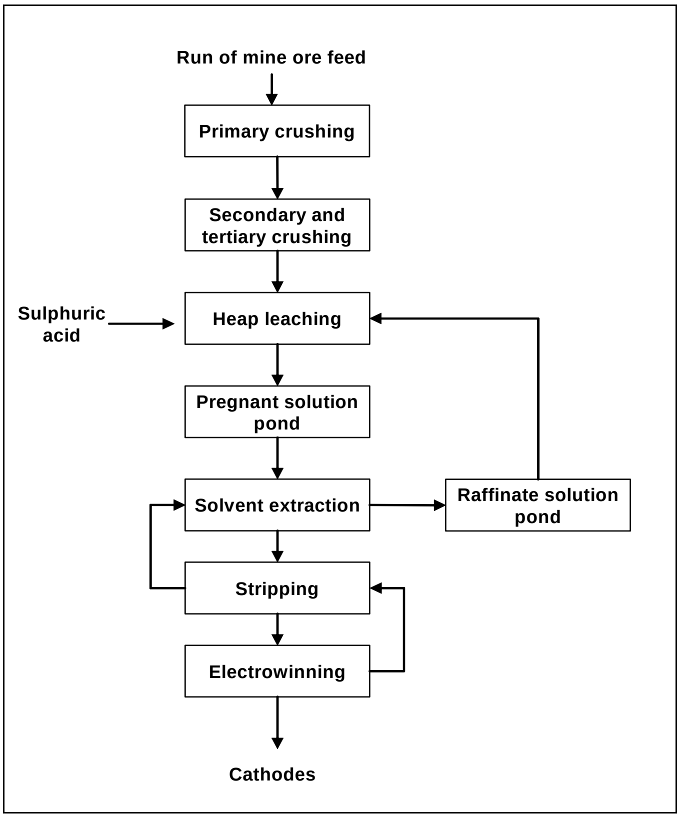


**Figure 3.2: Flow sheet of a heap leaching process**
[ 137, Riekkola-Vanhanen, M. 1999 ]

The hydrometallurgical route involves the crushing of the ore followed by leaching using sulphuric acid, sometimes in the presence of biological species, using heap, vat or agitation processes [ 134, Metallurgical Consulting Traulsen GmbH 1998 ]. The liquor produced from leaching is then clarified and purified and concentrated by solvent extraction.

A further variation of leaching is used by Umicore in Belgium where black copper is produced in an Ausmelt/ISA Smelt furnace. The black copper granules are dissolved in an autoclave and the pure copper is electrowon from the resulting solution [ 238, ECI Copper Installations 2008 ], [ 229, Umicore etc 2007 ]. The electrowinning process uses an inert anode such as lead or titanium and the metal ions are removed from the solution and deposited on the cathode in the same manner as electrorefining. Cathodes are then stripped in the same way if permanent cathode blanks are used. The electrolyte is circulated through a series of cells and finally is depleted of copper. Electrolyte is then returned to the solvent extraction circuit. Some electrolyte is normally bled for the control of impurities, which might have been carried over during solvent extraction.

### 3.1.2 Secondary copper production

Secondary copper is produced by pyrometallurgical processes. The process stages used depend on the copper content of the secondary raw material, its size distribution and the other constituents [ 90, Traulsen, H. 1998 ] [ 121, Rentz, O. et al. 1999 ]. As in primary copper, the various stages are used to remove these constituents and to recover metals as far as possible from the residues that are produced [ 219, VDI (D) 2102 2007 ].

Secondary feed material can contain organic materials like coatings, or be oily in nature and installations take this into account by using de-oiling and de-coating methods or by correct design of the furnace and the abatement system. The aim is to accommodate the increase in combustion gas volumes, destroy VOCs and to minimise the formation of PCDD/F or destroy them. The type of pretreatment applied or the furnace used depends on the presence of organic materials, the type of feed, i.e. copper content and other metals contained, and whether the material is oxidic or metallic.

If a furnace such as a converter is used to smelt impure brass scrap to separate the metals contained in it, the alloying elements are fumed from the copper to produce black copper and a zinc-rich filter dust.

A wide range of secondary raw materials are used and some of them are described in Table 3.4.

| Type of material | Cu content (wt- %) | Sources |
|---|---|---|
| Mixed copper sludges | 1 - 25 | Electroplating |
| Computer scrap | 15 - 20 | Electronics industry |
| Copper mono-sludges | 2 - 40 | Electroplating |
| Copper-iron material (lumpy or comminuted) from armatures, stators, rotors, etc. | 10 - 20 | Electrical industry |
| Brass dross, ashes and slags that contain copper | 10 - 40 | Foundries, semi-finished product plants |
| Red brass dross, ashes and slags that contain copper | 10 - 40 | Foundries, semi-finished product plants |
| Shredder material | 30 - 80 | Shredder plants |
| Copper-brass radiators | 60 - 65 | Cars |
| Mixed red brass scrap | 70 - 85 | Water meters, gear wheels, valves, taps, machine components, bearing boxes, propellers, fittings |
| Light copper scrap | 88 - 92 | Copper sheets, eaves, gutters, water boilers, heaters |
| Heavy copper scrap | 90 - 98 | Sheets, copper punchings, slide |

| | | |
|---|---|---|
| | | rails, wires, pipes |
| Mixed copper scrap | 90 - 95 | Light and heavy copper scrap |
| Copper granules | 90 - 98 | From cable cominution |
| Pure No. 1 scrap | 99 | Semi-finished products, wire, cuttings, strip |

**Table 3.4: Secondary raw materials for copper production**
[ 121, Rentz, O. et al. 1999 ]

The stages used for secondary copper production are generally similar to those for primary production but the raw material is usually oxidic or metallic and process conditions are therefore varied. Smelting of secondary raw materials therefore uses reducing conditions.

### 3.1.2.1 Secondary smelting stage

A number of furnaces such as the blast, Mini Smelter, top blown rotary furnaces (TBRC), sealed submerged arc electric furnace, Ausmelt/ISA Smelt furnace (KRS or Kayser recycling system), reverberatory, and rotary are used for low and medium grade material [ 26, McLellan and Partners Ltd 1993 ], [ 90, Traulsen, H. 1998 ] [ 121, Rentz, O. et al. 1999 ]. Contimelt systems are used for high grade copper scrap (>99 % Cu).

The type of furnace and the process steps used depends on the copper content of the secondary raw material, its size and other constituents. The smelting and refining of secondary copper is therefore complex and the type of secondary material, which can be processed is dependent on the particular facilities and furnaces available [ 90, Traulsen, H. 1998 ]. Details of furnaces are given in Chapter 2. The secondary copper production route is shown in Figure 3.3.

Iron (in the form of irony copper, normal iron scrap, etc.), carbon (in the form of coke or natural gas) and fluxing agents are added to reduce metal oxides if required and the processes are operated to suit the feed material. Reduction smelting results in the volatilisation of mainly zinc, tin and lead which are discharged as oxides with the off-gas and are collected in the dust collection system. Contents of dust, sulphur dioxide, PCDD/F and VOCs in the fume from the furnaces depend on the raw materials. For a further clean-up after dust separation, the off-gas can be routed to a contact process sulphuric acid production unit after additional wet scrubbing [ 219, VDI (D) 2102 2007 ]. The collected flue dust is sent to further processing to recover the metals separated from the input materials.

The Mini-Smelter is also used for secondary copper production using scrap that contains iron and tin. In this application the iron is the reducing agent in the first stage to produce metallic copper and then oxygen is blown into the melt to oxidise iron and the other metals (lead and tin) present which are recovered in the slag. The oxidation of the iron content provides the heat to drive the process and excess heat is recovered.

The KRS process uses the Ausmelt/ISA Smelt furnace (see Section 2.8.2.6) [ 234, UBA Copper, lead, zinc and aluminium 2007 ]. The combination is an advanced technology which replaces the conventional blast furnace/converter technology in non-ferrous metals recovery from secondary raw materials. Typical input materials include copper and precious metal-bearing secondary raw materials from copper smelting and refining, copper casting plants, the metal processing industry or recycling plants for copper-bearing materials such as electric and electronic scrap, copper alloy scrap, copper-rich slags, copper dross, filter and cyclone dust, precipitation sludges and wire-drawing sludge.

In principle, electric furnaces process the same materials as the KRS or the blast furnace. The electric furnace requires a lower material input per tonne of black copper output than the blast furnace which, unlike electric furnaces, cannot normally be operated without return slag.

### 3.1.2.2 Converting, fire-refining, slag treatment and electrorefining, processing of pure alloy scrap

Converting and refining furnaces are the same as those used for primary production and the slag treatment systems and electrorefining processes are also the same. The main difference is that converters used for secondary production treat metal and not matte. They use coke as fuel for melting and, to make up for process heat deficits while in primary converters, the matte provides the necessary process heat [ 90, Traulsen, H. 1998 ]. Secondary converters also oxidise and slag minor elements like iron and separate other metals like zinc or tin by volatilisation. They produce a converter copper in a quality that suits fire-refining. The heat of the reaction when air is blown into the converter is used to volatilise metallic components, slagging agents are used to remove iron and some lead. Fire refining furnaces are also used to melt higher grade scrap. There are potential sources of diffuse emissions from secondary converters.
The electrorefining slimes and spent solutions are also sources of precious metals and other metals such as nickel. These are recovered in the same manner as those from primary production.

Copper alloys such as bronzes and brasses are also used as secondary raw materials in a number of processes. If impure or mixed with other alloys they are processed in the secondary smelting and refining circuits as described in Section 3.1.2.1 above [ 219, VDI (D) 2102 2007 ].

The pure alloy is used directly for semis fabrication. Induction furnaces are used to melt the clean material followed by casting into shapes suited for the further fabrication step. Charge analysis and control is practised to produce the desired alloy without major additions of virgin metal. Zinc oxide can be collected from the filter dust.

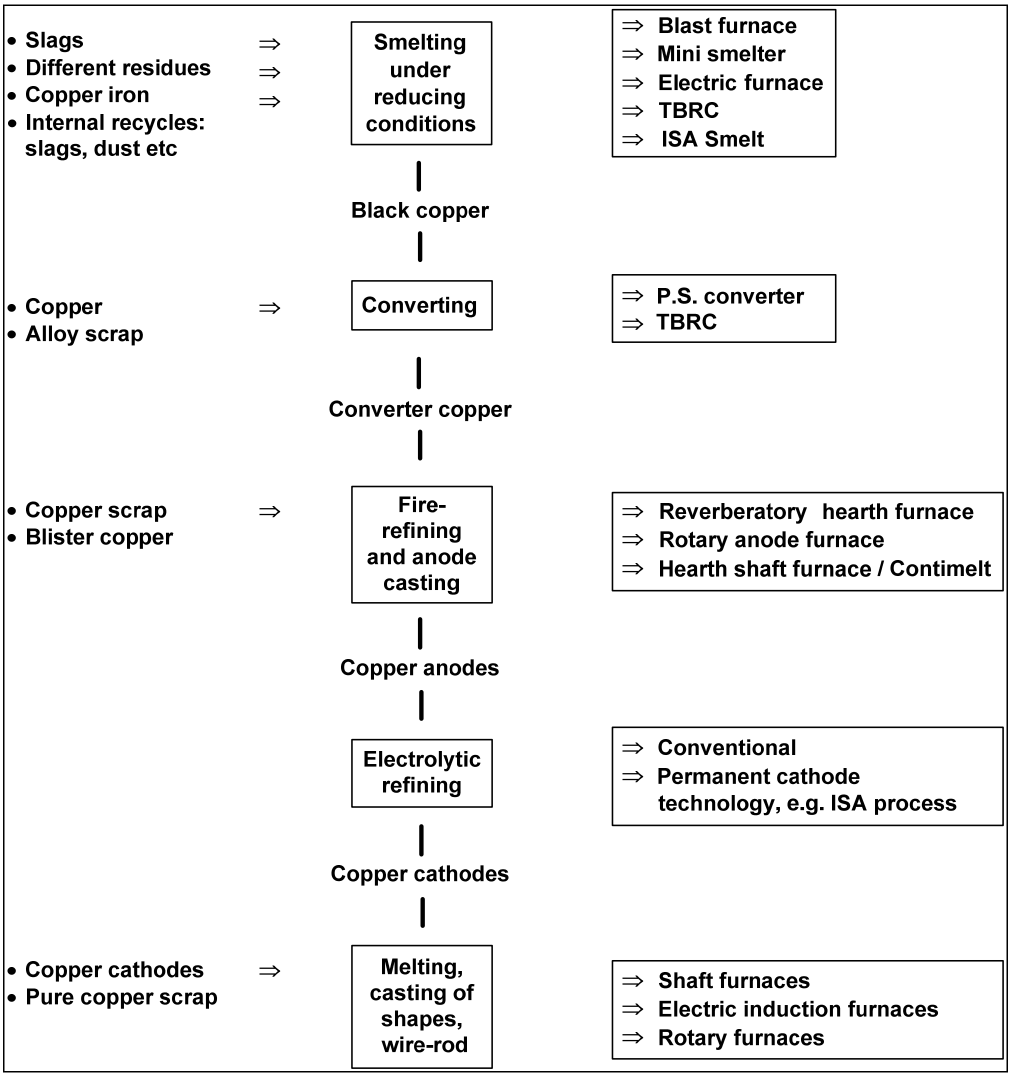


**Figure 3.3:** **Generic flow sheet for secondary copper production**
[ 90, Traulsen, H. 1998 ].

Depending on the type of feed materials in some plants, a flue dust is produced in the first stage that is rich in zinc and lead, for example during blast furnace smelting of lower grade material. These dusts contain up to 65 % combined zinc and lead and are a feed material very suited to be processed in lead production processes for the production of lead and zinc.

### 3.1.3 Tin

Tin is recovered from the residues produced during some of the secondary copper refining processes, from the detinning of coated steel cans and from ores. There is no production of tin in the EU-27 directly from ores but the following techniques are practised in secondary copper smelters:

- At one secondary copper smelter, a second reduction stage is used [ 90, Traulsen, H. 1998 ]. Lead and tin are reduced with scrap steel or tin cans in a TBRC. Lead and tin scrap, slag and residues are added and a lead/tin alloy is produced. The alloy passes to a shaking ladle to remove residual copper, nickel and silicon and the decopperised alloy is then treated in a three-stage vacuum distillation system to separate lead and tin. The tin is refined by crystallisation before the second vacuum distillation stage.

- The flue dust from the secondary copper converter (sometimes also from the blast furnace) is used as feed material. Under reducing conditions, zinc is volatilised and recovered as oxide while lead and tin are produced in the form of an alloy.
- The tin lead alloy furnace technology is used [ 234, UBA Copper, lead, zinc and aluminium 2007 ]. It is a multi-stage reduction process to produce black copper, tin lead alloy and iron silicate slag from the KRS converter slag. As well as the molten converter slag, other intermediates from on-site production or from third parties and secondary materials are input materials. Materials or additives can be charged throughout the process. The slag composition is controlled within defined limits to obtain a marketable product. After a final granulation step, the slag can also be sold. The black copper is recirculated into the KRS furnace. The process and secondary hood off-gases are routed to filter systems. The collected flue dust being either marketed or returned to the KRS bath furnace. The refining of the tin lead alloy includes the following steps:
    - segregation and de-drossing (removal of copper, nickel);
    - removal of the rest of copper, zinc and arsenic with adding sulphur, ammonium chloride and aluminium.

Steel scrap can be detinned by either electrolytic or chemical leaching processes using caustic soda and sodium nitrite [ 8, Hatch Associates Ltd 1993 ]. In the latter case, ammonia is released (0.048 kg per kg tin). Tin is dissolved and then recovered by electrolysis, the tin is removed from the cathodes by dipping in a molten bath of tin. Ingots or tin powder are produced and these are used to produce a range of alloys and coating materials.

Tin is melted in kettles similar to those used for lead and alloys are produced. Scrap tin is also recovered in the melting processes. The most common range of alloys is known as solders and they use lead as the alloying material. Other melting furnaces are used but temperature control is not as easy.

Tin is refined using a number of processes. Electrorefining using steel cathodes is carried out and a pyrometallurgical refining process can also be carried out in a similar manner to lead refining. In the case of tin refining, iron is removed by liquation, copper is removed by the addition of sulphur and arsenic or antimony are removed by the addition of aluminium or sodium.

## 3.1.4 Wire-rod production

Wire-rod is manufactured from high purity electrorefined copper cathodes thus ensuring that trace impurities, which may affect conductivity, annealability and hot shortness, are minimised. Attention is paid to controlling the furnace conditions to minimise oxygen absorption with the metal. The processes are described below [ 114, Eurometaux 1998 ]:

### 3.1.4.1 Southwire process

Shaft furnaces are used for melting copper cathodes and other pure copper scrap material. Melting rates of up to about 60 t/h are achieved. An example of the Southwire process is shown in Figure 3.4.

The feed materials are melted by natural gas, propane or similarly fired burners arranged in rows around the furnace shell. The fuel is burnt under closely controlled combustion conditions to maintain a slightly reducing atmosphere (less than 0.5 to 1.5 % of CO or $H_2$) in the areas where the gases are in contact with the copper to minimise the oxygen content of the copper. This is achieved by independent control of the fuel/air ratio for each burner by monitoring the CO or $H_2$ content of the combustion gases from each burner in turn.

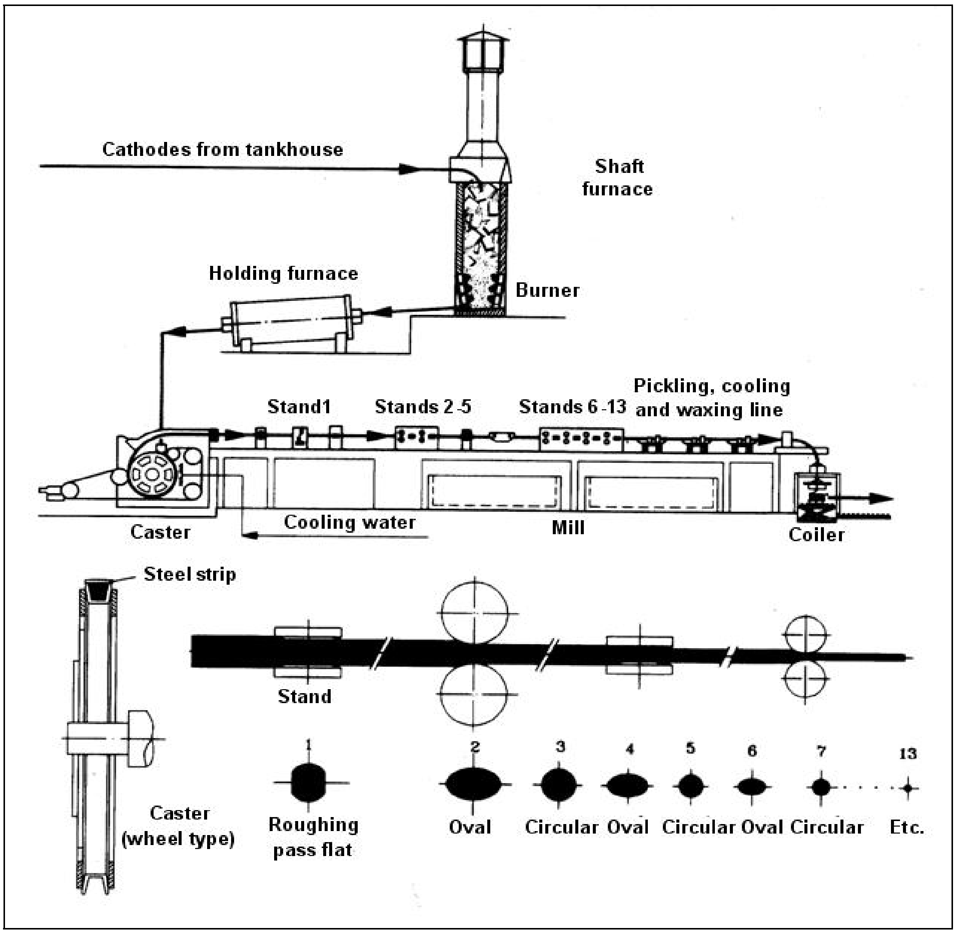


**Figure 3.4:** **Example of the Southwire process**
[ 121, Rentz, O. et al. 1999 ]

Gases from the furnace are cooled and dust is removed using fabric filters. Afterburning can also be used to destroy CO if the concentration is high.

Molten copper is discharged from the base of the shaft furnace and flows to a cylindrical holding furnace for temperature adjustment and balancing of the metal and for metallurgical treatment. Natural gas-fired burners are provided to maintain the temperature of the molten cooper and a reducing atmosphere in the launders. The holding furnace, which is also natural gas or similarly fuel fired, serves as a reservoir to provide a constant flow of metal to the casting process and, if required, can be used to superheat the metal.

Molten copper flows from the holding furnace via a tundish equipped with flow control to the casting wheel. A water-cooled, steel band encloses over half of the circumference of the wheel, forming the casting cavity into which the molten copper solidifies to form a trapezoidal cast bar ranging between 5000 and 8300 mm². Acetylene, burnt with air is used to produce a soot dressing for the casting wheel and steel band. After being levelled and shaved, the cast bar is fed by pinch rolls to a rolling mill consisting of a roughing section and one finishing section which reduces the bar to its final diameter. A mineral oil emulsion or synthetic solution in water is used as a rolling fluid [ 219, VDI (D) 2102 2007 ].

### 3.1.4.2 Contirod process

A shaft furnace as described above is used to melt copper. Molten copper from the furnace flows via a launder equipped with siphons into a rotating, gas heated holding furnace. The copper then flows to the pouring funnel, which automatically controls the feeding rates to the caster [ 114, Eurometaux 1998 ]. An example of the Contirod process is shown in Figure 3.5.

The twin belt Hazelett casting machine is used [ 121, Rentz, O. et al. 1999 ] [ 219, VDI (D) 2102 2007 ]. The two belts are cooled by a continuous film of water that moves at high speed along the length of their surface. The side blocks are automatically cooled in a specially designed cooling area located on the return strand of the loop. Depending on plant size, the cast bar area can range between 5000 mm$^2$ and 9100 mm$^2$ and production capacities between 25 and 50 tonnes per hour. The rectangular bar is cooled, the four corners are milled to remove any flash and the bar then enters a rolling mill comprising alternative horizontal and vertical passes to produce a final product. A mineral oil emulsion or synthetic solution in water is used as a rolling fluid.

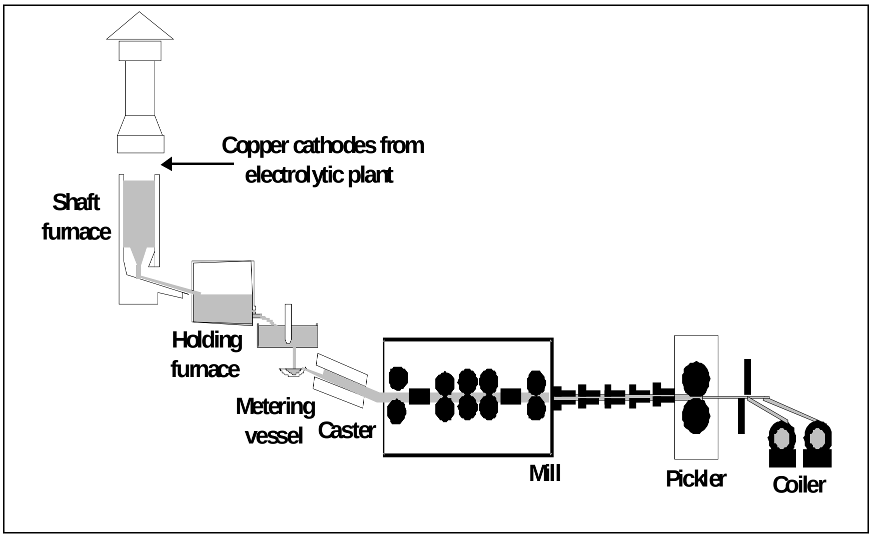


**Figure 3.5: Example of the Contirod process**
[ 121, Rentz, O. et al. 1999 ]

### 3.1.4.3 Properzi and Secor processes

The continuous Properzi and Secor processes are similar to the Southwire process (see Section 3.1.4.1) with variations in casting geometry [ 114, Eurometaux 1998 ]. The features described for the Southwire process are also valid for these two copper wire-rod fabrication systems.

### 3.1.4.4 Upcast process

Copper is melted in a channel induction furnace. The melt is transferred in batches into an induction holding furnace. For small production capacities, a single combined melting-holding furnace may be sufficient [ 114, Eurometaux 1998 ].

The Upcast withdrawal machine is located above the holding furnace. Water-cooled graphite dies are submerged a certain depth into the melt and the molten copper runs continuously into the dies where it solidifies and is drawn up to the pinch rollers. The solidified wire-rod is pulled upwards by the pinch rollers.

### 3.1.4.5 Dip forming process

The preheated feed material is discharged into a channel induction-melting furnace. Copper passes to the holding furnace and crucible that is attached to the holding furnace. A mother rod, 12.5 mm in diameter, is drawn through an inlet die at the base of the crucible. Drawing the core wire through the metal pool and controlling the final diameter through the upper die increases the diameter. The cast rod is directed via dancers to a three-stand rolling mill producing 8.0 mm and 12.5 mm rods [ 114, Eurometaux 1998 ].

### 3.1.5 Production of semi-finished products of copper and copper alloys

Copper and copper alloys are melted continuously or in batches and cast for the production of shapes suited to the further fabrication step [ 219, VDI (D) 2102 2007 ]. The cast products are precursors for a variety of materials such as sheets, strips, sections, bars, rods, wires and tubes. Generally the following routes are taken [ 114, Eurometaux 1998 ]:

- billets are mostly made from copper and copper alloys for the production of tubes or sections and rods;
- slabs and cakes are cast from copper and copper alloys for the production of sheets or strips;
- special processes are applied for specific products from copper and copper alloys: the Upcast process for wires and tubes, horizontal continuous casting for strip and sections, vertical strip casting and roll processes for the fabrication of copper tubes.

A general flow sheet of semi-finished product fabrication is shown in Figure 3.6:

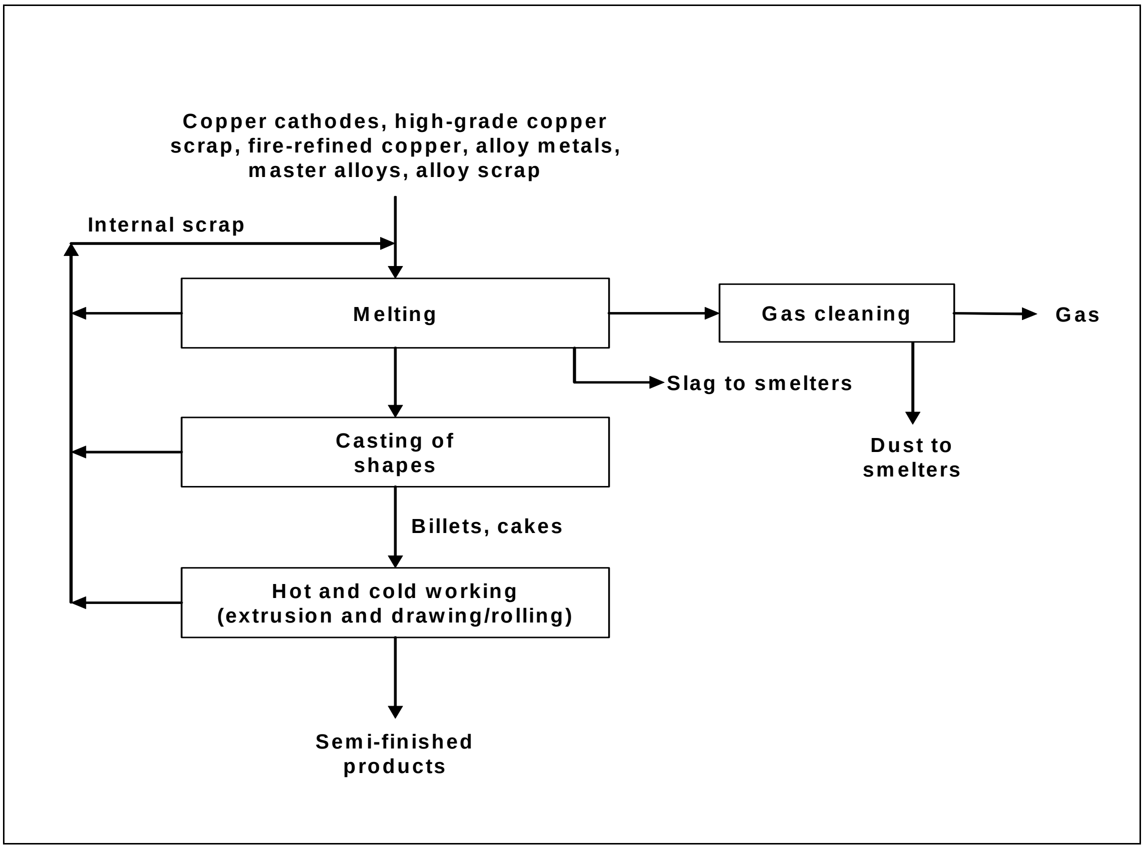


**Figure 3.6: General flow sheet of semi-finished product fabrication**
[ 121, Rentz, O. et al. 1999 ]

### 3.1.5.1 Melting processes

Copper or copper alloys can be melted in batches in an electric or induction furnace (crucible or channel type). When high melting rates are required, copper is also melted continuously in a shaft furnace. Crucible or reverberatory furnaces are also used for melting and fire-refining copper. The fume collection and abatement systems are chosen according to the raw material and the degree of contamination present. The gas collected from electric furnaces is normally cleaned in cyclones followed by fabric filters. For gas-fired shaft furnaces, the control of the burners is a critical factor to minimise the CO content of the gases emitted. An afterburner followed by heat recovery systems are in use if the CO content is high enough (e.g.>5 % CO); fabric filters are also used for dedusting in shaft furnaces.

Copper cathode and copper and alloy scrap is used as the raw material and is normally stored in open bays so that the different alloys can be blended to produce the final alloy. This pre-blending is an important factor to reduce the time taken in preparing the melt, which minimises the energy used and reduces the reliance on expensive master alloys. With induction furnaces ,scrap is cut into small sizes to improve the melting efficiency and allow easy deployment of hoods, etc.

Raw materials are also brasses or copper turnings and borings and in this case are coated with lubricants. Care is taken to prevent oil leaking from the storage area and contaminating ground and surface water. Similarly, swarf dryers or other furnaces and solvent or aqueous de-oiling methods are used to remove lubricants and other organic contamination [ 219, VDI (D) 2102 2007 ].

When brasses or bronzes are melted, zinc is fumed from the furnace, good control of the temperature can minimise this. Fume is collected in the gas extraction system and removed in a fabric filter. The zinc oxide is normally recovered. A degree of fire-refining is also carried out and the resulting fumes are taken into account in the design of the fume collection and abatement systems.

### 3.1.5.2 Casting

Normally molten metal from the furnace or holding section can be cast continuously or in batches [ 114, Eurometaux 1998 ]. Continuous casting uses either vertical or horizontal modes (see Figure 3.7) but discontinuous casting normally uses the vertical mode. Upcast techniques are also used. Billets and cakes/slabs are produced and are processed further.

The principle of continuous or semi-continuous casting is given in Figure 3.7.

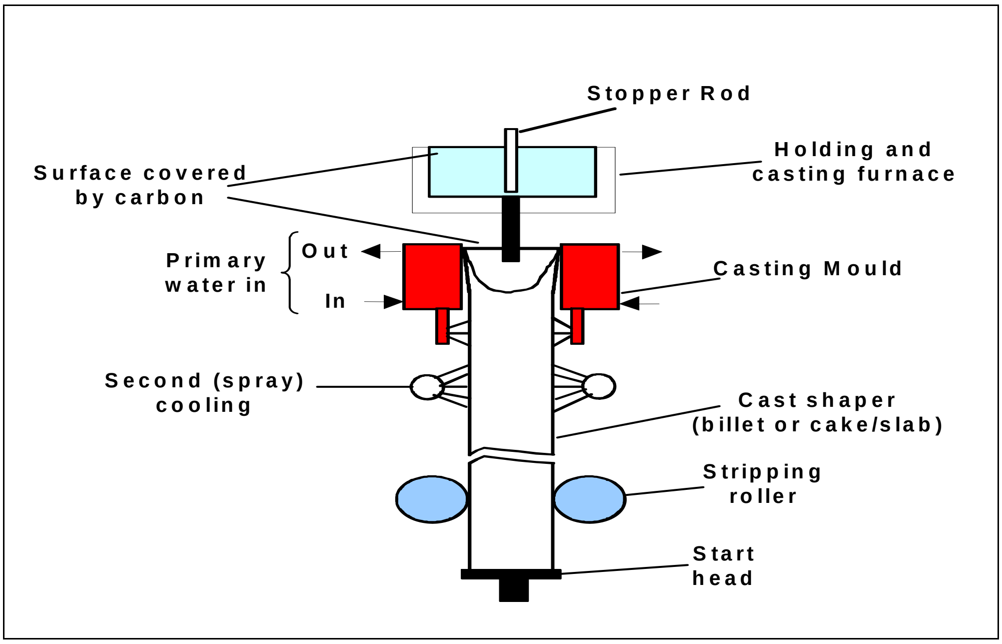


**Figure 3.7: Principle of continuous or semi-continuous casting**
[ 121, Rentz, O. et al. 1999 ]

The normal shapes produced by casting are:

- billets for the production of tubes, rods and sections using continuous or discontinuous casting
- slabs or cakes for the production of sheets and strips using continuous or discontinuous casting.

Metal is melted and passes via a holding furnace into a vertical or horizontal billet caster. Sections of billets are sawn off for further fabrication. Special processes are applied for specific products from copper and copper alloys: the Upcast process for wires and tubes, horizontal continuous casting for strip and sections, vertical strip casting and roll process for the fabrication of copper tubes.

The cast strand on vertical or horizontal casting units is cut using the flying saw technique. In a discontinuous casting unit, the format length is determined by the depth of the casting pit. After reaching the maximum format length, casting is interrupted and the cast shapes are extracted by crane or elevator. In the case of continuous casting, it is not necessary to interrupt the casting process. All casting operations need direct cooling water for final solidification and cooling down of the cast strand down to temperatures allowing further handling. The cooling water can be recycled after sedimentation and separation of solids (casting scales). If the scales are not contaminated with graphite or other particles, they are recirculated to a smelter for processing if not directly re-used in the casting shop.

A comparison of the plant data for typical continuous vertical and horizontal continuous casting installations is given in Table 3.5.

| Parameter | Vertical continuous casting | Horizontal continuous casting |
|---|---|---|
| Ingot diameter | 70 to 1500 mm | 150 to 400 mm |
| Capacity | 8 t/(h and strand) | 8 t/(h and strand) |
| Casting rate | 80 to 800 mm/min | 80 to 200 mm/min |
| Casting temperature | 980 to 1200 °C | 980 to 1200 °C |
| Operating mode | One strand or a number of strands | One or a number of strands |
| Withdrawal cycle | Continuous | Continuous or cyclical |
| Secondary cooling | Using sprayed water | Does not necessarily use sprayed water, although this is possible |
| Type of mould | Copper mould, graphite mould | Graphite mould |

**Table 3.5: Comparison of the plant data for typical continuous vertical and horizontal continuous casting installations**
[ 121, Rentz, O. et al. 1999 ]

### 3.1.5.3 Fabrication of tubes, sections and rods

The fabrication process lines can be subdivided into two product groups, with each product group following the same process steps:

- copper tubes in straight length and coils
- copper (alloy) tubes as well as copper and copper alloy rods, bars, wires and sections.

In both cases the starting materials for the fabrication process are copper or copper alloy billets. The billets in a first stage are electrically or indirectly preheated by gas-fired units and then pressed in unfinished tubes using hydraulically-operated extrusion presses [ 219, VDI (D) 2102 2007 ]. For the fabrication of copper tubes, depending of the type of product to be fabricated, different processes are industrially applied:

- tube extrusion followed by multi-step drawing to size
- tube extrusion followed by breakdown rolling followed by several steps of drawing to size
- hot piercing mill followed by breakdown rolling and drawing to size.

For billets, which are extruded or rolled into tubes with thick walls, breakdown rolling normally has the preference for being the first size reduction step.

For tubes extruded to thin walls, tube drawing machines are applied.

For the fabrication of copper alloy rods, bars, wires and sections the processes that are normally used are material extruding in coils or straight lengths followed by cleaning and pickling, drawing to size (using drawbenches or continuous drawing machines), heat treatment for certain alloys and straightening and sawing.

The whole process, starting with the extrusion press or the hot piercing mill, is a sequence of (mostly) reducing steps changing the shape and size. During these processing steps the tools of the equipment for size and shape changing are cooled and protected by adequate media, using emulsion for the breakdown rolling and lubricants for the drawing units. The emulsions for the breakdown rolling are cleaned up by filtration, thus increasing the lifetime and reducing the amount of lubricant to be disposed of after treatment. However, the lubricants used for the drawing steps are completely lost with the product and no oily materials have to be rejected from the drawing processes.

The products are normally annealed and degreased before transport and the off cuts are de-oiled in a furnace or other degreasing processes before being returned to the furnace for melting. Products are annealed in a variety of furnaces under reducing conditions using (as the protection gas) exogas or hydrogen/nitrogen mixtures.

Copper tubes may also be produced utilising an extrusion press with a piercer in which billet sections are extruded to tube shell pieces; the tube shell pieces are then rolled in a breakdown roller (pilger mill) and finally drawn to size in drawing blocks. The oil utilised (in small quantities) for the drawing operations is neutralised using in-line degreasing/pickling systems often connected with the annealing section.

#### 3.1.5.4 Fabrication of sheets and strips

Slabs and cakes from the casting shop are, in most cases, the starting material for the fabrication of sheets and strips. The key elements of the fabrication process for flat products are the hot and subsequent cold rolling operations. In detail the fabrication process comprises the following steps:

- preheating
- hot rolling and milling
- cold rolling
- intermediate annealing
- pickling, rinsing and drying
- re-rolling and strand annealing
- finishing:
    - sheets (cutting to length)
    - strips (cutting to width).

The hot rolling of the cast slabs takes around 15 to 20 slabs until the final shape is reached and is determined by the slab weight. There is no loss of metal during hot rolling so that slab and coil weight are identical. The hot rolling mill does not require protection gas. The noise development during rolling is controlled by protective measures [ 234, UBA Copper, lead, zinc and aluminium 2007 ].

Hot rolling is usually done with a dual rolling mill equipped with benches up to 200 m and a final coiling device. The cooling water for the rolls has small amounts of lubricant added for improving the attachment to the steel rolls. The vapour generated is vented and the vent gas is demisted prior to release to atmosphere.

Further cold rolling operations are then performed. Cold rolling results in a hardened metal. In most cases, the coil is annealed prior to cold rolling. Annealing is done under reducing conditions to avoid oxidation. A protection gas of exogas or nitrogen/hydrogen mixtures are used. Exogas is produced on site from natural gas in a special reactor, which is indirectly fired. Nitrogen and hydrogen are purchased and stored on site in special tanks. The $N_2/H_2$ protection gas mixtures are produced from the storage tanks by mixing the components in the ratio required. For annealing before cold rolling, bell-type furnaces are used with electric heating or indirectly fired by natural gas or fuel oil. Tower-type furnaces are applied for intermediate annealing of pre-rolled coils.

The sheet thickness is further reduced by stepwise cold rolling operations on different reversing mills. For cold rolling, different types of mills called Duo, Quarto, Sexto and Sendzimir (12 rolls) are used. Rolling mill designs such as single-stand mills which are combined to an in-line multi-stand rolling mill are also applied. It depends on the thickness of the sheet and on the desired dimensions of the coil which type of mill is used.

During cold rolling, an emulsion or oil is used for roll protection. Therefore, the roll stands are vented and the ventilation gases are cleaned by mechanical filters, wet electrostatic precipitators or scrubbing. The emulsion and the oil is cleaned from metal and cracked oil particles are removed by paper or textile band filters.

Typical data for a process to produce brass strip is given in Table 3.6.

| **Hot rolling** | **Process data** |
|---|---|
| Type of mill | Mainly Duo |
| Initial dimensions | 250 - 130 mm thickness,<br>450 - 1000 mm width |
| Final dimensions | 15 - 12 mm thickness,<br>450 - 1000 mm width |
| Temperature | 750 - 800 °C |
| Rolling force | ~ 10 - 12 kN/mm sheet width |
| Surface milling | 0.3 - 0.7 mm cutting of both surfaces |
| **First cold rolling** | |
| Type of mill | Mainly Quarto |
| Rolling force | ~ 15 - 20 kN/mm sheet width |
| Dimension reduction and rolling speed | Reduction 15 mm to 4 mm thickness in multiple passes, speed 100 - 200 m/min |
| Conversion ratio | 70 - 80 % |
| Annealing(1) (recrystallisation) | |
| Temperature | 550 - 600 °C |
| **Second and final rolling** | |
| Type of mill | Mainly Quarto, alternatively, depending on sheet thickness, Sexto or stands where 20 rolls are used |
| Rolling force | ~ 2 - 10 kN/mm sheet width, depending of type of mill used |
| Rolling speed | Reduction 4 to 1 mm: 300 - 500 m/min, multiple passes<br>or reduction 1 to 0.1 mm: 500 - 1000 m/min, multiple passes |
| **Cutting of sheets into strips** | |
| Type of equipment | Longitudinal strip cutting machine |
| (1)Annealing is required after every conversion ratio of more than 70 - 80 %; annealing temperatures selected depend on the material properties to be achieved. | |

**Table 3.6: Typical data for a process to produce brass strip**
[ 121, Rentz, O. et al. 1999 ]

### 3.1.6 Copper and copper alloy ingots

Ingots of copper or its alloys are produced for the foundry industry using a fixed mould casting process. A wide variety of alloys are produced with other metals such as nickel, tin, zinc, aluminium, etc.

The production of ingots requires the production of an accurate alloy composition. This is achieved at the raw material reception and storage stage by segregation and sorting. Old scrap is normally stored in open bays so that the different alloys can be blended to produce the final alloy. Preblending is an important factor to reduce the time taken in preparing the melt, which minimises the energy used and reduces the reliance on expensive master alloys. Copper or copper alloys can be melted in batches in rotary or induction furnaces. Rotary furnaces are normally used for dirtier scrap, and oxy-fuel burners are also used frequently. Fluxes can be added to separate unwanted components in particular iron and the slag is tapped separately from the metal. The yield of metal ranges from 70 to 97 % but depends on the raw materials used [ 103, Farrell, F. 1998 ].

The fume collection and abatement systems are chosen according to the raw material and the degree of contamination present. Access to an induction furnace for charging and tapping means that a movable hooding system is used. The hoods are robust so that they can withstand some mechanical impact. The gas collected from induction furnaces is normally cleaned in cyclones followed by fabric filters. An afterburner followed by a heat recovery system can be used for cases where there is organic contamination, alternatively the furnace combustion control system should be able to accommodate the combustion of contaminants.

When brasses or bronzes are melted, zinc is fumed from the furnace, but a good level of control of the furnace temperature can minimise this. Fumes are collected in the gas extraction system and are usually removed in a fabric filter. The zinc oxide is normally recovered. A degree of fire-refining is also carried out to adjust alloy composition and the resulting fumes are taken into account in the design of the fume collection and abatement systems.

The furnace melt is sampled and analysed and final alloy adjustments are made. Metal is then tapped in to covered launders that feed a chain of ingot moulds. The moulds are normally treated with a mineral to prevent sticking and oil fumes are produced. Oil can be collected and burnt.

Cooled ingots are stacked, bound and stored in the open on pallets.

#### 3.1.6.1 Master alloys

The furnace charge is normally pre-adjusted to suit the alloy to be used but molten metal can be transferred to a ladle or holding furnace so that the alloy composition can be finely adjusted before casting. Master alloys such as CuP, CuNi, CuZnPb, CuBe, etc. are used for this purpose. These master alloys are produced in similar furnaces to those described above, the nature of fumes and dust from the production of master alloys influences the process control, and collection and abatement systems that are used. More stringent operating and abatement systems are particularly appropriate when extremely hazardous materials such as beryllium are used or when reactive materials such as phosphorus are added to produce an alloy. For example phosphorcopper master alloy is made in the following way: Two furnaces (induction furnaces are commonly used) are operated in series; copper is melted in the first furnace and transferred to the second where molten phosphorus is injected by a lance to form the alloy; the rate of injection is controlled to minimise phosphorus pentoxide fume, particularly during the final stages when the metal is approaching saturation (<14 % P); the phosphor copper is then tapped into moulds; phosphorus pentoxide fumes continue to be emitted as the alloy cools if the phosphorous content is too high.

Phosphorus pentoxide is very hygroscopic and as a consequence the fumes cannot be filtered using a conventional fabric filter as the fumes will absorb moisture and coat the bags with phosphoric acid. Conventional wet scrubbing has a limited effect as the fine fumes form a fine mist and fail to contact the scrubbing medium. Effective reduction of the concentration of phosphorous compounds in the gas stream can be achieved by using high energy venturi scrubbers or fibrous mat filters. In theory, a weak acid could be produced for further processing but this is difficult in practice.

### 3.1.7 Pickling operations

Wire, tube, strip and some other materials are pickled to produce a bright finish before packing or, in the case of copper wire, to remove oxide from the surface prior to wire drawing. Sulphuric acid solutions are used and sometimes a mixture of dilute sulphuric and nitric acids are used. In the latter case, nitric fumes can be emitted if higher strength acids are used.

#### 3.1.7.1 Nonacid pickling of copper rods

This process operates in a sealed circuit. Rods can be pickled in an in-line system that consists of a compartmentalised horizontal steel pipe. A 2.5 to 3.5 % solution of isopropanol alcohol (IPA) in water is used. The process of converting the cuprous oxide scale with alcohol to form copper (partly left on the rod) is known as the Burns process [ 114, Eurometaux 1998 ]. In copper wire-rod fabrication, normal practice is to recycle the solution to pickling after copper sludge removal by settling or filtration; the IPA concentration is adjusted as required.

After pickling, the rod is dried using compressed air. Then it is given a coating of wax, applied as a fine spray with a 4 % wax emulsion which prevents oxidation of the surface of the rod. The rod is down coiled on to wooden pallets and compacted, strapped and wrapped in plastic sheet.

#### 3.1.7.2 Acid pickling of copper rods and semis of copper and copper alloys

**Copper wire rod**

Acid pickling of copper wire-rod uses a compartmentalised horizontal stainless steel pipe [ 114, Eurometaux 1998 ]. In a first stage, the rod is pickled with diluted sulphuric acid; then the residual acid is washed in several stages from the rod surface by water sprays followed by drying using compressed air and coating by wax.

Alternatively, after partial cooling in a long water-filled tube, the rod is formed into spirals corresponding to the diameter of the coil. These spirals are spread onto a roller table where the temperature is reduced to 20 ºC by water sprinklers. An acid-resistant alloy conveyor carries these spirals into the pickling tanks where the rod is pickled with a 20 % sulphuric acid solution. The acid pickling system ensures a perfect removal of all oxides from the rod surface. The loops are then washed with rinsing water and finally protected by a wax solution.

Electrowinning to recover the copper dissolved by the pickling acid is used or the wash solution may also be transferred as make-up to a tankhouse at the same site or treated by ion exchange.

**Semis of copper and copper alloys**

Surface pickling of sheets and strips is usually performed with sulphuric acid (8 - 10 %) but for some special alloys, mixtures of sulphuric and nitric acids are used in continuous lines or automatic systems. Gas cleaning is used to remove nitric acid fumes. The acid is changed from time to time in order to ensure that surface quality is not affected [ 114, Eurometaux 1998 ].

Spent acid is sent for treatment and for the recovery of metal in internal or external treatment plants. The pickling systems are vented for worker protection. The products are rinsed, the rinse water is then sent for treatment, and the sludges are recycled if possible. For surface degreasing of rolled products, water that contains detergents are used. The spent water is cleaned by ultrafiltration.

## 3.2 Current emission and consumption levels

The main environmental issues of the refined copper industry are air and water pollution [ 27, M. Barry et al. 1993 ], [ 206, Traulsen, H. 1999 ]. The facilities generally have their own waste water treatment facilities and waste water recycling is usually practised. Most potential wastes are re-used.

Some local aspects, like noise, are relevant to the industry.

Due to the hazardous nature of some solid and liquid wastes, there is also a significant risk of soil contamination unless these wastes are stored and handled correctly.

Diffuse emissions can be highly significant (see Section 2.4). Measurements have been carried out at one major copper smelter producing primary and secondary copper. The results clearly show that diffuse emissions predominate even after improvements were made to secondary fume capture systems [ 158, Petersen, K. 1999 ]. In this example the dust loads that were measured are as follows in Table 3.7[rr12].

| | Dust emission (kg/yr) | |
|---|---|---|
| | Before additional secondary gas collection (1992) | After additional secondary gas collection (1996)(1) |
| Anode production t/yr | 220000 | 325000 |
| Diffuse emissions:<br>• total smelter<br>• smelter roofline | <br>66490<br>56160 | <br>32200<br>17020 |
| Primary smelter stack emissions:<br>• smelter/acid plant<br>• stack-secondary hoods | <br>7990<br>2547 | <br>7600<br>2116 |
| (1) Emissions after an investment of EUR 10 million to give an improved diffuse gas capture and treatment system. Additional energy = 13.6 GWh/yr | | |

**Table 3.7: Comparison of abated and diffuse dust loads at a primary copper smelter**
[ 158, Petersen, K. 1999 ]

### 3.2.1 Energy consumption~~usage~~ in copper production[rr13]

Copper production requires energy in most stages and the energy used in the electrolytic process is most significant [ 25, OSPARCOM 1996 ]. The production energy (net) requirement for a number of processes using copper concentrate is in the range of 14 - 20 GJ/t copper cathode [ 206, Traulsen, H. 1999 ]. The exact figure depends mainly on the concentrate (% sulphur and iron), but the smelting unit used, the degree of oxygen enrichment and the collection and use of process heat also have an influence. Comparative data based solely on the type of smelter are therefore liable to inaccuracies. The utilisation of the energy content of the concentrate is more important and smelters that achieve autogenic operation have lower energy use.

The energy consumed by the electrorefining stage of copper production is reported to be 300 - 400 kWh per tonne of copper but the energy used is considerably higher when high impurity anodes are electrorefined [ 134, Metallurgical Consulting Traulsen GmbH 1998 ]. The type of blank cathode used (stainless steel or copper) mainly influences the efficiency of the tankhouse [ 90, Traulsen, H. 1998 ] and this can range from 92 to 97 % in terms of current efficiency.

Data on energy consumption for abatement systems ~~use is~~are given in Annex I, Table 14.11, Table 14.12, Table 14.13, Table 14.14, Table 14.15, Table 14.16, Table 14.17, Table 14.18, Table 14.19 and Table 14.20.

## 3.2.2 Emissions and consumption data

The main sources of emissions and consumption for the production of copper are described below:

### 3.2.2.1 Primary copper input and output

The input and output data for a primary smelter depends on the copper content of the concentrate, the concentration of other metals (As, Se, Hg, Ag, Au, etc.) and the use of copper scrap or other material that contain copper in the various parts of the process.

Figure 3.8 illustrates the inputs and potential outputs from a typical process for the production of primary copper and Figure 3.9 shows

the gas treatment system.

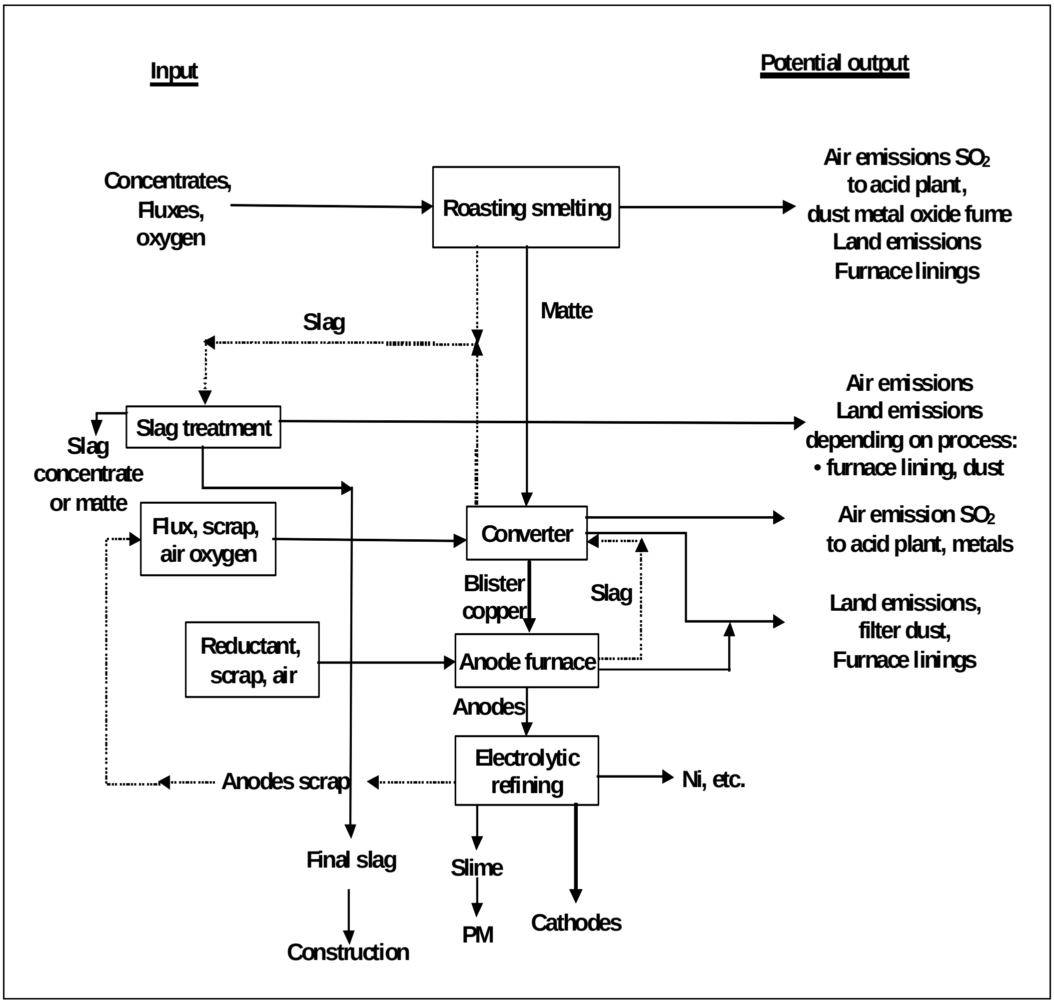


**Figure 3.8: Generic input and output diagram for primary copper**
[ 234, UBA Copper, lead, zinc and aluminium 2007 ]

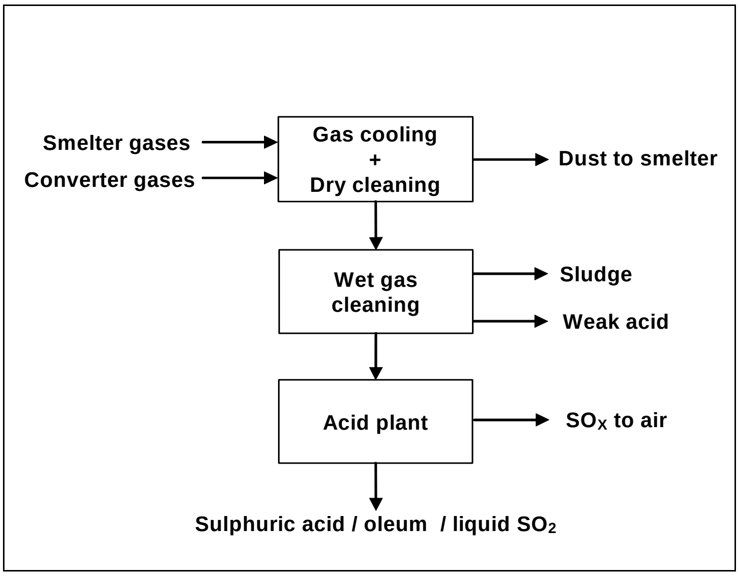


**Figure 3.9: Treatment of smelter and converter gases**
[ 234, UBA Copper, lead, zinc and aluminium 2007 ]

*(Check whether this is a sufficient flow chart for the off-gas treatment in primary copper production. It seems to be unclear, does dry gas cleaning always takes place prior to the aicid plant, where is wet gas cleaning applied? I.e. for the electric furnace for alloy converter)*

Some primary copper smelters are integrated with secondary smelting facilities or with the production of lead or zinc oxide dust from mixed concentrates, etc. The input and output data are therefore very difficult to compare. Values for a complex process are given in Table 3.8 below. It should be noted that the main influence on the input and output data is the copper content of the concentrate or other raw material and so there can be variations of the data and comparisons are not significant. The recovery of copper during smelting and refining is more meaningful and is greater than 96 %.

| Input materials | Quantity (t/yr) | Products | Quantity (t/yr) |
|---|---|---|---|
| Copper concentrates | 1040000 | Copper cathode | 366000 |
| Copper scrap | 65000 | Copper salts | |
| Shredded material from electronic scraps | 3600 | Nickel sulphate | |
| External intermediate products | 56000 | Precious metals | 960 |
| | | Refined lead | 17000 |
| | | Sulphuric acid | 1018000 |
| | | Slags | 690000 |

**Table 3.8: Example input and output data for a primary copper smelter/refinery**
[ 121, Rentz, O. et al. 1999 ], [ 234, UBA Copper, lead, zinc and aluminium 2007 ]

### 3.2.2.2 Secondary copper input and output data

As reported above, secondary raw material can be fed into various parts of the secondary processes depending on the purity, contents of other metals and degree of surface contamination [ 219, VDI (D) 2102 2007 ]. The degree of organic contamination affects the potential emissions, and in several process stages, afterburners are used to destroy organic components such as PCDD/F depending on the degree of organic contamination present. Figure 3.10 and Figure 3.11 show generic input and output diagrams for secondary copper.

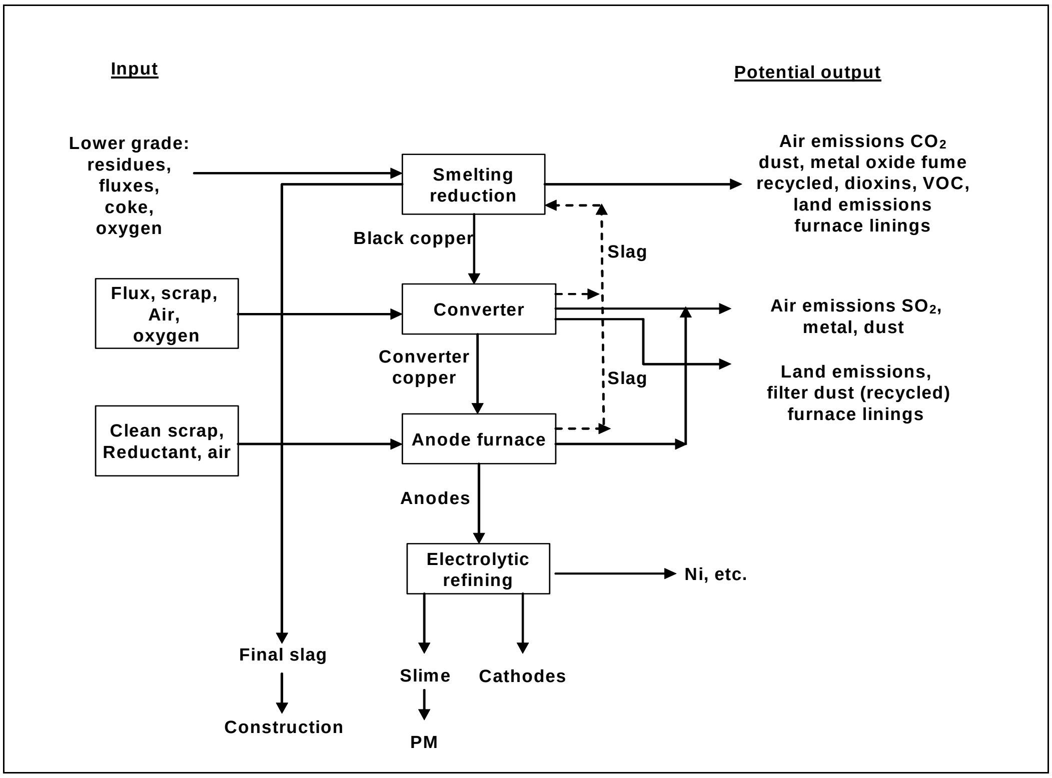


**Figure 3.10:** Generic input-output diagram for secondary copper smelting
[ 234, UBA Copper, lead, zinc and aluminium 2007 ]

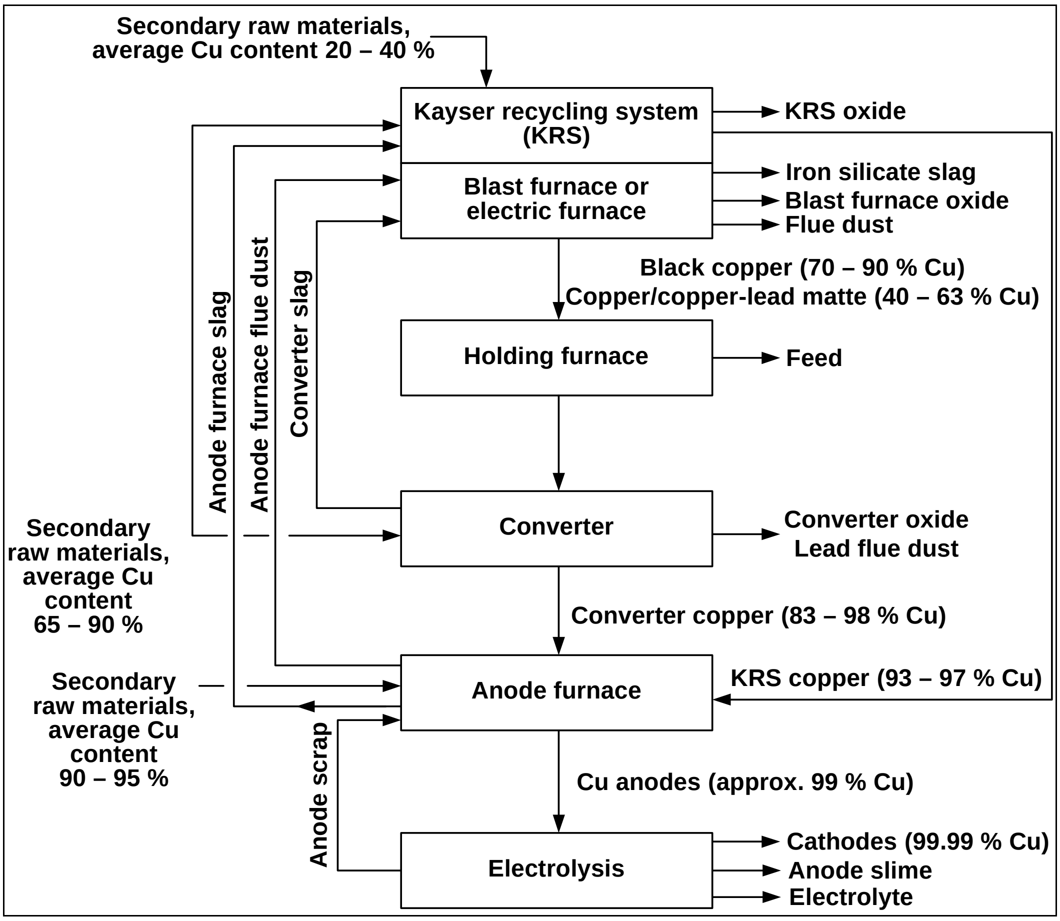


**Figure 3.11: Example of an input-output diagram from a secondary copper production site with a tin/lead recovery process**
[ 234, UBA Copper, lead, zinc and aluminium 2007 ].

Many residues are recycled within the process and to other associated processes. Producers of non-ferrous metals, for example lead, zinc and tin, use many of the residues as raw materials for their processes [ 219, VDI (D) 2102 2007 ]. Several sites have incorporated on-site processes to recover other metals from these residues.

Table 3.9 and Table 3.10 reflect one example of~~the typical~~ inputs and outputs of a secondary copper smelter, existing of a KRS furnace, a lead/tin alloy plant, a reverberatory hearth furnace and electrolysis. The ranges depend on the availability of materials.

| Inputs | Quantity (t/yr) | Outputs | Quantity (t/yr) |
|---|---|---|---|
| Copper scrap | 100000 - 120000 | Copper cathodes | 185000 |
| Blister copper | 10000 - 30000 | Copper sulphate | 10500 - 2000 |
| Copper anodes | 0 - 40000 | Nickel sulphate | 2500 - 3000 |
| Copper alloy scrap | 20000 - 30000 | Zinc oxides | 12000 - 15000 |
| External residues and wastes (e.g. slags, dusts, ashes, sludges, sweeps, etc.) | 50000 - 70000 | Lead/tin alloys | 2500 - 3000 |
| Copper-iron material (1) | approximately 50000 | Anode slime | 1500 - 1800 |
| Limestone | 5000 - 7000 | Slag | 100000 - 120000 |
| Silica | 10000 - 15000 | $CO_2$ | 73000 – 103720 |
| Coke | approximately | | |

| | |
|---|---|
| | 1000 |
| Fuel (Oil) | 20000 - 30000 |
| NB: ($^1$) including electronic scrap<br>$CO_2$ output equivalent to 0.4 – 0.56 t per t copper | |

**Table 3.9: Input-output data for the secondary copper process shown in Figure 3.11**
[ 234, UBA Copper, lead, zinc and aluminium 2007 ]

| Parameter | KRS furnace | Shaft Furnace |
|---|---|---|
| t steam (GJ)/t burden | 0.6 (1.7) - 0.7 (2.0) | 0.7 (1.8) |
| Burden throughput (t/h) | 25 to 50 (including iron) | 5 - 20 |
| Volumetric off-gas flow ($m^3/h$) | 300000 | 50000 - 100000 |
| Dust content ($mg/m^3$) | 5000 - 10000 | 20000 - 40000 |
| **Main dust constituents (filter dust, depending on operating mode)** | | |
| Cu (% by mass) | 3 - 6 | <5 |
| Pb (% by mass) | 15 - 20 | 10 - 40 |
| Zn (% by mass) | 35 - 50 | 30 - 60 |
| Sn (% by mass) | 2 - 4 | 1 - 5 |
| **Clean gas** | | |
| Dust content ($mg/m^3$) | 1 - 5 | 1 - 5 |
| $SO_2$ ($mg/m^3$) | <500<br>Daily mean<br>Peak half hourly value<br>1500 | 10 - 100 |
| $NO_X$ ($mg/m^3$) | 10 - 100 | 30 - 100 |
| PCDD/F (ng ITEQ/$m^3$) | <0.1 – 0.4 | 2.3 to 29.5 without reduction measures<br><0.5 with oxygen injection |
| Off-gas temperature at stack outlet (°C) | 80 - 90 | 75 - 90 |

**Table 3.10: Differences in the operating parameters between a KRS and a shaft furnace**
[ 234, UBA Copper, lead, zinc and aluminium 2007 ]

### 3.2.2.3 Emissions to air

Dust, metal compounds, organic carbon (which can result in the formation of PCDD/F) and sulphur dioxide can be emitted to air [ 121, Rentz, O. et al. 1999 ]. The potential sources and relevance of potential emissions to air are shown in Table 3.11 and they are discussed later in this section.

| Emission source | Dust and metal compounds | PCDD/F | Organic carbon | Sulphur compounds |
|---|---|---|---|---|
| Material handling | •• | | | |
| Storage of raw materials | ••• | | | |
| Drying | ••• | | • | • |
| Scrap treatment | •• | ••• (secondary) | ••• (secondary) | |
| Smelting | ••• | ••• (secondary) | •(secondary) | ••• (Treated in a recovery plant) |
| Converting | •• | • (secondary) | • (secondary) | ••• (Treated in a recovery plant) |

| | | | | |
|---|---|---|---|---|
| Refining | •• | • (secondary) | • (secondary) | • |
| Melting/casting | • (•• for alloys) | | • (secondary)<br>+ CO | |
| Ladle transfers | ••• | | | • |
| Electrolysis | | | | |
| Slag treatment | •• | | •CO<br>(from electric furnace) | |
| NB: ••• more significant – • less significant | | | | |

**Table 3.11: Significance of potential emissions to air from copper production processes**

*How has this table to be understand? If secondary is inserted does it mean that these emissions appear only in secondary copper production and if nothing is mentioned does it mean that in primary and secondary copper production these emissions are relevant?*

Oxides of nitrogen are relatively insignificant [ 23, DFIU-University Karlsruhe 1996 ] but may be absorbed in the sulphuric acid produced from a primary process; the use of oxygen enrichment can sometimes reduce the formation of nitrogen oxides by the thermal route. This depends on the point where oxygen is added, sometimes a higher concentration of nitrogen oxides is produced due to the increase in temperature, however the gas volume and total quantity is lower. Low-$NO_X$ burners can be used.

The formation of PCDD/F in the combustion zone and in the cooling part of the off-gas treatment system (de novo synthesis) may be possible. To safeguard against harmful effects on the environment, emissions must be reduced. Accordingly, off-gases have to be captured at their source of generation and routed to an off-gas-cleaning device (e.g. a capture system followed by a dust collector and scrubber) [ 219, VDI (D) 2102 2007 ].

The emissions can escape the process either as stack emissions or as diffuse emissions depending on the abatement systems used and the quality of plant maintenance. Stack emissions are normally monitored continuously or periodically and reported by on-site staff or off-site consultants to the competent authorities.

#### 3.2.2.3.1 Carbon monoxide

In addition to the emissions outlined above, the melting processes using furnaces that need to maintain a reducing atmosphere can produce a significant concentration of carbon monoxide. This is particularly the case for the melting of high-grade copper in shaft furnaces in combination with shape casting or the production of wire-rod as the products require controlled oxygen levels to obtain high conductivity. The process therefore operates under reducing conditions and the carbon monoxide content of the gases can be elevated and typical levels are approximately 5000 mg/$Nm^3$. The burner control systems that are used can also minimise CO and maintain product quality. CO alarms can also be incorporated into the process. Typical CO production in a shaft furnace used for wire-rod or semis production is 2000 to 11000 grams per tonne of copper [ 114, Eurometaux 1998 ]. In some installations, afterburning is used to remove hydrocarbons from the gases when scrap coated with organic matter is processed. CO is also destroyed at the same time and the emissions are reported to be ~ 45 grams per tonne of copper [ 121, Rentz, O. et al. 1999 ].

It is possible to predict ground level concentrations of CO and this may be used to determine the effect of CO on local air quality (there is a proposed EU AQS for CO) so that further abatement needs can be assessed locally. CO elimination by combustion of the shaft furnace gases with these levels of CO would require additional fuel and so the emission of $CO_2$ would increase exponentially.

Carbon monoxide is also produced during the operation of the slag-cleaning furnace and the blast furnace and in some circumstances can be emitted in the off-gases. Afterburning can be used to remove the CO, giving typical concentrations in the range of 10 to 200 mg/Nm$^3$. There is at least one example where oxygen is lanced into the top of a blast furnace above the reaction zone to provide an afterburning zone in the furnace body. This measure also destroys organic compounds such as PCDD/F. The electric furnaces used for slag cleaning and reduction processes are normally operated with afterburning either within the furnace or in a special reaction chamber.

### 3.2.2.3.2 Dust and metal compounds

These can be emitted from most stages of the process. The techniques for dealing with emissions from the handling, storage, drying and treatment stages are covered in Chapter 2 and the application of these techniques should be used to prevent and minimise these emissions.

Direct and diffuse dust emissions from the smelting, converting and refining stages are potentially high. The significance of the emissions is also high as these process stages are used to remove volatile metals such as Zn, Pb some As and Cd from the copper and these metals are present in the gas and partly in the dust.

The primary smelters usually contain dust very well and are effectively sealed to minimise diffuse emissions; concentrate burners or lances are used and are therefore[rr14] easier to seal. Good maintenance of the furnaces and ducts is practised to minimise diffuse emissions and the collected gases are treated in dust removal systems[rr15] prior to the sulphur recovery processes.

Secondary smelters are more prone to diffuse emissions during charging and tapping cycles. These furnaces have large charging doors and the warping and miss-sealing of these doors is a significant factor. In secondary bath smelters, the burden is charged via an enclosed charging system, diffuse emissions occur at the tap-hole and runners, and are captured by hoods and routed to the gas-cleaning system. The gases that are collected are usually cooled and dust is removed from gas streams by electrostatic precipitators or fabric filters. High filtration efficiency is usually achieved and dust concentrations after abatement are in the range of ~~<~~<1 - 5 mg/Nm$^3$ [ 157, Winter, B. et al. 1999 ], [ 206, Traulsen, H. 1999 ].

Because of the batch type of operation, the conversion and fire-refining stages can usually not be sealed as well as in the smelting stage. The feeding and transfer of matte, slag and metal is a significant potential source of diffuse fumes. More importantly the use of a ladle or boat transfer system can inhibit the effectiveness of fume collection hoods, particularly with the Peirce-Smith or similar style of converters. To capture or reduce emissions occurring during charging or emptying, converters are either enclosed or provided with secondary capture hoods (see Chapter 2). The off-gas extracted from the enclosure or hood should be treated in a manner depending on the $SO_2$ content. Gases from matte conversion will have higher concentrations of $SO_2$ and in all cases, metal oxides (As, Pb, etc.) need to be removed. Through hood additions of flux and other material can minimise the rollout time of converters and so reduce the time when converters are separated from the primary gas collection system[rr16]. The production of higher-grade matte reduces the number of ladle transfers and therefore reduces the potential for fumes. Diffuse or non-collected emissions are therefore[rr17] very important. These issues are dependent on efficient and effective primary and, in some cases, secondary fume collection.

The melting and casting stages used during the production of wire-rod, semis, etc. are also potential sources of dust and metals. The production of copper alloys such as brasses results in significant fumes (ZnO) at the casting stage and these require efficient collection. The dust burden is generally low but[rr18] heat/energy recovery, if practicable, can be used. Efficient fume collection and fabric filters are usually used [ 114, Eurometaux 1998 ].

Emissions of metals are strongly dependent on the composition of the dust produced by the processes. The composition varies widely and is influenced ~~a)~~ by the process that is the source of dust and ~~b)~~ by the raw materials that are being processed. For example the dust produced from a scrap converter is totally different from that of a matte converter and this will vary depending on the operating phase of the process (charging, blowing, casting, poling, etc.) at the time of the measurement, on the input material, etc. Table 3.12 and Table 3.13 show the percentage of metals in the dust from various processes and the measured ranges from a number of copper processes.

| Component | Concentrate to matte smelting furnace ESP dust | Blast furnace dust | Scrap converter dust | Matte converter ESP dust | Electric slag cleaning furnace dust | Anode furnace dust |
|---|---|---|---|---|---|---|
| Pb % | 0.1 - 5 | 5 - 50 | 5 - 30 | 2 - 25 | 2 - 15 | 2 - 20 |
| Zn % | 0.1 - 10 | 20 - 60 | 25 - 70 | 5 - 70 | 25 - 60 | 5 - 40 |
| Sn % | 0.1 - 1 | 0.2 - 5 | 1 - 20 | 0.1 - 4 | | |
| Cu % | 5 - 30 | 2 - 12 | 2 - 15 | 10 - 25 | 0.5 - 2.5 | 15 - 25 |
| As % | 0.1 - 4 | | | | | 0.5 - 10 |
| Ni % | 0.1 - 1 | 0.1 - 1 | | 0.1 - 1 | | |

**Table 3.12: Main constituents of dust from copper processes**
[ 206, Traulsen, H. 1999 ]

The variations between the individual measurements in a plant are greater than the differences between blast furnaces, electric furnaces, converters and anode furnaces[rr19]. Typical ranges of measured concentrations downstream of a filtering separator of all copper-producing processes are shown in Table 3.13.

| Gas constituents | Unit | Typical range in clean gas |
|---|---|---|
| Mercury (Hg) | (mg/m$^3$) | 0.001 - 0.05 |
| Thallium (Tl) | (mg/m$^3$) | <0.02 |
| Lead (Pb) | (mg/m$^3$) | 0.04 - 1 |
| Cobalt (Co) | (mg/m$^3$) | <0.02 |
| Nickel (Ni) | (mg/m$^3$) | 0.01 - 0.1 |
| Selenium (Se) | (mg/m$^3$) | 0.01 - 0.1 |
| Tellurium (Te) | (mg/m$^3$) | <0.02 |
| Antimony (Sb) | (mg/m$^3$) | <0.01 - 0.1 |
| Chromium (Cr) | (mg/m$^3$) | 0.01 - 0.1 |
| Cyanide (CN) | (mg/m$^3$) | <0.05 |
| Fluoride ($F^-$) | (mg/m$^3$) | <0.05 |
| Copper (Cu) | (mg/m$^3$) | 0.02 - 1 |
| Manganese (Mn) | (mg/m$^3$) | <0.02 |
| Vanadium (V) | (mg/m$^3$) | <0.02 |
| Tin (Sn) | (mg/m$^3$) | 0.01 - 0.15 |
| Arsenic (As) | (mg/m$^3$) | <0.01 - 0.15 |
| Cadmium (Cd) | (mg/m$^3$) | <0.001 - 0.05 |
| PCDD/F (total of dust borne and gaseous fractions) | ng I-TEQ/m$^3$ | 0.01 - 0.4 |

**Table 3.13: Concentrations of dust constituents and PCDD/F in the clean gas of all unit processes from a secondary copper smelter**
[ 206, Traulsen, H. 1999 ]

#### 3.2.2.3.3 Organic carbon compounds

Organic carbon compounds can be emitted during primary production from the drying stage depending on materials used for ore treatment and the fuel used for drying. For secondary production the most significant sources are from the scrap treatment, smelting and refining stages. The conversion stage for secondary copper is also a potential source if scrap contaminated with organic material is added to the converter and complete combustion is not achieved; this is particularly the case for diffuse emissions. ~~VOCs~~ Organic carbon compounds[rr20] can be emitted if oily material is used as feed and can account for 5 - 100 g per tonne of copper or between 1 and 10 mg/Nm$^3$ [ 249, Austria Brixlegge Report 2007 ]. VOCs may also be emitted from solvent degreasing or solvent extraction processes.

#### 3.2.2.3.4 PCDD/F

The organic carbon compounds that can be emitted include PCDD/F resulting from the poor combustion of oil and plastic in the feed material and from de novo synthesis if the gases are not cooled rapidly enough. Scrap treatment to remove organic contamination can be practised but more usually afterburners are used to treat the gases produced followed by rapid cooling. In cases where it is not possible to treat the gases from the furnaces in an afterburner, they can be oxidised by adding oxygen above the melting zone. It is also possible to identify organic contamination of secondary raw materials so that the most appropriate furnace and abatement combination can be used to prevent the emissions of smoke and fumes and the associated PCDD/F. Melting scrap that is contaminated with organic material is also a potential source of PCDD/F in the semis industry [ 219, VDI (D) 2102 2007 ].

It has been reported that, in the case of primary smelting and converting, the high operating temperatures used destroy organic components and the presence of sulphur dioxide inhibits de novo synthesis of PCDD/F.

Chapter 2 describes some of the factors that influence the emissions of PCDD/F and BAT is given in Section 2.20.5. The techniques used for abatement of PCDD/F in this sector include afterburning, controlled gas handling and cooling and effective dust removal; activated carbon adsorption is also used.

PCDD/F emissions of <0.001 to 0.14[rr21] ng I-TEQ/m$^3$ were measured downstream of a KRS, an electric furnace and two converters not equipped[rr22] with secondary PCDD/F control devices. Another study reports PCDD/F levels of 0.25 - 1.81 ng I-TEQ/m$^3$ downstream of a converter which has meanwhile been shut down. PCDD/F emissions measured downstream of an anode reverberatory furnace were of the order of 0.13 ng I-TEQ/m$^3$ on average. Being designed as a countercurrent reactor, the blast furnace has relatively low off-gas temperatures resulting in elevated PCDD/F emissions. Before the implementation of emission control measures, PCDD/F levels of between 2.3 and 29.5 ng I-TEQ/m$^3$[rr23] were measured in blast furnace units. At a blast furnace with cold top gas the dioxin emissions downstream the afterburning chamber were reduced to <0.2 ng ITE/Nm$^3$ by the application of a carbon-lime additives [219].

If major amounts of electronic scrap with brominated flame retardants are used as feedstocks, this may result in the formation of mixed halogenated dioxins. In case of copper remelting/refining, the conditions may exist for the formation of PCDD/F, in particular when using scrap materials and chips contaminated with chlorine from the cutting fluids used.

#### 3.2.2.3.5 Sulphur dioxide

The most significant sources of sulphur dioxide are the roasting, smelting and converting stages of primary copper production using sulphide concentrates [ 23, DFIU-University Karlsruhe 1996 ]. Diffuse emissions are expected but can be collected in several ways [ 121, Rentz, O. et al. 1999 ]. Sulphur dioxide can also be emitted from the concentrate drying stage (mainly from the fuel used in the burner) and from the primary refining stages where the blister copper contains 0.03 to 0.1 % dissolved sulphur. The concentration in the gas is usually very low and simple scrubbing of the gases is generally used if required.

If not applying partial roasting and calcine smelting to matte in separate units because of special feed material, the roasting of copper concentrates is carried out simultaneously with smelting. The use of sealed furnaces for smelting allows the sulphur dioxide to be collected efficiently. All of the smelters in the EU-27 use oxygen enrichment that produces a high sulphur dioxide concentration. This therefore allows the off-gas volumes to be minimised and the gas handling systems including the sulphuric acid plants to be reduced in size. Very high levels of oxygen enrichment can increase the concentration of sulphur trioxide in the gases passing to an acid plant. This increased amount of sulphur trioxide in the gas from the furnace is absorbed in the scrubbers and increases the amount of weak acid for treatment, other uses or disposal. Contact sulphuric acid plants with four or five passes are used to convert the gases. In some cases, single contact plants are used if there is a low (<5 %) sulphur dioxide content, otherwise double contact plants are used [ 90, Traulsen, H. 1998 ]. If required, liquid sulphur dioxide can be produced from part of the sulphur dioxide contained in the gas.

The matte conversion stage also produces a significant concentration of sulphur dioxide. There are two potential problems when using batch fed converters such as the Peirce-Smith or similar style of converter. Firstly, gas collection is not totally efficient and the same remarks apply as those made above in Section 3.2.2.3.2. Secondly, the sulphur dioxide concentration in the gases varies significantly depending on the stage of conversion and can cause problems with sulphur dioxide removal systems unless they are designed specifically to take account of this variation. These gases are mixed with the steady, more concentrated gases produced by the primary smelter to maintain autothermal operation of the sulphuric acid plant. Using several converters in a phased sequential operation combining the off-gases can also reduce this effect.

Continuous processes such as the Mitsubishi process and the Kennecott/Outotec flash smelt/flash conversion process maintain a high and constant concentration of sulphur dioxide and do not need ladle transfers [ 66, George, D.B. et al. 1995 ], [ 72, Shibasaki, T. et al. 1993 ]. The gas volumes that are produced are consequently lower. This means that the concentration of sulphur dioxide is higher in the effluent gas but the mass is much smaller, at least during gas handling, cleaning and cooling. In the contact plant the $SO_2$ to $O_2$ ratio should be adjusted and the $SO_2$ concentration is diluted down to the maximum tolerable concentration.

After heat recovery and cleaning of the gases, the sulphur dioxide in the gas from the smelting stages is converted to sulphur trioxide ($SO_3$). Sulphuric acids plants in the European copper industry have a conversion efficiency reported as 99.5 to more than 99.9 % (excluding start-up, etc.) [ 90, Traulsen, H. 1998 ]. A very small amount of $SO_3$ is not absorbed and is emitted together with the residual $SO_2$ [ 121, Rentz, O. et al. 1999 ]. During start-up and shut-down there may be occasions when weak gases are emitted. These events need to be identified for individual installations and many companies have made significant improvements to the process control equipment to reduce these emissions. The height of the stack used for the acid plant gases usually takes these factors into account to reduce local impact.

Sulphur dioxide may also be present in the gases produced during secondary smelting stages due to the sulphur content of the fuel or raw materials. In some cases, scrubbers are used to remove the $SO_2$ and in one case the gases from an electric furnace (and a Cu/Pb converter) are diverted to a primary copper smelter sulphuric acid plant when certain raw materials are present[rr24].

Section 2.20 describes some of the factors that influence the emissions of sulphur dioxide and BAT is given.

### 3.2.2.3.6 Diffuse emissions

In pyrometallurgical plants, diffuse emissions may occur both during charging and tapping operations as well as during the transfer of the molten products or intermediates from one operation to another. Of particular importance in this connection is the fact that the prevailing temperatures of the various metal, slag or matte fractions are above the volatilisation points of the low boiling accompanying metals (e.g. Zn, Pb and Sn) and their oxides so that the latter accumulate in the emitted vapours (see Chapter 2[rr25]). As far as possible, diffuse emissions should be captured at the source via secondary hoods and the extracted off-gas is to be routed to the gas-cleaning system.

In secondary smelters with the low dust loads of the secondary hood off-gas, it is sometimes advantageous to combine this off-gas stream with the furnace off-gas prior to cleaning since this can improve the filtration properties of the total off-gas stream. Further diffuse emissions may occur during transport due to the resuspension of dust, the handling of the molten materials, in particular, during transfer or pouring operations. Moreover, dust emissions are generated during the handling and pretreatment of the secondary raw materials (e.g. size reduction, shredding, pelletising). The emission at secondary copper smelters can be dominated by diffuse dust emissions which account for approximately 70 % of total emissions. [ 234, UBA Copper, lead, zinc and aluminium 2007 ].

### 3.2.2.3.7 Nitrogen oxides

The production stages for copper usually rely on high temperatures but are also associated with the use of oxygen. This reduces the partial pressure of nitrogen in the flame and reduces nitrogen oxide formation provided that nitrogen is not present in great amounts in the very hot areas. Typical levels for the emissions of nitrogen oxides for secondary copper are reported to be in the range of 50 to 500 mg/Nm$^3$ depending on the furnace and type of operation. For $NO_X$, the use of highly efficient processes (e.g. Contimelt) requires a balance to be established locally between energy use and achieved value[rr26].

Nitrogen oxides from primary processes are mainly absorbed in the sulphuric acid produced [ 130, Eurometaux Copper Industry 1998 ] see also Table 2.26[rr27].

### 3.2.2.3.8 Summary of air emissions

Emissions are summarised in Table 3.14[rr28], Table 3.15 and Table 3.16.

| Process type | Dust (g/t of product metal) | Sulphur dioxide (g/t of product metal) | Cu (g/t of product metal) | Pb (g/t of product metal) | As (g/t of product metal) |
|---|---|---|---|---|---|
| Primary Cu | 130 - 800 | 6000 - 18000 | 25 - 130 | 6 - 45 | 2 - 27 |
| Secondary Cu | 100 - 1000 | 500 - 3500 | 8 - 100 | 10 - 60 | 0.5 - 5 |
| Melt shop semis fabrication | 21 | NA | 4 | NA | 0.15 |
| Wire-rod production | 10 | NA | 4 | NA | 0.05 |

**Table 3.14: Specific emissions to air from some primary and secondary processes**
[ 234, UBA Copper, lead, zinc and aluminium 2007 ].

| **Parameter** | **CO** | **Dust** | **PM$_{10}$** | **PM$_{2.5}$** | **NO$_X$** | **SO$_2$** | **CO** | **SO$_X$** | **HCl** | **HF** | **Pb** | **Zn** | **Cu** | **O$_2$** | **Sn** | **V** | **As** | **Hg** | **Ni** | **Cd** | **Temp.** | **Organic C** | **PCDD/PCDF** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Units** | **(mg/Nm$^3$)** | | | | | | | | | | | | | **(%)** | **(mg/Nm$^3$)** | | | | | | **(°C)** | **(mg/Nm$^3$)** | **(ITEQ ng/m$^3$)** |
| Shaft Furnace | <0.1 | 0.5 | 0.53 | 0.39 | 45 | 0.2 | <0.1 | | | | 0.012 | 0.009 | 0.008 | 12 | | | 0.001 | 0.006 | 0.001 | 0.0001 | 199 | 1.2 | 0.603 |
| Converter Furnace | | 0.75 | | | 7.3 | | 11.3 | 4.7 | | | 0.097 | 0.126 | 0.0334 | 17.8 | | | 0.0012 | 0.0028 | 0.0033 | 0.0006 | 30 | 1.4 | |
| Anode Furnace | | 2.3 | 1.5 | 1.02 | 179 | 24.5 | | 24.5 | 7.17 | 3.9 | 0.36 | 0.636 | 0.507 | 17.5 | 0.337 | <0.0005 | | 0.17 | | 0.0001 | 98 | 3.4 | |
| Slag Production Unit | | <0.3 | | | | | | | | | | | | | | | | | | | | | |
| Asarco Furnace | | 0.5 | 0.25 | 0.25 | 21 | 17 | | 17 | 2.62 | | | | 0.0098 | 17.4 | | | | | | | 112 | 9.34 | 0.202 |
| Thermal treatment of chips | | 5 | | | 200 | | | | | | | | | | | | | | | | | 20 | 0.1 |
| Electrically-heated furnaces | | 5 | | | | | | | | | | | | | | | | | | | | 20 | 0.1 |
| Rotary drum furnace | | 5 | | | 300 | | | | | | | | | | | | | | | | | 50 | 0.1 |
| Shaft furnace (Asarco) | | 0.5 - 5 | | | 21 - 300 | | | | | | | | | | | | | | | | | 9 - 50 | 0.2 - 0.4 |
| Milling<br>Plant A)<br>Plant B) | | <10 | | | | | | | | | | | | | | | | | | | | <50 | |

**Table 3.15: Achievable emissions from some secondary smelting, remelting/refining processes (with semis fabrication)**
[ 234, UBA Copper, lead, zinc and aluminium 2007 ], [ 249, Austria Brixlegge Report 2007 ][rr29]

| **Operating parameter** | **Unit** | **Typical value or range** | |
|---|---|---|---|
| | | **Scrap converter** | **Matte converter** |
| Converter copper yield per batch | (t) | 8 - 25 | 30 - 300[rr30] |
| Number of batches per day | | 4 - 6 | 2 - 3 |
| Batch duration | (h) | 4 - 6 | 5 - 8 |
| Blowing time/batch | (h) | 2 - 3.5 | 4 - 7 |
| **Raw gas (including secondary hood off-gas)** | | | |
| Volumetric off-gas flow | ($m^3/h$) | 80000 - 150000 | 80000 - 150000 |
| Dust content | ($mg/m^3$) | 10000 - 30000 | 10000 - 30000 |
| **Main dust constituents (depending on operating mode)** | | | |
| Zn | (% by mass) | 25 - 70 | 1 - 10 |
| Sn | (% by mass) | 1 - 20 | 1 - 5 |
| Pb | (% by mass) | 5 - 30 | 30 - 55 |
| **Clean gas (including secondary hood off-gas)** | | | |
| Dust content(1) | ($mg/m^3$) | 1 - 5 | -(2) |
| $SO_2$ | ($mg/m^3$) | 200 - 500(3) | -(2) |
| $NO_X$ (expressed as $NO_2$) | ($mg/m^3$) | 20 - 30 | -(2) |
| Off-gas temperature at stack outlet | (°C) | 80 - 90 | -(2) |

(1) For dust constituents, see Table 3.10
(2) Matte converter off-gases are routed to the contact process unit for sulphuric acid production[rr31].
(3) Continuous monitoring: daily mean value <500 $mg/m^3$; max. half-hour mean value <1500 $mg/m^3$

**Table 3.16: Emissions and operating data from converters in secondary copper production**
[ 206, Traulsen, H. 1999 ], [ 234, UBA Copper, lead, zinc and aluminium 2007 ].

### 3.2.2.4 Emissions to water

Pyrometallurgical processes use significant quantities of cooling water (cooling systems are covered in Chapter 2 and in a separate horizontal BREF on Industrial Cooling Systems [ 342, European Commission 2001 ]). Suspended solids, metal compounds and oils can be emitted to water from these sources. All waste water is treated to remove dissolved metals and solids. In a number of installations, cooling water and treated waste water including rainwater is re-used or recycled within the processes but all sources should be treated separately as required [ 206, Traulsen, H. 1999 ], [ 234, UBA Copper, lead, zinc and aluminium 2007 ]. The potential sources and relevance of potential emissions to water are shown in Table 3.17 and they are discussed later in this section [ 219, VDI (D) 2102 2007 ].

| **Emission Source** | **Suspended solids** | **Metal compounds** | **Oil** |
|---|---|---|---|
| Surface drainage | (3) | (2) | (3) |
| Cooling water for direct cooling | (3) | (3) | (1) |
| Cooling water for indirect cooling | (1) | (1) | |
| Granulating water | (3) | (2) | |
| Leaching (if not closed circuit) | (3) | (3) | (1) |
| Pickling | (2) | (3) | (3) |
| Tankhouse (if not closed circuit) | | (3) | |
| Scrubbing systems | (3) | (3) | |

NB: (3) more significant – (1) less significant
Open leaching circuits and open circuits in tankhouses are not used in the EU.

**Table 3.17: Significance of potential emissions to water from copper production processes**

The ecotoxicology of metals in water is discussed in Section 2.3.2.2 and a methodology for determining their impact is given under the MERAG report [ 301, MERAG Guidance 2007 ].

### 3.2.2.4.1 Suspended solids and metal compounds

These can be emitted from several stages of the process, the most significant being waste waters and rinses from pickling operations. The techniques for dealing with emissions from the raw material handling and storage areas are covered in Chapter 2 and the application of these techniques are used to prevent and minimise these emissions. Surface water can result from either rainfall or from the wetting of stored material to prevent dust formation.

Potential sources of suspended solids and metal compounds are the cooling, granulating and leaching systems. In general, these systems are either sealed and the water is recirculated or are non-contact.

Wash-waters, spent electrolyte and process effluents are also produced in the tankhouses, pickling lines and from scrubbers. These effluents contain significant quantities of metal compounds in the solution and are treated along with liquors bled from the sealed cooling and granulating systems before discharge to water [ 27, M. Barry et al. 1993 ]. System leakage can occur and monitoring arrangements are needed for the pipework and storage tanks, specifically for pipelines outside the plant and in cases when they are in areas without a collection system. Waste water treatment processes are described in Chapter 2 and the methods used depend on the contaminants that are present, the destination of the treated water and local environmental quality.

The amount of water discharged is also a significant issue as some installations used extensive water recirculation systems. One copper smelter reported that the daily discharge volume is 3000 m$^3$/d while similar plants that do not recirculate to the same extent discharge more than 100000 m$^3$/d. The mass emission of pollutants is therefore the factor that should be used [ 238, ECI Copper Installations 2008 ].

Waste water emissions are summarised in Table 3.18, Table 3.19, and Table 3.20. Further data is also given in Table 2.37.

| | Main components before treatment (mg/l) | | | | | |
|---|---|---|---|---|---|---|
| **Source** | **Cu** | **Pb** | **As** | **Ni** | **Cd** | **Zn** |
| Process water | 2000 | 500 | 10000 | 1000 | 500 | 1000 |
| Precipitation water(1) | 15 - 30 | <5 | <2 | <2 | <0.5 | 1 - 10 |
| Direct cooling water | <3 | <0.5 | <0.1 | <0.1 | <0.05 | <0.5 |
| (1) Calculated back from the analysis of the precipitation sludge and based on emission values which are accessible to the authority | | | | | | |

**Table 3.18: Annual concentrations of the main constituents in the untreated waste water from a primary copper smelter**
[ 234, UBA Copper, lead, zinc and aluminium 2007 ]

| | Flow | Main components (mg/l) | | | | | |
|---|---|---|---|---|---|---|---|
| | **(m³/yr)** | **Cu** | **Pb** | **As** | **Ni** | **Cd** | **Zn** |
| Process water | 180000 | 0.01 - 0.2 | 0.001 - 0.04 | 0.01 - 0.1 | 0.004 - 0.15 | 0.0001 - 0.1 | 0.01 - 0.2 |
| Surface run-off | 700000 | 0.01 - 0.4 | 0.005 - 0.2 | 0.003 - 0.07 | 0.002 - 0.4 | 0.0002 - 0.1 | 0.03 - 0.4 |
| Direct cooling water | 11300000 | 0.01 - 0.25 | 0.001 - 0.1 | 0.001 - 0.1 | 0.002 - 0.06 | 0.0001 - 0.003 | 0.02 - 0.5 |
| Cooling water (total) | 65000000 | | | | | | |
| NB: Table refers to a combined primary/secondary copper smelter/refinery complex located on a river close to the sea producing 370000 tonnes of Cu cathode per year. Metal concentrations (mg/l) are given as annual averages. | | | | | | | |

**Table 3.19: Example of the metal content in various waste waters after treatment**
[ 121, Rentz, O. et al. 1999 ]

| **Main components**<br>Overall pollutant rate (g/t) | **Cu** | **Pb** | **As** | **Ni** | **Cd** | **Zn** |
|---|---|---|---|---|---|---|
| Plant A) producing Cu cathodes referred to above in Table 3.19. | 1 - 2.3 | 0.03 - 0.3 | 0.05 - 0.23 | 0.1 - 0.2 | 0.02 - 0.05 | 0.16 - 0.8 |
| Plant B) treating all waste water and surface water from areas that are historically polluted | 5 – 10 | 0.3 – 1.0 | 2.5 – 5.0 | 5 – 10 | 0.1 – 0.3 | 2 – 5 |

**Table 3.20: Overall pollutant rate of waste water discharges from two complex primary copper plants**
[ 238, ECI Copper Installations 2008 ]

In the example quoted above in Table 3.19, 20 to 50 kg sludge per $m^3$ of waste water arise, mainly depending on the arsenic content of the raw material and this varies from 5 to 20 % As, and the iron content is 25 to 45 %. [ 234, UBA Copper, lead, zinc and aluminium 2007 ].

| **Substance** | **Value (kg/yr)** |
|---|---|
| Cu | 11 |
| Ni | 3 |
| Zn | 25 |
| Pb | 1 |
| Cr | 1 |
| As | 0.01 |
| Cd | 0.01 |
| Hg | 0.01 |
| Sn | 1 |
| NB: Effluent discharge 35000$m^3$/yr. | |

**Table 3.21: Annual loads discharged to water from a copper semis production plant**
[ 121, Rentz, O. et al. 1999 ]

Sludges from all of the processes are produced and these are usually sent for controlled disposal. In some cases, they are returned to the smelter to recover the metallic fraction.

#### 3.2.2.4.2 Oil

This can be present on secondary raw materials and can be washed from the storage areas. The techniques used for storage are covered in Chapter 2.6. Waxes and oils are used in the coating and drawing processes associated with the production of rods and other shapes and their presence is taken into account to prevent contamination of water.

### 3.2.2.5 By-products, process residues and waste

*Waste catalogue 2000/532/EC replacing Decision 94/3/EC establishing a list of wastes pursuant to Article 1(a) of Council Directive 75/442/EEC on waste and Council Decision 94/904/EC establishing a list of hazardous waste pursuant to Article 1(4) of Council Directive 91/689/EEC on hazardous waste*

Some intermediate products generated during copper production may be covered by the Hazardous Waste List (Update, see above)~~Council Decision 94/904/EEC~~) shown in Section 2.13.1. Most of these materials however contain recoverable quantities of copper and other non-ferrous metals and are therefore used as raw materials in their own right. For example, slag from the production of tin from cassiterite is the main source of tantalum and niobium. Flue dusts from all sources can also be re-used in the smelting process and to prevent dust formation during handling they are carefully handled, usually in specially-designed systems or, already pretreated for the further processing requirements [ 219, VDI (D) 2102 2007 ]. Some furnace linings can also be re-used as tap-hole mass or in the process and may be incorporated in the slag. In other cases the linings are disposed of.

The sources of some intermediate products, by-products, residues and their potential uses are given in Table 3.22, Table 3.23 and Table 3.24.

| Process Source | Intermediate product or residue | End use |
|---|---|---|
| Abatement systems | Filter dusts<br>Mercury compounds<br>Spent catalysts and acid<br>Sulphuric acid sludges<br>Weak acid. | Raw material for Cu (returned to smelter),<br>Gypsum for sale<br>Calcium source for smelter<br>Pb, Zn and other metals<br>Raw material for Hg<br>Chemical industry<br>Neutralisation<br>Other uses, e.g. leaching decomposition<br>For $SO_2$ |
| Smelter | Slag<br>Furnace linings | To slag furnace or other separation<br>Internal recycle<br>Recovered or disposed |
| Converter | Slag | To smelter - internal recycle |
| Slag furnace | Slag | Abrasive, construction material |
| Refining (anode) furnace | Slag | To smelter - internal recycle |
| Tankhouse | Electrolyte bleed<br>Anode remnants<br>Anode slime | Ni salts, cu recovery, acid recovery<br>Other internal recycling: converter (cooling) or anode furnace<br>Precious metals recovery |
| Melting/smelting | Skimmings and slag | Raw material for metal recovery |
| Slag flotation | Slag | Filler in cement production |
| Waste water treatment | ~~Glean~~ Clean gypsum | re-use in smelter as source of calcium |
| General | Oils | Oil recovery |
| Hydrometallurgy | Depleted electrolyte | Leaching |
| Semis production | Acid pickling solutions and rinses | Disposal as waste if low in non-ferrous metals or sold for metal recovery |
| Rod production | Acid pickling solutions (if applied)<br>Scale | Recovery in separate electrolytic cell<br>Copper recovery |

**Table 3.22: Wastes, intermediate products and residues from the production of copper**
[ 130, Eurometaux Copper Industry 1998 ]

| Production step | By-product, intermediate product, residue or waste | Quantity (t/yr) | Use or treatment option |
|---|---|---|---|
| **Primary smelting and electrolysis (460000 t anodes/yr)** | | | |
| Flash smelting furnace | Dust | 100000 | Internal use at the flash smelting furnace |
| | Slag | 700000 | Further processing in the electric furnace |
| Electric furnace (slag cleaning) | Dust | 400 | External use for Zn/Pb production |
| | Slag | 700000 | External use as construction material |
| Copper converter | Dust | 4000 | Internal recycling to the flash smelter or electric furnace (secondary plant) |
| | Slag | 160000 | Internal use at the flash smelting furnace |
| Anode furnace | Dust | 200 | Internal use at the flash smelting furnace |

| Production step | By-product, intermediate product, residue or waste | Quantity (t/yr) | Use or treatment option |
|---|---|---|---|
| | Slag | 20000 | Internal use at the copper converter |
| Electrolysis | Anode sludge (wet) | 3000 | To recovery of precious metals and Se, Te, Pb |
| Sulphuric acid plant | Sulphuric acid | 1000000 | By-product for sale |
| | Final liquor | 70000 | Internal use in the chemical plant for the production of nickel sulphate, $As_2O_3$ |
| **Secondary smelting & electrolysis** | | | |
| Electric furnace off-gas treatment | Dust | 10000 | By-product for sale to recover Zn |
| | Slag | 60000 | External use as construction material |
| Converter | Dust | 400 | Internal use at electric furnace |
| | Slag | 15000 | Internal use at electric furnace |
| Contimelt process | Dust | 1000 | Internal use at the flash smelter/electric furnace |
| | Slag | 2000 | Internal use at the copper converter |
| Scrap converter/TLA plant | Dust | 1000 | Further processing in the TLA plant |
| | Slag | 2000 | Internal use at the electric furnace |
| Process waste water treatment plant | Sludge | 2000 | Disposal as hazardous waste |
| General | Household refuse | 500 | |
| **Secondary smelting and electrolysis** | | | |
| KRS, off-gas treatment | Iron silicate slag | 120 - 200 | Construction material on disposal site |
| | KRS oxide | 20 - 40 | Sale |
| Mixed tin furnace | Mixed tin | 50 | Sale |
| Electrolysis | Anode slime | 13 | Sale |
| | Nickel sulphate | 20 | Sale |
| Waste water treatment | Precipitated sludge | NA | Disposal as hazardous waste |
| All steps | Anode remains, | NA | Internal recirculation |

**Table 3.23: Wastes, intermediate products and residues from primary and secondary smelting processes in Germany**
[ 234, UBA Copper, lead, zinc and aluminium 2007 ]

| Production step | Intermediate product or residue | Quantity (kg/t copper product) | Use or treatment option |
|---|---|---|---|
| **Remelting/refining (with semis fabrication)** | | | |
| Shaft furnace | Dross | NA | NA |
| | Flue dust | 0.7 - 1 | To secondary copper production |
| | Refractory lining | 0.5 - 1.5 | Controlled disposal |
| | Sludge | 2 - 4 | Controlled disposal |
| | Production scrap | 39 | Internal recirculation |
| Induction furnace | Dross | 8 - 15 | Internal recirculation |
| | Flue dust | 4 - 7 | To secondary copper production |
| | Refractory lining | 2 | Recovery of metals |
| | Copper mould | NA | |
| | Graphite mould | <<0.01 | Recovery of graphite |

**Table 3.24: Wastes, intermediate products and residues from some remelting/refining processes (with semis fabrication)**
[ 206, Traulsen, H. 1999 ]

Wastes destined for disposal are kept to a minimum and mainly consist of acid slimes from the sulphuric acid plants that are treated and sent for disposal or furnace linings some of which cannot be recovered in the process. In some cases, tailings from the processing of smelter or converter slag by flotation are produced. These tailings are disposed of on site or at the mine site if it is close. Other wastes are either domestic or demolition wastes.

Table 3.25 and Table 3.26 shows the potential use of the process residues. Many of the residues are used as raw materials for the production of other metals or as materials recycled within the copper production route [ 206, Traulsen, H. 1999 ].

| Process unit | By-product or residue | Amount (t/yr) | Use/treatment option |
|---|---|---|---|
| **Primary plant: Annual cathode production: primary copper 220000 t/yr;** | | | |
| Flash smelting furnace | Dust | 100000 | Internal use at the flash smelting furnace |
| | Slag | 400000 | Further processing in the electric furnace |
| Electric furnace | Dust | 400 | External use for Zn/Pb production |
| | Slag | 400000 | External use as construction material |
| Copper converter | Dust | 4000 | Internal recycling to the flash smelter or electric furnace (sec. plant) |
| | Slag | 150000 | Internal use at the flash smelting furnace |
| Anode furnace | Dust | 200 | Internal use at the flash smelting furnace |
| | Slag | 20000 | Internal use at the copper converter |
| Sulphuric acid plant | Sulphuric acid | 656000 | By-product for sale |
| **Secondary plant: Annual cathode production: secondary copper 150000 t/yr.** | | | |
| Electric furnace | Dust | 10000 | By-product for sale to recover Zn |
| | Slag | 40000 | External use as construction material |
| Converter | Dust | 400 | Internal use at electric furnace |
| | Slag | 10000 | Internal use at electric furnace |
| Contimelt process | Dust | 1000 | Internal use at the flash smelter/electric furnace |
| | Slag | 2000 | Internal use at copper converter |
| Scrap converter/TLA plant | Dust | 1000 | Further processing in TLA plant |
| | Slag | 2000 | Internal use at the electric furnace |
| **Others:** | | | |
| Electrolysis | Anode slime (wet weight) | 3000 | Internal use at the chemical plant for the recovery of precious metals and Se, Te, Pb |
| | Final liquor | 35000 m$^3$ | Internal use at the chemical plant for the production of nickel sulphate, $As_2O_3$,$H_2SO_4$ |
| Process waste water treatment plant | Sludge (wet weight) | 1500 | Disposal as hazardous waste |
| General | Household refuse | 400 | |

**Table 3.25: Potential uses and examples of the quantity of residues produced by a complex primary and secondary installation**

[ 121, Rentz, O. et al. 1999 ]

| Process unit | By-product, or residue | Amount (t/yr) | Use/treatment option |
|---|---|---|---|
| Blast furnace | Slag | 30000 - 35000 | Sold as construction material |
| | Oxide from afterburning chamber, boiler and cooler | 700 - 800 | Internal use at the blast furnace |
| | Filter oxide | 1000 - 1300 | External use to recover Zn, Pb, etc. |
| Converters | Slag | 17000 - 19000 | Internal use at the blast furnace |
| | Oxide from afterburning chamber | 250 - 300 | Internal use at the blast furnace |
| | Oxide from cooler | 100 | Internal use at the blast furnace |
| | Residues | 300 | Internal use at the blast furnace |
| | Filter oxide | 3500 - 3700 | External use to recover Zn, Pb, etc. |
| Anode furnace | Anode copper residues | 7000 - 8000 | Internal use at the blast furnace |
| | Filter oxide | 150 | Internal use at the blast furnace |
| | Residues from furnace | 200 | Internal use at the blast furnace |

| | | | |
|---|---|---|---|
| Electrolysis | Anode slime | 360 | External use |
| | Nickel sulphate | 700 | External use |
| General | Household refuse | NA | |
| NB: Annual production 60000 t/yr cathode. | | | |

**Table 3.26: Potential uses and examples of the quantity of residues produced by a secondary installation**
[ 121, Rentz, O. et al. 1999 ]

Slags contain varying amounts of copper and many are re-used or treated to recover the metal content. Slag treatment is often carried out in a thermal process to produce an inert slag. The composition of some copper smelting slags before slag cleaning treatment is shown in Table 3.27.

| Component | Flash furnace | Pierce-Smith converter | Combined slag after electric furnace slag cleaning |
|---|---|---|---|
| | (wt- %) | | |
| Copper | 1 - 2.5 | 3 - 5 | 0.3 - 0.8 |
| Iron (total) | 38 - 45 | 40 - 45 | 40 - 43 |
| Silica | 30 - 33 | 25 | 28 - 32 |
| Magnetite | 4 - 18 | 25 | <2 |

**Table 3.27: Composition of some copper smelting slags before slag cleaning treatment**
[ 121, Rentz, O. et al. 1999 ]

Many of the slags produced by slag treatment processes contain very low levels of leachable metals and are stable. They are frequently sold as products for the abrasive and construction industries as they have excellent mechanical properties which are sometimes superior to those of competing natural minerals [ 206, Traulsen, H. 1999 ]. Oils from various sources within the process can be recovered.

### 3.2.2.6 Operating data from some copper production processes[rr32]

Operating data for some copper processes are given in Table 3.28, Table 3.29, Table 3.30, Table 3.31, Table 3.32, Table 3.33, Table 3.34, Table 3.35, Table 3.36 and Table 3.37.

| Operating parameter | Unit | Typical value or range |
|---|---|---|
| Total power consumption | (kWh/t copper cathode) | 360 - 380 |
| Current density | (A/m²) | 320 - 350 |
| Anode slime yield | (kg/t copper cathode) | 5 - 12 |
| Electrolyte temperature | (°C) | 60 - 68 |
| Yield | ( %) | >95 |
| Anode scrap | ( %) | 10 - 12 |
| **Electrolyte composition** | | |
| $H_2SO_4$ | (g/l) | 150 - 200 |
| Cu | (g/l) | 40 - 50 |
| Ni | (g/l) | 16 - 22 |
| As | (g/l) | 5 - 12 |

**Table 3.28: Operating data of the copper electrolysis unit**
**Applies to the permanent cathode system**
[ 234, UBA Copper, lead, zinc and aluminium 2007 ]

| Operating parameter | Unit | Typical value or range |
|---|---|---|
| Rated electric power | (MWh) | 13.5 |
| Coke consumption | (kg/t burden) | 25 - 60 |
| Smelting capacity | (t/h) | 10 - 25 |
| **Raw gas (furnace)** | | |
| Volumetric off-gas flow | (m$^3$/h) | 15000 |
| Dust content | (mg/m$^3$) | approximately 30000 |
| **Main dust constituents (mean values)** | | |
| Cu | (% by mass) | 0.3 - 6 |
| Pb | (% by mass) | 15 - 50 |
| Zn | (% by mass) | 10 - 50 |
| Sn | (% by mass) | 1 - 4 |
| Off-gases with a $SO_2$ content of >500 mg/m$^3$ are subjected to wet scrubbing after dust collection and routed to a contact process, sulphuric acid production unit | | |
| **Raw gas (secondary hoods)** | | |
| Volumetric off-gas flow | (m$^3$/h) | 150000 |
| Dust content | (mg/m$^3$) | <5000 |
| **Main dust constituents (mean values)** | | |
| Cu | (% by mass) | approximately 8 |
| Pb | (% by mass) | approximately 27 |
| Zn | (% by mass) | approximately 8 |
| As | (% by mass) | approximately 1 |
| Cd | (% by mass) | approximately 1 |
| **Clean gas** | | |
| Dust content | (mg/m$^3$) | 1 - 5 |
| $SO_2$ content | (mg/m$^3$) | <500(1) |
| Off-gas temperature downstream of filter | (°C) | <85 |
| (1) Continuous monitoring: daily mean value <500 mg/m$^3$; max. half-hour mean value <1500 mg/m$^3$ | | |

**Table 3.29: Electric furnace operating data**
[ 234, UBA Copper, lead, zinc and aluminium 2007 ]

| Operating parameter | | Unit | Typical value or range |
|---|---|---|---|
| Burden throughput including iron | | (t/h) | 25 - 50 |
| Fuel consumption (fuel oil) | | (kg/t burden) | 50 - 70 |
| Reducing agent consumption (e.g. coke) | | (kg/t burden) | approximately 10 |
| Yield | Iron silicate slag | (kg/t burden) | 300 - 500 |
| | Converter slag | (kg/t burden) | 150 - 200 |
| | Converter copper | (kg/t burden) | 200 - 300 |
| | KRS oxide (filter dust) | (kg/t burden) | 50 - 100 |
| Volumetric off-gas flow (furnace including secondary hoods) | | (m$^3$/h) | 300000 |
| Raw gas dust content | | (mg/m$^3$) | 5000 - 10000 |
| Specific heat recovery rate | | t steam (GJ)/t burden | 0.6 (1.7) - 0.7 (2.0) |
| **Main dust constituents (filter dust; depending on operating mode)** | | | |
| Cu | | (% by mass) | 3 - 6 |
| Pb | | (% by mass) | 15 - 20 |
| Zn | | (% by mass) | 35 - 50 |
| Sn | | (% by mass) | 2 - 4 |
| **Clean gas** | | | |
| Dust content | | (mg/m$^3$) | 1 - 5 |
| $SO_2$ | | (mg/m$^3$) | 50 - 500(1) |
| $NO_X$ (expressed as $NO_2$) | | (mg/m$^3$) | 10 - 100 |
| Off-gas temperature at stack outlet | | (°C) | 80 - 90 |
| (1)Continuous monitoring: daily mean value <500 mg/m$^3$, half-hourly mean value <1500 mg/m$^3$. | | | |

**Table 3.30: Operating data of the KRS**
[ 234, UBA Copper, lead, zinc and aluminium 2007 ]

| **Operating parameter** | | **Unit** | **Typical value or range** |
|---|---|---|---|
| Anode copper yield per batch | | (t) | 300 - 600 |
| Number of batches per day | | | approximately 1 |
| Batch duration | | (h) | 22 - 27 |
| Fuel consumption (fuel oil) | | (kg/t Cu | 60 - 80 |
| Reducing agent consumption | Pole gas or | ($m^3$/t Cu) | approximately 10 |
| | Pole wood | (kg/t Cu) | approximately 20 |
| **Raw gas (including secondary hood off-gas)** | | | |
| Volumetric off-gas flow | | ($m^3$/h) | 100000 - 150000 |
| Dust content | | (mg/$m^3$) | approximately 1000 |
| Specific heat recovery rate | | (t steam (GJ)/t burden) | 0.5 (1.4) |
| **Main dust constituents** | | | |
| CaO (from off-gas conditioning) | | (% by mass) | 30 - 50 |
| Cu | | (% by mass) | 15 - 25 |
| Zn | | (% by mass) | 5 - 10 |
| Sn | | (% by mass) | 1 - 3 |
| Pb | | (% by mass) | 5 - 15 |
| As | | (% by mass) | 0.5 - 5(1) |
| **Clean gas (including secondary hood off-gas)** | | | |
| Dust content | | (mg/$m^3$) | 1 - 5 |
| $SO_2$ | | (mg/$m^3$) | 150 - 500(2) |
| $NO_X$ (expressed as $NO_2$) | | (mg/$m^3$) | 100 - 350 |
| Off-gas temperature at stack outlet | | (°C) | approximately 100 |

(1) depending on the input material

(2)Continuous monitoring: daily mean value <500 mg/$m^3$; max. half-hour mean value <1500 mg/$m^3$

**Table 3.31: Operating data of an anode reverberatory furnace**
[ 234, UBA Copper, lead, zinc and aluminium 2007 ]

| **Plant data** | **Unit** | **Range or typical value** |
|---|---|---|
| Charge materials | | Cathodes, wire bars, scrap materials, blister (in small quantities) |
| Capacity | (t) | 35 |
| Melting temperature | (°C) | 1100 |
| Melting capacity | (t/h) | 4 |
| Type of heating | | Fuel-heated with natural gas |
| Specific energy consumption (1) | (MJ/t) | Approximately 700<br>(60 to 70 $m^3$ natural gas) |
| Waste-gas temperature (clean gas in the stack) | (°C) | 80 |
| Waste-gas volumetric flowrate | ($m^3$/h) | 20000 |
| Waste-gas-cleaning method used | | Quenchers, fabric filters |
| **Total dust in the untreated gas** | **(g/$Nm^3$)** | **up to 3** |
| **Emission data from recorded sources (clean gas, half hourly means)** | | |
| Total dust | (mg/$Nm^3$) | 3 |
| **Dust constituents** | | |
| Nickel | (mg/$Nm^3$) | 0.1 |
| Cadmium | (mg/$Nm^3$) | 0.04 |
| Lead | (mg/$Nm^3$) | 0.02 |
| Copper | (mg/$Nm^3$) | 4 |
| Arsenic | (mg/$Nm^3$) | 0.007 |
| Total carbon (TOC) | (mg/$Nm^3$) | 50 |

(1) Including holding and realigning times

(2) The plant and emission data given are examples which represent the results of individual measurements.

**Table 3.32: Operating data for a rotary drum furnace**
[ 234, UBA Copper, lead, zinc and aluminium 2007 ]

| Plant data (1) | Unit | Range or typical value |
|---|---|---|
| Charge materials | | Cathodes, return scrap (internal and external scrap) |
| Capacity (theoretical) | (t) | 50 |
| Melting temperature | (°C) | 1100 |
| Melting capacity | (t/h) | 25 |
| Type of heating | | Fuel-heated (natural gas) |
| Specific energy consumption (2) | (MJ/t) | 1300 - 1500 |
| Waste-gas temperature (cleaned gas) | (°C) | 100 |
| Waste-gas volumetric flowrate | (m$^3$/h) | 40000 |
| Waste-gas-cleaning method used | | Thermal afterburning, conditioning with lime injection and fabric filters |
| Total dust in the untreated gas | (g/m$^3$) | Up to 1.5 |
| **Emission data from recorded sources (clean gas, half hourly means given)** | | |
| Total dust (3) | (mg/Nm$^3$) | 1 |
| Dust constituents | | |
| Nickel | (mg/m$^3$) | 0.1 |
| Cadmium | (mg/m$^3$) | 0.05 |
| Lead | (mg/Nm$^3$) | 0.5 |
| Cobalt | (mg/Nm$^3$) | <0.1 |
| Copper | (mg/Nm$^3$) | 0.5 |
| Arsenic | (mg/Nm$^3$) | 0.05 - 015 |
| CO | (mg/Nm$^3$) | 9000 (4) |
| Total carbon (TOC) | (mg/Nm$^3$) | 50 |

(1) The plant and emission data given represent, by way of example, the results of individual measurements.
(2) including holding and realigning times
(3) also using materials with organic impurities
(4) the cathodes were melt reductive

**Table 3.33: Operating data for a shaft furnace of a continuous-casting installation**
[ 234, UBA Copper, lead, zinc and aluminium 2007 ]

| Plant data (1) | Unit | Range or typical value |
|---|---|---|
| Charge materials | | Electrolytic copper (copper cathodes and own scrap) |
| Melting capacity | (t/h) | 50 - 60 |
| Type of heating | | Fuel-heated (natural gas) |
| spec. energy consumption | (MJ/t) | 1000 - 1050 |
| Waste-gas temperature (cleaned gas) | (°C) | 120 - 160 |
| Waste-gas volumetric flowrate | (m$^3$/h) | 50000 - 80000 |
| Waste-gas-cleaning method used | | - |
| **Emission data from recorded sources (clean gas, half hourly means given)** | | |
| Total dust | (mg/Nm$^3$) | <4 |
| $NO_X$ | (mg/Nm$^3$) | 60 - 110 |
| $SO_2$ | (mg/Nm$^3$) | 15 - 30 |
| HCl | (mg/Nm$^3$) | <20 |
| CO (2) | (mg/Nm$^3$) | 3500 - 9000(3) |
| Total carbon (TOC) | (mg/Nm$^3$) | 10 - 21 |

(1) The plant and emission data given represent, by way of example, the results of individual measurements
(2) Without afterburning
(3) the cathodes were melt reductive

**Table 3.34: Operating data for a shaft furnace of a cast-and-rolled wire installation**
[ 234, UBA Copper, lead, zinc and aluminium 2007 ]

| Plant data(¹) | Unit | Range or typical value |
|---|---|---|
| Charge materials | | Lumpy charge material, chips |
| Capacity (theoretical) | (t) | 6 - 60 |
| Capacity (utilised) | (t) | 3 - 50 |
| Melting temperature | (°C) | 1050 - 1300 |
| Melting capacity | (t/h) | 2.4 - 25 |
| Type of heating | | Electrical |
| spec. energy consumption (²) | (MJ/t) | 900 - 1600 |
| Waste-gas temperature (clean gas in the stack) | (°C) | 60 - 120 |
| Waste-gas volumetric flowrate | ($m^3$/h) | 17000 - 70000 |
| Waste-gas-cleaning method used | | Cyclone with downstream fabric filter |
| **Total dust in the untreated gas** | (g/$m^3$) | 3 (³) |
| **Emission data from recorded sources (clean gas, half hourly means) (³)** | | |
| Total dust | (mg/$m^3$) | <5 |
| **Dust constituents** | | |
| Chromium | (µg/$m^3$) | <10 |
| Nickel | (µg/$m^3$) | <10 |
| Cadmium | (µg/$m^3$) | <5 |
| Lead | (µg/$m^3$) | <20 |
| Copper | (µg/$m^3$) | <50 |
| Manganese | (µg/$m^3$) | <20 |
| Tin | (µg/$m^3$) | <20 |
| Zinc | (µg/$m^3$) | <100 |
| Arsenic (gas phase) | (µg/$m^3$) | <20 |
| Total carbon (TOC) | (mg/$m^3$) | <10 - 50 |
| (¹) The plant and emission data given represent, by way of example, the results of individual measurements<br>(²) including holding and relining times<br>(³) during production of brass | | |

**Table 3.35: Operating data for crucible induction furnaces for the production of copper alloys**
[ 234, UBA Copper, lead, zinc and aluminium 2007 ]

| Plant data(¹) | Unit | Range or typical value |
|---|---|---|
| Charge materials | | Lumpy charge material, chips |
| Capacity (theoretical) | (t) | 7 - 25 |
| Capacity (utilised) | (t) | 7 - 20 |
| Melting temperature | (°C) | 1050 - 1300 |
| Melting capacity | (t/h) | 2.5 - 8.8 |
| Type of heating | | Electrical |
| Specific energy consumption(²) | (MJ/t) | 1290 |
| Waste-gas temperature (cleaned gas) | (°C) | 50 - 90 |
| Waste-gas volumetric flowrate | ($m^3$/h) | 10000 - 20000 |
| Waste-gas-cleaning method used | | Cyclone with fabric filter |
| **Total dust in the untreated gas** | (g/$m^3$) | 3 (³) |
| **Emission data from recorded sources (clean gas, half-hourly means) (³)** | | |
| Total dust | (mg/$m^3$) | <1 |
| **Dust constituents** | | |
| Chromium | (µg/$m^3$) | <1 |
| Nickel | (µg/$m^3$) | <1 |
| Cadmium | (µg/$m^3$) | <0.1 |
| Lead | (µg/$m^3$) | <5 |
| Copper | (µg/$m^3$) | <10 |
| Manganese | (µg/$m^3$) | <1 |
| Tin | (µg/$m^3$) | <1 |
| Arsenic (solid phase) | (µg/$m^3$) | <0.1 |
| Arsenic (gas phase) | (µg/$m^3$) | <2 |
| Total carbon (TOC) | (mg/$m^3$) | <10 |
| (¹) The plant and emission data given represent, by way of example, the results of individual measurements<br>(²) including holding and realigning times<br>(³) during production of low-alloy copper grades | | |

**Table 3.36: Operating data for channel induction furnaces for the production of copper alloys**

[ 234, UBA Copper, lead, zinc and aluminium 2007 ]

| Inputs | Quantity | Outputs | Quantity |
|---|---|---|---|
| Metal | 110000 t/yr | Rolling products | 125600 t/yr |
| Master alloy | 4000 t/yr | extruded and drawn products | 134000 t/yr |
| Scrap | 308300 t/yr | pipes | 69000 t/yr |
| Natural gas | 538 $kWh/t_{product}$ | Casting products | 10.24 $kg/t_{product}$ |
| Butane gas | 34 $kWh/t_{product}$ | Recycling of waste | 69.83 $kg/t_{product}$ |
| $NH_x$ | 12220 $m^3/t_{product}$ | Disposal of waste | 1306 t/yr |
| Nitrogen $N_2$ | 15834 $m^3/t_{product}$ | Sanitary sewage | 0.14 $m^3/t_{product}$ |
| Hydrogen $H_2$ | 1289 $m^3/t_{product}$ | treated waste water | 0.71 $m^3/t_{product}$ |
| Current | 1117 $kWh/t_{product}$ | Cooling water | 26699 $m^3/t_{product}$ |
| Water power | 21 $kWh/t_{product}$ | Evaporation | 0.80 $m^3/t_{product}$ |
| Groundwater | 28229 $m^3/t_{product}$ | Cooling tower overflow | 0.021 $m^3/t_{product}$ |
| Drinking water | 0.145 $m^3/t_{product}$ | Carbon complete | 25416 kg/yr |
| Cover material | 4.1 $kg/t_{product}$ | Nitrogen oxide $NO_2$ | 63072 kg/yr |
| Charcoal | 0.85 $kg/t_{product}$ | Dust | 952 kg/yr |
| Technical gas(1) | 17.8 $m^3/t_{product}$ | $CO_2$ emission | 0.12 $t/t_{product}$ |
| chemical solid | 0.85 $kg/t_{product}$ | | |
| chemical liquid(2) | 4.96 $kg/t_{product}$ | | |
| Processing liquids and fats(3) | 1.73 $kg/t_{product}$ | | |
| Butane gas(4) | 2.72 $kg/t_{product}$ | | |
| Petrol | 0.04 $l/t_{product}$ | | |
| Diesel | 2.42 $l/t_{product}$ | | |
| (1) Annealing inert gas<br>(2) predominant as pickle and leach<br>(3) Oil, cooling lubricant, degreasing agent<br>(4) Process gas as an alternative for natural gas | | | |

**Table 3.37: Operating data for a secondary copper process (remelting)**
[ 234, UBA Copper, lead, zinc and aluminium 2007 ]

## 3.3 Techniques to consider in the determination of BAT

The sections of this document entitled 'Techniques to consider in the determination of BAT' set out techniques considered generally to have potential for achieving a high level of environmental protection in the industries within the scope of the document. The background to the way the techniques are described is given in Section 2.1.2 and Table 2.2.

This section presents a number of techniques for the prevention or reduction of emissions and residues as well as techniques for reducing the overall energy consumption. They are all commercially available. Examples are given in order to demonstrate techniques which illustrate a high environmental performance. The techniques that are given as examples depend on information provided by the industry, European Member States and the valuation of the European IPPC Bureau. The general techniques described in Chapter 2, common processes, apply to a large extent, to the processes in this sector and influence the manner in which the main and associated processes are controlled and operated.

The control of furnace operating parameters and the prevention of diffuse emissions from furnaces and the tapping and pouring processes is also important. Techniques used by other sectors are also applicable particularly those relating to the use of sulphur recovery systems.

The appropriate techniques are strongly influenced by the raw materials that are to be processed on a site by site basis, in particular the type and variability of the concentrate or secondary raw materials can be crucial to the choice of process. On a worldwide basis, some operations have a dedicated single source of raw material but the majority of the plants in Europe buy concentrate from the open market and need to maintain flexibility in processing a range of raw materials that can contain varying amounts of other metals which directly affect the success of waste water treatment systems as well as the smelter operation. The smelter pays the market price for the concentrate based on the value of the copper and precious metal content less the fixed amounts for treating (smelting) the concentrate (Tc) and refining the anodes (Rc). It is these fixed charges that provide the income for the smelter and not the world price of copper.

In a similar manner, the standard of collection and abatement systems used worldwide in the industry reflects local, regional or long-range environmental quality standards and direct comparison of the environmental performance of process combinations is therefore difficult. It is possible however, to judge how a particular process can perform with the appropriate, modern abatement equipment [ 206, Traulsen, H. 1999 ].

For $SO_2$ or total carbon removal, the variation in raw gas concentration during batch processes may affect the performance of the abatement system. For example converter blows will produce peak raw gas concentrations and consequently the number of cycles per day influences the associated range (given as a daily average). A similar effect may be seen with other batch process stages. Peak concentrations in the treated gas may be up to three times the reported range. For $NO_X$, the use of highly efficient processes (e.g. Contimelt) requires a balance to be established between energy use and achieved value.

### 3.3.1 Materials storage, handling and pretreatment processes

#### 3.3.1.1 Primary raw materials

**Description**

The raw materials are concentrates, fluxes and fuel. Important aspects are the prevention of leakage of dust and wet material, the collection and treatment of dust and liquids and the control of the input and operating parameters of the handling and feeding processes.

The issues specific to this group are:

- The potentially dusty nature of some concentrates and some fluxes (e.g. lime) means that enclosed storage, handling and treatment systems are techniques to consider in these instances. The dust generated by some slag-crushing operations means that collection and abatement may be applicable for this process. Similarly, slag granulation water may require settlement or other treatment prior to discharge [ 233, Farrell Nordic Mission 2008 ].
- Concentrates are mixed with fluxes to produce a fairly constant feed. Therefore, the general practice of sampling and analysis to characterise the concentrates and storage of individual concentrates separately so that an optimum blend can be prepared for smelting are techniques to be considered [ 274, Farrell Mission in DE 2008 ].
- Feed blends prepared from bedding plants or from dosing bin systems using weighing systems such as belt weighers or loss in weight systems are techniques to consider. They form a sandwich mix on the extraction belt. Final mixing and homogenisation takes place in the conveying and drying systems. Enclosed conveyors or pneumatic transfer systems are used. Hot gas rotary dryers, fluidised bed, flash or steam coil dryers, etc. can be used. Steam coil dryers use waste heat from other parts of the process provided that the heat balance allows it. The drier and associated dust abatement stage, therefore, depends on site-specific conditions such as the reliability of the steam supply. Fabric or ceramic filters achieve better dust removal efficiencies than ESPs [ 103, Farrell, F. 1998 ].
- In some cases, the dry material is reported to have an ignition temperature of between 300 and 400 °C but this factor can be dealt with in a number of ways. For example the oxygen content of the gases in a hot air drier is low and the operating temperature is controlled at a maximum tolerable level, mostly by mixing it with cold air. Nitrogen may also be used; auto-ignition may not be a problem in these cases. Similarly, steam coil dryers can maintain a low temperature in the concentrate and a low airflow rate, which can achieve the same effect. Some techniques are also used to prevent auto-ignition. Heat or spark detection can identify hot spots and these devices can be used to trigger nitrogen quenching [ 103, Farrell, F. 1998 ].
- The storage of acid produced during the process in double-walled tanks or tanks placed in chemically-resistant bunds are techniques to be considered. The treatment of acid slimes from the sulphuric acid plant and weak acid from scrubbing systems depends on local processing or disposal requirements unless there is a local use for the material. Anode slimes and other residues that contain metals and are destined for recovery off site should be stored in drums or other suitable ways depending on the material [ 233, Farrell Nordic Mission 2008 ].

**Achieved environmental benefits**
The environmental benefits are the prevention of diffuse emissions of metals, dust and other compounds.

**Cross-media effects**
None are reported.

**Operational data**
None are available.

**Applicability**
These techniques are generally applicable to most plants.

**Economics**
None was provided but the processes are operating economically.

**Driving force for implementation**
The reduction of emissions and saving raw materials.

**Example plants**
Plants in SW, DE, BG, BE, PL and ES.

**Reference literature**

[ 233, Farrell Nordic Mission 2008 ], [ 274, Farrell Mission in DE 2008 ], [ 103, Farrell, F. 1998 ].

### 3.3.1.2 Raw material sampling and reception system

**Description**
The concentrate reception and sampling system uses an enclosed vehicle tipping area, sealed transfer system and computerised sampling. The storage and blending area, and conveyors are enclosed [ 103, Farrell, F. 1998 ].

**Achieved environmental benefits**
The prevention of diffuse dust. Defined feed for the process which minimises variation in process parameters.

**Cross-media effects**
No data has been reported.

**Operational data**
No data has been reported.

**Applicability**
This technique is applicable to most primary copper processes.

**Economics**
No detailed economic data is available but it can be concluded by common practice that these techniques are economically viable. Production efficiency increased and one plant reported a payback period of 18 months.

**Driving force for implementation**
The knowledge of the correct mix of input material allows the optimum operational conditions to be established resulting in an increased yield and reduction of emissions. The elimination of losses of raw materials by wind effects is also a driving force.

**Example plants**
ES, BE and DE.

**Reference literature**
[ 103, Farrell, F. 1998 ], [ 291, Competitive Report 2001 ].

### 3.3.1.3 Secondary raw materials

**Description**
There are a variety of secondary raw materials used for secondary production and they range from fine dusts to large single items. The copper content varies for each type of material and so does the content of other metals and contaminants. Size and copper content (low, medium and high) can be used to classify the materials. Techniques used for storage, handling and pretreatment will vary according to the material size and the extent of any contamination. These factors vary from site to site and the techniques discussed in Chapter 2 are techniques to be considered. The site-specific issues that apply to this group are [ 103, Farrell, F. 1998 ]:

- the storage of fine dusts in enclosed buildings or in sealed packaging;
- the storage of secondary raw materials that contain water-soluble components under cover;
- the storage of non-dusty, non-soluble material in open stockpiles and large items individually in the open;

- large items including lumps of slag, metal (blister, etc.) may damage concrete surfaces causing hidden cracks and the specific case influences the technique used.

Pretreatment stages are often used to remove organic components such as cable insulation and printed circuit board remnants and to separate other metals, e.g. tin or lead and the following techniques are techniques to be considered in the determination of BAT.

- The use of milling and grinding techniques with good dust extraction and abatement are techniques to consider. The fine dust that is produced may be treated to recover precious metals, pneumatic or other density separation techniques are used.
- Cryogenic techniques to make cable coverings friable and more easily separated.
- Thermal de-coating and de-oiling processes are also techniques to consider and will feature an afterburning stage to destroy any organic material in the off-gas.
- Fine dusts are stored and handled in a manner that prevents the emission of dust. They are often blended and agglomerated to provide a consistent feed to the furnace.

The storage, handling and pretreatment techniques to consider for copper are given in Table 3.38.

| Raw Material | Storage | Handling | Pretreatment | Comment |
|---|---|---|---|---|
| Coal or Coke | Covered bays<br>Silos | Covered conveyors if non-dusty.<br>Pneumatic | | |
| Fuel and other oils | Tanks or drums in bunded areas | Secure pipeline or manual system | | |
| Fluxes, if dust Forming | Open on concrete or similar floors.<br>Enclosed (Silo), if required | Enclosed conveyors with dust collection.<br>Pneumatic | Blending with concentrates or other material | |
| Concentrates | Enclosed unless non-dust-forming | Enclosed with dust collection.<br>Pneumatic | Blending using bedding plant or conveyors, drying | |
| Copper products cathodes, wire-rod, copper billets and cakes | Open concrete area or covered storage | | | |
| Fine dust | Enclosed | Enclosed with dust collection.<br>Pneumatic | Blending,<br>Agglomeration | |
| Coarse dust (raw material or granulated slag) | Covered bays | Mechanical loader | De-oiling | Oil collection if present |
| Lump (raw material or slag) | Open | Mechanical loader | | Oil collection if present |
| Whole Items | Open or covered bays | Mechanical loader | | Oil collection if present |
| Swarf | Covered storage | Charge skips | Swarf drying or de-oiling | Oil collection if presently |
| Cable | Open | Mechanical loader | De-coating | |
| Circuit Boards | Covered bays | Mechanical loader | Grinding + density separation | Plastic content may provide heat input |
| Process residues for recovery | Open, covered or enclosed depending on dust formation | Depends on conditions | | Appropriate drainage system |
| Wastes for disposal (e.g. furnace linings) | Open covered or enclosed bays or sealed (drums) depending on the material | Depends on conditions | | Appropriate drainage system |

**Table 3.38: Storage, handling and pretreatment techniques to consider for copper**

**Achieved environmental benefits**
The environmental benefits are the prevention of diffuse emissions of metals, dust and other compounds.

**Cross-media effects**
None are reported.

**Operational data**
None are available.

**Applicability**
These techniques are generally applicable to most plants.

**Economics**
None was provided but the processes are operating economically.

**Driving force for implementation**
The reduction of emissions and saving raw materials.

**Example plants**
Plants in DE, AT, FR, BE and ES.

**Reference literature**
[ 103, Farrell, F. 1998 ], [ 231, FF Mission 2007 ], [ 274, Farrell Mission in DE 2008 ]

### 3.3.2 Primary smelting processes

*This information about the applied furnaces is not considered to be a technique to consider in the determination of BAT. Part of it can be used in Section 3.1. Attention has to be paid avoiding repetition.*

The copper smelting processes practised in the EU-27 are [ 238, ECI Copper Installations 2008 ]:

- Outotec flash smelting using high oxygen enrichment for normal copper concentrate to matte smelting; matte conversion in Peirce-Smith converters to produce blister copper. Slag cleaning in electric furnace or by flotation.
- Direct to blister smelting in a flash furnace with slag cleaning in an electric furnace.
- Partial roasting of concentrates in a fluid bed roaster, electric furnace smelting to matte. Matte conversion to blister copper in Peirce-Smith converters. Slag cleaning by fuming. The raw materials processed contain zinc and some lead as well as copper.
- Smelting and conversion to blister copper of primary and secondary lead/copper and some raw materials that contain zinc in an Ausmelt/ISA Smelt furnace; lead production by slag cleaning in a blast furnace.
- Smelting in a blast furnace of primary materials with low iron and sulphur contents and high carbon content and next converting obtained copper mat into blister copper.

The Outotec flash furnace produces a high-grade matte that assists and simplifies the process of conversion.

In some instances the furnace can produce blister copper directly without a converting stage. The use of the Outotec flash furnace in this manner is characterised by blister copper production in one smelting step when using specific concentrates [ 134, Metallurgical Consulting Traulsen GmbH 1998 ]. For example, this process is used in Poland for direct blister production from concentrates with a low iron content.

The Outotec flash smelting process features heat recovery in the form of steam and electricity and also the collection and recovery of sulphur dioxide as sulphuric acid. Furnace lining life is approximately 5 to 10 years (depending on various factors, like furnace size, production rate and operating parameter practised, etc.).

In addition to those above, several other furnaces are used for the smelting stage worldwide [ 134, Metallurgical Consulting Traulsen GmbH 1998 ] and several of these can also be considered. The use of the reverberatory furnace for primary copper concentrates is not included.

There is a distinction between these processes as two of the processes, the Mitsubishi and the Kennecott/Outotec processes, combine the smelting and converting stages and so do not use a separate converter. The Mitsubishi process uses three interconnected furnaces with gravity flows of molten material between the furnaces. The Kennecott/Outotec process uses a matte granulation and grinding process between the smelting and conversion flash furnaces so that the unit operations are uncoupled.

An overview of primary copper smelting furnaces is given in Table 3.39 which summarises the advantages and disadvantages of the various processes. All of the furnaces mentioned have been described earlier.
*It doesn't make sense to have the furnaces in section 2.8 and 2.9 and here again.*

| Furnace | Applied capacity (x1000 t/yr) | Gas collection | Advantages | Disadvantages | Comments |
|---|---|---|---|---|---|
| ***Smelting process*** | | | | | |
| Outotec flash smelting | ~ 150 to 400 (mostly 200 to 300) | Sealed furnace | High smelting rate.<br>High quality matte.<br>Long furnace lining life | Comparatively higher furnace investment but lower overall installation and operating costs | Vast process knowledge available |
| Electric (with partial roasting) | ~ 40 to 220 | Sealed furnace | Primary and secondary.<br>Compact | Two-stage process | |
| Ausmelt/ISA Smelt | ~ 170 to 230 | Hooded | Primary and secondary.<br>High smelting rate.<br>Variety of fuels | Requires a settler to separate matte and slag | Moist feed can increase gas volumes |
| Blast furnace | 100 to 200 | Hooded | Smelts poor copper concentrates, high Pb and Zn removal | Requires settler to separate matte and slag | |
| Noranda and El Teniente (for one unit) | ~ 120 to 150/ and 70 to 190 | Hooded | Compact.<br>Lower cost | Furnace lining life ~ 2 years | Processes are developing rapidly and their status will improve over time |
| INCO flash | ~ 120 to 200 | Sealed furnace | High smelting rate.<br>High quality matte. | Autogeneous 100 % $O_2$ used resulting in narrow operating window. | |
| Contop | ~ 120 | Sealed furnace | High Bi and Zn removal. | Low throughput | Only one plant. |
| Vanyukov process | ~ 100 or more | Hooded | Similar to Noranda | | Too little data to assess. |
| Baiyin process | ~ 70 | Hooded | Similar to Noranda.<br>Divided furnace to give integral settler | | Too little data to assess. |
| ***Continuous, coupled process*** | | | | | |

| Furnace | Applied capacity (x1000 t/yr) | Gas collection | Advantages | Disadvantages | Comments |
|---|---|---|---|---|---|
| Mitsubishi | ~ 120 to 240 | Sealed furnace | Can also melt purchased and anode scrap.<br>High smelting rate.<br>No ladle transfer | Some limitation in feed. Coupled unit operation with effect on efficiency of the complete line.<br>Sulphur content of blister copper | 3rd plant being constructed. |
| ***Continuous uncoupled Process*** | | | | | |
| Kennecott/ Outotec flash smelting and converting process | ~ 300 | Sealed furnaces | Surge storage of ground matte<br>No ladle transfer | Comparatively higher investment cost but lower direct operating costs | The only process with uncoupled unit operation |

**Table 3.39: Overview of primary copper smelting furnaces**
[ 134, Metallurgical Consulting Traulsen GmbH 1998 ]

#### 3.3.2.1 Reduction of environmental impact by incorporating a new smelter and converters

**Description**
The copper production capacity was increased by 100000 tonnes to a total copper capacity of 240000 tonnes. The project included a new smelter feed mixing facility, a new new copper furnace flash smelter, an enlarged converter hall with new converters and a new charge system, a new converter hall ventilation system and filter and a new anode casting plant.

A new sulphuric acid plant, including new mercury-removal technique was also installed.

**Achieved environmental benefits**
The environmental impact has not been increased despite the increase in the throughput of the installation. *Try to get data comparing the situation before and after incorporating the new smelter.*

**Cross-media effects**
No data has been reported.

**Operational data**
Recent information is available for a specific process upgrade. In this instance the published costs are given below. 100000 t/yr extra production of copper is achieved. Proven and best available technology combined with experienced personnel results in high availability of processes and reduced emissions.

**Applicability**
These techniques are applicable to a new smelter or the modernisation of an existing smelter.

**Economics**
Total project cost 2 billion Swedish crowns (EUR 224 million). Anticipated pay back period is 6.5 years. The environmental considerations in this expansion were estimated to cost about EUR 70 (about 30 % of the project cost).

**Driving force for implementation**
Increased throughput and modernisation to produce high-purity copper at lower costs and with minimal environmental impact were the driving forces.

**Example plants**

Rönnskär, Sweden.

**Reference literature**
[ 238, ECI Copper Installations 2008 ], [ 233, Farrell Nordic Mission 2008 ], [ 134, Metallurgical Consulting Traulsen GmbH 1998 ].

### 3.3.2.2 Direct to blister copper smelting

**Description**
High grade and low iron concentrate is smelted in an Outotec flash furnace to produce blister copper directly without the need for a converter. The disadvantage of omitting the converter stage is that there is no surplus heat available to melt anode scrap and reverts. The solution to this is to have an integrated approach with another plant that uses converters or to use reverberatory anode furnaces to melt the scrap [ 287, Tuominen, Anjala, Bjorklund; Kojo, Lahtinen; Peuraniemi; Lahtinen, Kojo TMS 2006 ].

The furnace slag produced in the direct to blister process has a high copper content and so the slag is treated in an electric furnace to produce a copper/lead/iron alloy. This is subsequently treated in bath furnaces to separate additional blister copper.

Gases from the flash furnace have a high $SO_2$ concentration and pass to a double contact sulphuric acid plant for conversion to the acid.

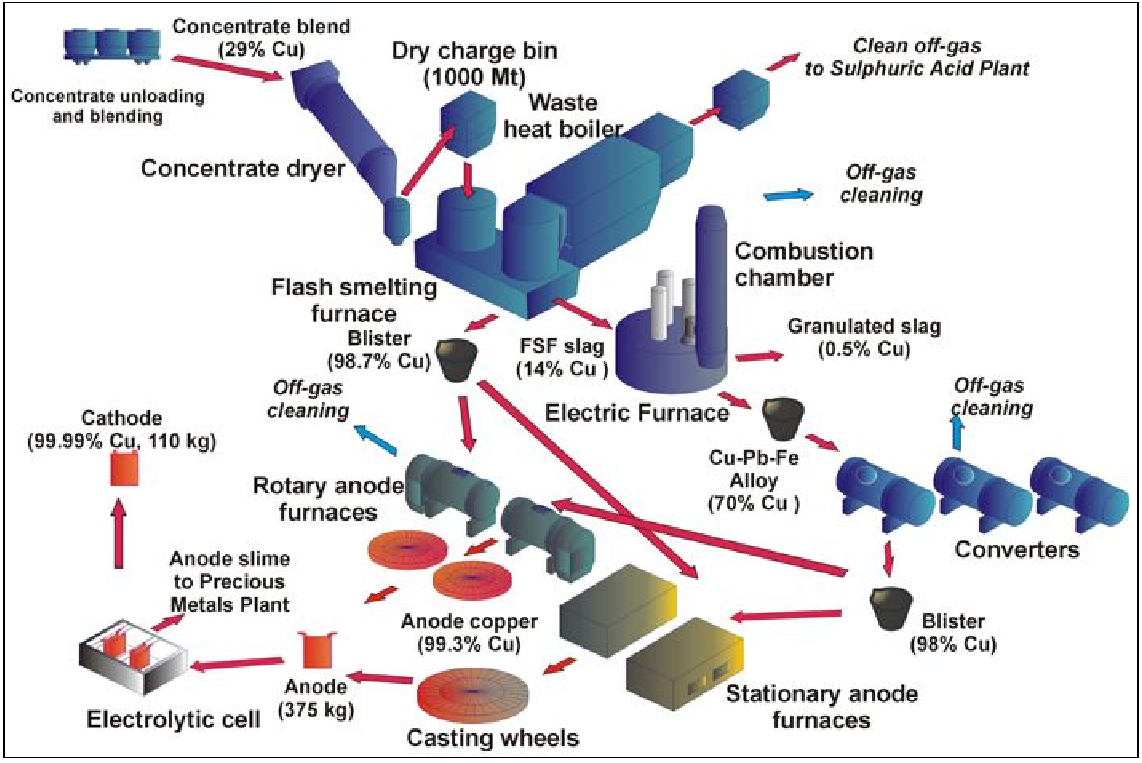


**Figure 3.12: Direct to blister smelting Głogów 2 Smelter - KGHM**

**Achieved environmental benefits**
The sources of diffuse emissions are much smaller than those from a conventional smelting/converting process. *Are there any data available.*

**Cross-media effects**
No adverse impacts have been reported.

**Operational data**
Included in the description and Figure 3.12.

**Applicability**
This technique was originally applicable to low slag fall concentrates but is now being applied to lower concentrate grades.

**Economics**
No details on economics gave been provided but claims have been made for lower investment costs and a reduced size of acid plant. Three plants are operating reliably and the first one was installed in 1978.

**Driving force for implementation**
Reduced diffuse emissions and reduced processing costs.

**Example plants**
Głogów, Poland; Olympic Dam, Australia; Konkola, Zambia.

**Reference information**
[ 287, Tuominen, Anjala, Bjorklund; Kojo, Lahtinen; Peuraniemi; Lahtinen, Kojo TMS 2006 ], [ 238, ECI Copper Installations 2008 ]

### 3.3.2.3 Use of a blast furnace for primary copper production

*Try to use one name, either blast or shaft furnace. From the heading it should be clearer what this BAT aims at. Even after reading this section it remains unclear what is the dominat target of this technique. Energy saving, SO2 reduction or what?*

**Description**
The smelter uses shaft furnaces with oxygen enrichment, to smelt low grade copper concentrate from the local mine and concentrator which has a low sulphur content.

The concentrate is mixed with coke and converter slag and is made into briquettes using black liquor from the pulp industry as a binder. This is fed by a double interlocked system into the top of the shaft furnace. The briquettes are smelted to produce a copper matte which is transferred by ladle to Hoboken converters where it is converted into blister copper. The blister copper is then transferred again to one of two anode furnaces and anodes are cast for electrorefining to LME Grade A standard using standard copper starter sheets.

The gases from the shaft furnaces have a very low $SO_2$ concentration and are passed to a single or double sulphuric acid plant for conversion to the acid. The gases from the powerplant and the acid plant are desulphurised. The desulphurisation takes place in a semi-dry scrubber or in a polyether-based adsorption/desorption process (Solinox), from which clean gas is emitted into the air and concentrated gas is recycled to the sulphuric acid plant. In this case, the sulphuric acid plant (which processes converter gases) has only a single contact, but instead its residue gas is also desulphurised in the Solinox process [ 230, FF Mission report 2007 ], [ 143, Byrdziak, H. et al. 1998 ].

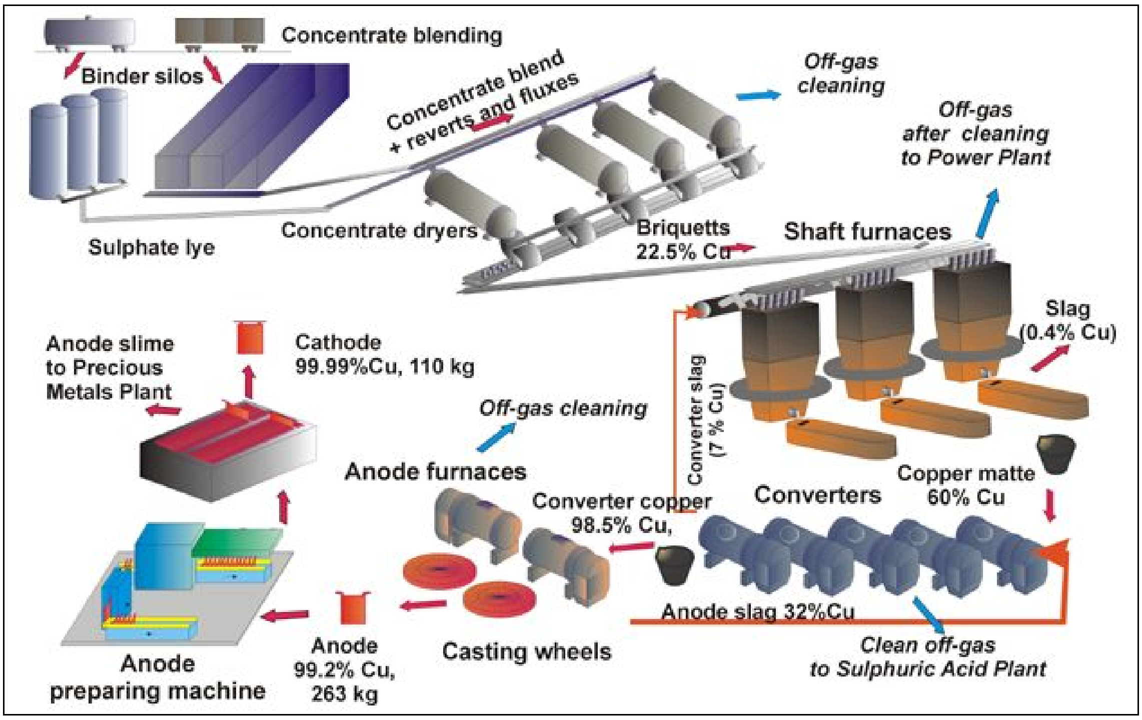


Figure 3.13: Blast furnace process for primary copper

### Achieved environmental benefits

The gases from the power plant and the acid plant are desulphurised in a polyether-based adsorption/desorption process to produce a cleaned gas to be emitted to air and a concentrated gas to be recycled to the sulphuric acid plant. The overall $SO_2$ removal efficiency is therefore high. Energy is recovered from the hot gases and from the CO content.

### Cross-media effects

The $SO_2$ adsorption stage is a very high energy consumer. The gases from the shaft furnaces have a very low $SO_2$ concentration and so are passed directly to a power plant to recover energy and use the CO content of the gases.

### Operational data

See Figure 3.13.

### Applicability

This technique is applicable to this type of concentrate. The concentrate also contains a relatively high concentration of carbon which means that other methods of smelting this particular concentrate will result in excessive energy release that will cause damage to the furnace. This process is therefore the only reliable process for this raw material.

This process is also suitable for smelting low copper content concentrate or solid material up to 150 mm in diameter.

### Economics

No data has been reported.

### Driving force for implementation

A reduction of the impact of $SO_2$ emissions on the environment is the driving force.

**Example plants**
Legnica, Poland.

**Reference literature:**
[ 230, FF Mission report 2007 ], [ 143, Byrdziak, H. et al. 1998 ].

## 3.3.3 Sulphur dioxide removal

### 3.3.3.1 Production of liquid sulphur dioxide from high strength gases

*(100% exactly the same section is used under 2.11.3.3. What is the sense then in having horizontal sections?)*

**Description**
Sulphur dioxide is absorbed in cold water (e.g. cold seawater) followed by vacuum stripping and recovery as liquid sulphur dioxide. These processes are used in conjunction with a sulphuric acid plant to recover sulphur dioxide that is not dissolved. The potential for the production of liquid sulphur dioxide depends on the existence of a local market. The process to produce liquid sulphur dioxide is shown in Figure 3.14. Liquid sulphur dioxide is also produced in a cryogenic process [ 233, Farrell Nordic Mission 2008 ].

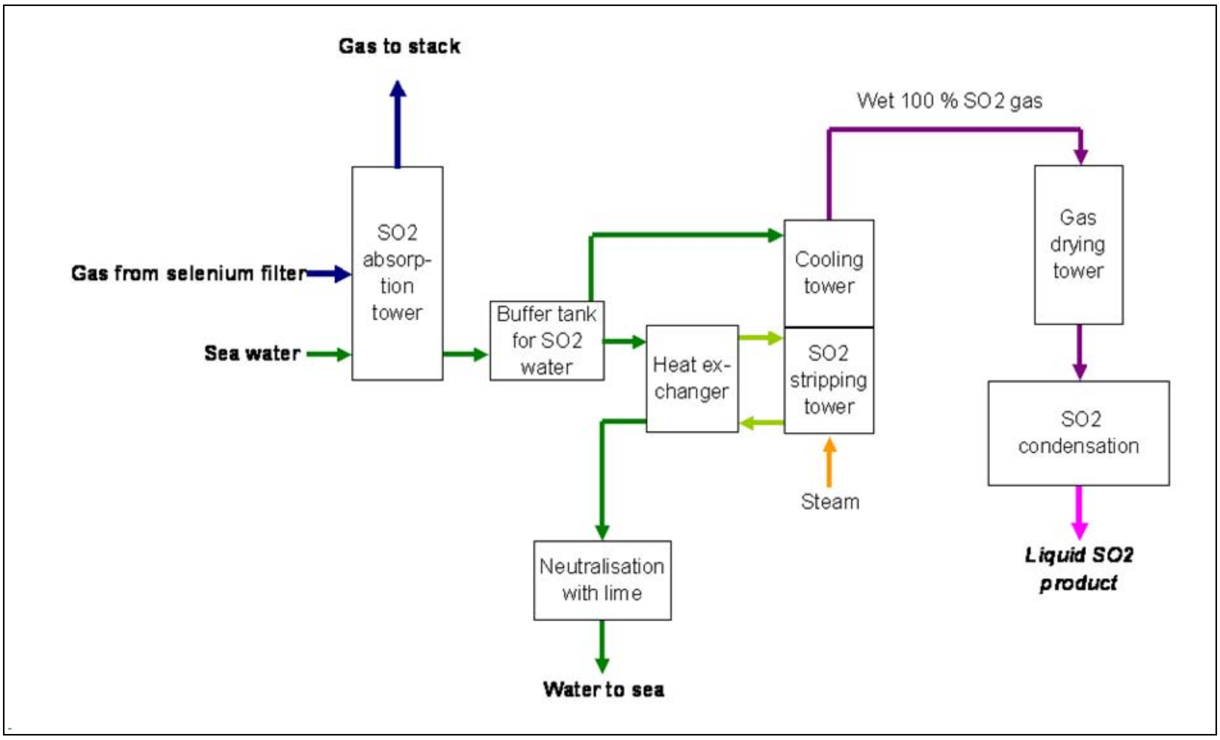


**Figure 3.14:** **The process to produce liquid sulphur dioxide**

**Achieved environmental benefits**
Provision of a supply of sulphur dioxide that can be used to maintain an even inlet concentration to a sulphuric acid plant. The annual average emissions of sulphur dioxide are shown in Table 2.29.

| Year | Tail gas concentration (mg/Nm$^3$) |
|---|---|
| 2006 | 213 |
| 2007 | 155 |
| 2008 | 153 |
| 2009 | 124 |

**Table 3.40: The annual average emissions of sulphur dioxide**

**Cross-media effects**
No data has been reported.

**Operational data**
Non provided.

**Applicability**
Applicable to installations where there is a local market for liquid sulphur dioxide.

**Economics**
One plant is operating under economic conditions.

**Driving force for implementation**
The production of sulphur dioxide for sale.

**Example plants**
Boliden, Sweden.

**Reference literature**
[ 233, Farrell Nordic Mission 2008 ].

### 3.3.3.2 Sulphur dioxide removal using lime injection

*It should be clear from the heading that secondary fume treatment lakes place only.*
*Exactly the same section is included in 2.11.3.6. Delete it there! Maybe relocate the information for the Swedish plant in Bergsoe to the lead chapter.*

**Description**
Lime is injected in the gas flow with a resulting formation of gypsum. When possible, simultaneous injection of water increases the reactivity of the lime, hence increasing the removal efficiency of the lime. The gypsum and the process dust are removed from the gas flow by a fabric filter which must have sufficient capacity for the additional dust load. The resulting mixture of lime and gypsum can be re-used in other metallurgical or water treatment processes [ 346, SO2 - Lime injection FINAL 4.2.2010 ].

Desulphurisation efficiency is influenced by the temperature of the gases (minimum 60 °C), the moisture content, and the contact time between lime particles and the gas. Turbulence of the gas flow, high specific surface of the lime particles and the quantity of lime also influence efficiency. A reactor chamber with sufficient residence time can be used to create a turbulent flow if there is space available, but direct injection of lime and water into the gas upstream of a fabric filter is used where there is not sufficient space for a reactor.

Lime injection can be combined with the simultaneous injection of other components, e.g. active carbon for Hg or PCDD/F removal. In existing gas cleaning installations, lime injection can be simple to implement, provided there is a sufficient temperature of the gases and reaction time.

**Achieved environmental benefits**
Dust and $SO_2$ removal is achieved with the same fabric filter. Removal efficiencies range from 50 to 95 % *(for dust or SO2 or both?).* Removal rates at the higher end of this range are only possible in ideal conditions in newly-designed, dedicated installations. The addition of lime has a positive effect on dioxin emissions.

**Cross-media effects**

If the gypsum produced is impure it can either be treated/recirculated in the process or disposed of. The impure gypsum can be used in metallurgical processes requiring calcium, e.g. for slag formation or in a waste water treatment facility where the excess lime that didn't react can still be useful. The use of a mixing chamber creates an additional pressure drop, resulting in higher energy use by the fan. The use of energy, lime and water are also cross-media effects.

**Operational data**

A minimum temperature of 60 °C is needed for the process to operate effectively. The removal efficiency at a temperature of 150 °C and 5% moisture content of the gas is about 45 %. When the moisture content increases to 25 %, the removal efficiency is increased to 75 %. At lower temperatures, the removal efficiency drops to 20 - 40 %, and high lime injection rates are needed. Where the gas temperature is close to the dew point, additional water injection is not possible because of the adverse effect on the fabric filter.

**Example operational data.**

**1) (Hoboken, Belgium).** Newly designed batch process and new gas cleaning system, with varying $SO_2$ concentrations in the process gases. Combined dust abatement and process dust removal system with injection of lime and water in a mixing chamber with residence time of 6 seconds $SO_2$ concentration of the gases vary from 0 up to 1 %. Injection rate: +/- 250 kg/h at 150 °C and moisture content of 30 vol/%. Because of the metal content of the process dust, the flue dust which is removed by the fabric filter is re used in another process. Also the gypsum can be used in this process. Because of lime injection, the filter capacity is 40 % higher than for dust abatement reasons only. A test of dry lime injection in a cool gas showed poor performance and high operating costs and the system was rejected.

2) **Beerse, Belgium.** Existing continuous process with varying $SO_2$ concentrations. Dry lime is injected at two points in the process that have high and low temperatures respectively. Clogging and blocking of the tubes restricts the usable lime injection rate. The mixture of dust and gypsum cannot be recycled internally and the disposal costs for gypsum/dust is high.

**3) Hamburg, Germany**. Secondary fume collection system with added lime injection in a copper smelter. A secondary fume collection system is used to reduce the diffuse emission of dust. A system to inject slaked lime into the gas flow was fitted to reduce the $SO_2$ present in the gas flow. The dust/lime mixture with an average dust and absorbent content of 1500 mg/ $Nm^3$ is removed in a fabric filter with a dust removal efficiency of 99 %. As the system treats secondary fumes, the temperature of the gases is relatively, which affects the removal rate.

The performance data for the example plants is shown in Table 3.41.

| Plant | $SO_2$ mg/$Nm^3$ | | Dust mg/$Nm^3$ | | Comment |
|---|---|---|---|---|---|
| | Inlet | Outlet | Inlet | Outlet | |
| Hoboken (New batch process) | Up to 1% | 50 – 400 | | | Six second residence time in a reaction chamber. Dust is used in another process |
| Hoboken (Test on secondary fume treatment) | 60 – 250 | 30 – 125 | | | Very high lime use due to low gas temperature. |
| Beerse (Whole battery smelter) | 3000 | 650 | | | Two point injection |
| Hamburg (Secondary fume collection) | 100 – 1500 | 450 – 750 | 1500 | < 2 | Lime addition prior to fabric filter. Dust is used in process |

**Table 3.41: Performance data for example plants**

[ 346, SO2 - Lime injection FINAL 4.2.2010 ]

*Unclear: What means battery smelter? We are here in the copper section!*
*Hamburg: Inlet 100 to 1500 and oult 450 to 750??*

**Applicability**
Optimum conditions can be incorporated in new installations in the copper sector. When using existing gas-cleaning equipment with a fabric filter that is designed to remove process dust, it can be used to capture gypsum if the filter capacity allows for this. When a filter is already used, direct injection is possible when temperature, moisture content and contact time are sufficient. An existing filter installation might be not sufficient because the amount of dust increases drastically and thus might need to be replaced.

**Economics**
Investment cost for plant 1: EUR 550.000 (mixing chamber: EUR 100.00, additional cost for fabric filter: EUR 190.000 , injection system including silo: 2EUR 60.000).

Investment costs for plant 3: EUR 10 million plus approximately EUR 7 million for measures to capture fugitive emissions of the anode furnace and casting wheel.

Simultaneous injection of water decreases the quantities of lime needed as the reaction between $SO_2$ and lime takes place at the surface of the lime particles, a relatively high amount of lime is needed. The quantities that are needed can be reduced by using a lime with a high specific surface and/or by recirculation of the fabric filter dust. Lime cost ranges from EUR 60/ton for calcium hydroxide to EUR 200/ton for expanded calcium hydroxide.

When the flue dust must be disposed of, the cost of this technique can be very high.

**Driving force for implementation**
The treatment of dust and SO2 simultaneously and the utilisation of existing fabric filters.

**Example plants**
Hoboken, Belgium; Beerse, Belgium; Hamburg, Germany; ~~Bergsöe, Sweden.~~*The Bergsoe site is a lead smelter and should be deleted here.*

**Reference Literature**
[ 346, SO2 - Lime injection FINAL 4.2.2010 ]

### 3.3.4 Secondary smelting processes

**Description**
The range of secondary materials and the variation in the copper content and the degree of contamination has lead to the development of a range of smelters for secondary materials [ 135, Gershel, T. 1998 ]. In Europe, the Mini Smelter, the blast furnace, the Ausmelt/ISA Smelt furnace, the TBRC and the sealed submerged arc electric furnace are used for a wide range of materials. They are all techniques to consider depending on the type of raw material. The Mini Smelter is used for secondary materials and slag using iron and high iron content scrap as a reducing agent. The converter is used for the treatment of black copper that contains iron from the smelting furnaces and for the smelting of alloy scrap. The reverberatory hearth furnace is used for refining converter copper and scrap with higher copper contents.

Table 3.42 gives an overview of the advantages and disadvantages of the secondary smelting furnaces for lower grade feed materials.

| Furnace | Capacity range | Gas collection and abatement requirement | Advantages | Disadvantages | Comments |
|---|---|---|---|---|---|
| Blast furnace | ~150 to 200 tonnes per | Semi-sealed.<br>Gas cooling(1) | Low grade material | Lack of process control | Improvement in process control for |

| | | | | | |
|---|---|---|---|---|---|
| | day per furnace | afterburning and cleaning (fabric filter) | | development | inclusion.<br>Production rate depends on type of feed and copper content |
| Submerged arc electric furnace | For a 8 MVA furnace: 8 - 25 tonnes per hour melting rate | Sealed.<br>Afterburning, gas cooling and cleaning(2) | Established for computer scrap.;<br>Low gas volume | Some feed restrictions | Formed CO burns in the furnace to provide heat.<br>Production rate depends on type of feed copper content and furnace rating |
| Mini Smelter | | Enclosed.<br>Gas cooling and cleaning (fabric filter) | High smelting rate, compact | Some feed restrictions | |
| TBRC | Up to ~ 40 to 70 tonnes per batch | Enclosed.<br>Gas cooling(1) and cleaning (fabric filter) | Range of material. High smelting rate, compact.<br>rotation used | Expensive | |
| Ausmelt/ISA Smelt and KRS furnace | ~ 30000 to 40000 tonnes per year. | Hoods.<br>Gas cooling(1) and cleaning(2) | Range of material;<br>high smelting rate | Developed for mixed primary and secondary raw materials | In full operation |
| Converter | ~15 to 35 tonnes per batch per converter | Hooded.<br>Gas cooling and cleaning(2) (fabric filter) | | | For treatment of black copper from melting furnaces and smelting of copper alloys |
| Hearth shaft furnace | ~ 250 t/d | Sealed and hooded, afterburning, cooling & cleaning (fabric filter) | Use for melting and refining of metal; good energy efficiency | Some feed restrictions | Fire refining of higher grade scrap, anode and blister copper. |
| Contimelt process | 50 - 100 t/h | Afterburning (reduction furnace), waste heat boiler, cleaning (fabric filter) | High production rate, high energy utilisation | Some feed restrictions | Fire refining of higher grade scrap, anode and blister copper |
| Reverberatory hearth furnace | ~ 250 to 400 tonnes per day | Semi-sealed and hooded.<br>Gas cooling(1) afterburning and cleaning (fabric filter) | Use for converting and refining | Sealing; some feed restrictions | Can use tuyères along with tilting system.<br>Fire refining of higher grade scrap and blister copper |

(1) If the temperature level is high enough, waste heat recovery may be considered; for cleaning in fabric filters, further cooling is required.

(2) In the EU plants, the off-gas may contain sulphur dioxide during certain campaigns and therefore is treated in a scrubber or sent to an acid plant at these times.

**Table 3.42: Overview of secondary smelting furnaces**

[ 206, Traulsen, H. 1999 ]

Several of the techniques described in Chapter 2 are applicable to fume extraction and abatement and the process control systems used by these furnaces. These techniques are not routinely used by all installations. The process control system for the blast furnace is considered suitable for development and its potential inclusion is subject to this factor.

Gases from secondary smelters usually contain little or no sulphur dioxide provided sulphidic material is avoided but can contain significant quantities of the more volatile metals such as lead and zinc, etc. They can also contain VOCs, PCDD/F, CO and dust and so the abatement stages for secondary smelting involve gas cooling (with heat/energy recovery), afterburning to destroy organic carbon and PCDD/F, coarse particle separation and fabric filtration. The collected dusts are recycled to recover these metals.

Secondary copper smelters are able to recover copper and precious metals from waste electrical and electronic equipment and many use a dedicated pretreatment plant to prepare this material.

**Achieved environmental benefits**
Containment of process gases and destruction of PCDD/F depending on the furnace are achieved. There is a reduction of main emissions. When copper cathodes are produced from recycled materials, there are savings of approximately 650000 t of $CO_2$ because specific direct emissions of secondary smelters are four times lower than those of primary smelters. $CO_2$ emissions at one secondary smelter have been reduced from 1.9 t $CO_2$/t copper in 1990 to 0.6 t $CO_2$/t copper in 2008.

**Cross-media effects**
Energy usage contributes to cross-media effects.

**Operational data**
Table 3.42 provides the overview of the techniques.

The production of copper from secondary raw materials has become more energy efficient with the introduction of newer techniques. The energy consumption of the KRS installation is 1.080 kWh/t of raw material, which is considerably lower than the old system of blast furnaces, converters and a lead tin alloy plants which are 2.300 kWh/t [ 234, UBA Copper, lead, zinc and aluminium 2007 ].

**Applicability**
These techniques are applicable to a change of furnace and are only applicable for a major modernisation or plant upgrade.

**Economics**
The capital cost of the KRS installation was EUR 40 million without the filter units and the stack which were existing [ 234, UBA Copper, lead, zinc and aluminium 2007 ].

**Driving force for implementation**
Compliance with environmental permits.

**Example plants**
Germany, Austria, Sweden, Belgium.

**Reference literature**
[ 121, Rentz, O. et al. 1999 ], [ 233, Farrell Nordic Mission 2008 ], [ 234, UBA Copper, lead, zinc and aluminium 2007 ], [ 219, VDI (D) 2102 2007 ], [ 206, Traulsen, H. 1999 ].

## 3.3.5 Converting

### 3.3.5.1 Primary copper converters

**Description**
The converting stage used in Europe is the Peirce-Smith (or similar) converter. It is also commonly used worldwide [ 90, Traulsen, H. 1998 ]. This type of converter has a very robust and efficient level of performance. It is capable of a high level of metallurgical treatment and can be used to fume off metals such as lead and zinc which can then be recovered. The heat generated during processing is also available to melt copper scrap (e.g. anode scrap) and this factor is an important advantage. Its disadvantage is that it relies on the feed and transfer of material by ladle, skip or mould.

Transfer by ladle is a potential source of diffuse fumes that contains dust, metals and sulphur dioxide. The ladle or skip used for feeding can interfere with the efficient positioning of the fume collector hoods. Good operation of the converter therefore relies on the use of primary and secondary fume collection hoods during charging and pouring to collect as many diffuse fumes as possible. Dusts, fluxes, carburant, scrap, etc. can be added through the hood. Automatic controls can prevent blowing during the periods that the converter is rolled out or rolled in again.

These processes and the techniques for control and fume collection reported in Section 2.4.5.1 are suitable for use with new and existing installations and are techniques to consider.

Other converter processes are also used worldwide [ 135, Gershel, T. 1998 ] and are also techniques to consider. The converter stages that are used in the continuous Mitsubishi and Outotec/Kennecott flash smelting/flash converting processes do not require ladle transfer and therefore remove this source of secondary fumes. Both of these processes however, still require some fume collection at launders and tap-holes and the flash converting process is dependent on furnace matte and converting slag granulation matte grinding and handling, which may be a potential source of some emissions to air and water. Nevertheless these processes are inherently cleaner and emission control does not rely as much on maintenance and operator care as other converter types. In the Mitsubishi converting furnace, matte flowing into a molten copper bath and reacts by forming slag and metal; due to this reaction the blister copper leaving the converters and entering the anode furnace is high in sulphur. The off-gases are therefore comparatively higher in sulphur dioxide and require $SO_2$ removal at the fire-refining stage.

An overview of converters for primary and secondary copper production is given in Table 3.43.

| Converter | Capacity range | Gas collection | Advantages | Disadvantages | Comments |
|---|---|---|---|---|---|
| ***Batch converters*** | | | | | |
| Peirce-Smith (or similar) | ~100 to 250 (primary) and ~15 to 35 (secondary) tonnes per batch copper | Primary and secondary hoods | Simple proven technology. Melting of anode and other scrap. Robust and flexible. Good metallurgical performance. Fuming of some metallic inclusions | Relies on ladle transfers | Vast process knowledge available. Use in primary and secondary production. Though-hood charging is used |
| Hoboken | ~50 - 100 tonnes per batch of copper | Siphon for primary gas collection | Easier gas collection | Blockages in goose neck. Ladle transfer | Use also for copper/lead matte conversion |
| TBRC | ~40 - 70 tonnes per batch of copper | Enclosed | Secondary smelting of scrap | | Use in secondary production |
| Ausmelt/ISA Smelt | ~40000 tonnes per year | Hoods, gas cooling and cleaning | | | Primary and secondary production |
| ***Integrated converters*** | | | | | |
| Mitsubishi | Up to ~240000 tonnes per year of copper | Sealed | High $SO_2$ | Difficult arrangement in existing plants. Closely coupled with smelting process | Primary production only. Practices additional Cu scrap treatment. May be applicable to other smelters |
| Kennecott/ Outotec | ~300000 tonnes per year of copper | Sealed | High $SO_2$ concentration<br>Surge storage of Matte | Melting of anode scrap not yet available | Primary only |

**Table 3.43: Overview of converters for primary and secondary copper production**
[ 90, Traulsen, H. 1998 ]

The gases collected from the converting cycles are cooled, cleaned and sent to a sulphur recovery system. As reported earlier, the $SO_2$ content of gases from the converter operation is variable between 6 and 12 % throughout the converting cycle, the gases are mixed with the strong gases from the smelting stage. The continuous converting processes have strong, constant concentrations of $SO_2$ and therefore enable comparatively smaller gas handling, cleaning and cooling systems and somewhat smaller sulphur conversion stages can be used

The Ausmelt/ISA Smelt furnace is also used in a combined process of batch wise smelting and copper/lead matte converting to blister copper.

The Hoboken converter is also used for alloy conversion to separate copper from a mixed alloy with lead and iron.

**Achieved environmental benefits**
Containment of process gases and the destruction of PCDD/F depending on the furnace are the achieved environmental benefits.

**Cross-media effects**
No data has been reported.

**Operational data**
Table 3.43 provides the overview.

**Applicability**
These techniques are applicable to a change of furnace and are only applicable for a major modernisation or plant upgrade.

**Economics**
No data has been reported but the techniques are all operating viably.

**Driving force for implementation**
Compliance with environmental permits and improved efficiency and reliability of the process are the driving forces for implementation.

**Example plants**
DE, AT, FI, SE, US.

**Reference literature**
[ 90, Traulsen, H. 1998 ], [ 233, Farrell Nordic Mission 2008 ], [ 238, ECI Copper Installations 2008 ].

### 3.3.5.2 Secondary copper converters

**Description**
As reported [ 134, Metallurgical Consulting Traulsen GmbH 1998 ], the most common converting stage for secondary production uses the Pierce-Smith (or similar converters), the TBRC and the Ausmelt/ISA Smelt furnace. The TBRC, when used as a converter, is compact and is normally totally enclosed allowing collection of the secondary fumes. Copper alloy scrap additions are made to the converter. Carbon additions are made for heat balancing and for the separation of elements like zinc or tin by volatilisation under reducing conditions. The same remarks apply to the fume collection systems that are used in primary copper production. Good operation of the converter therefore relies on the use of primary and secondary fume collection

hoods during charging and pouring to collect as many diffuse fumes as possible; dusts such as fluxes and carburant can be added through the hood. Automatic controls can prevent blowing during the periods that the converter is rolled out. Gases from the conversion of secondary copper secondary processes are treated by gas cooling (with heat/energy recovery if practicable), coarse particle separation, sulphur dioxide removal and fabric filtration.

**Achieved environmental benefits**
Containment of process gases and the destruction of PCDD/F depending on the furnace are the achieved environmental benefits. The batch converter section of Table 3.43 provides the overview.

**Cross-media effects**
No data has been reported.

**Operational data**
Table 3.43 provides the overview.

**Applicability**
These techniques are applicable to a change of furnace and are only applicable for a major modernisation or plant upgrade.

**Economics**
No data has been reported but the techniques are all operating viably.

**Driving force for implementation**
Compliance with environmental permit and improved efficiency and reliability of the process.

**Example plants**
DE, AT, BE.

**Reference literature**
[ 229, Umicore etc 2007 ], [ 238, ECI Copper Installations 2008 ], [ 219, VDI (D) 2102 2007 ].

## 3.3.6 Examples for other process stages

### 3.3.6.1 Fire refining

**Description**
Fire refining is described earlier (see Sections 3.1.2.2 and 3.1.1.1.3). Rotary furnaces, reverberatory hearth furnaces, hearth shaft furnaces and the Contimelt process are all techniques to consider for primary and secondary smelters. They feature gas additions via tuyères or lances. The hearth shaft furnace and the Contimelt process are designed for solid feed. The reverberatory hearth furnace takes solid and molten copper feed and the rotary furnace takes mainly molten copper feed. Molten copper feed normally requires the use of ladle transfer for filling and some diffuse emissions may have to be considered as potential problems at this point. Additions of scrap to refining furnaces can give rise to diffuse fumes and therefore scrap that is contaminated with organic material should be avoided. The rate of addition of scrap can be controlled [ 238, ECI Copper Installations 2008 ].

Fume collection systems are used for the fire-refining furnaces. The abatement system required will vary depending on the material used. The gas and fumes from the furnace are collected, afterburnt during the reduction stage, cooled and cleaned in fabric filters or scrubbers. Depending on the sulphur carryover from the converter, sulphur dioxide may need to be removed, e.g. by caustic scrubbing. For example, when fire-refining blister copper from the Mitsubishi converting furnace, the off-gases can be comparatively higher in sulphur dioxide and require $SO_2$ removal [ 134, Metallurgical Consulting Traulsen GmbH 1998 ].

Heat recovery from the refining furnace off-gas should be used at units melting solid material at high rates. Gases from anode furnaces should be considered for use in drying or other process stages. Hot gases extracted from launders can be used as preheated combustion air.

The casting of molten copper from the anode furnace into a casting wheel or continuous caster are techniques to consider.

**Achieved environmental benefits**
The environmental benefits are the prevention of diffuse emissions of metals, dust and other compounds.

**Cross-media effects**
None are reported.

**Operational data**
None are available.

**Applicability**
The processes and the techniques for control, fume collection and sulphur dioxide removal are suitable -for use with new and existing installations.

**Economics**
None was provided but the processes are operating economically.

**Driving force for implementation**
The reduction of emissions and saving raw materials.

**Example plants**
Plants in DE, AT, FR, BE, PL and NL.

**Reference literature**
[ 196, Finkeldei, L. 1999 ], [ 134, Metallurgical Consulting Traulsen GmbH 1998 ], [ 238, ECI Copper Installations 2008 ].

#### 3.3.6.2 Electrorefining

**Description**
Electrorefining processes that feature optimised cell dimensions (spacing, cell size, etc.), and the use of stainless steel cathode blanks or copper starter sheets are techniques to be considered. For existing tankhouses, the expense of conversion to stainless steel preformed cathodes may not be appropriate and copper starter sheets will be used in these instances. Mechanised (and automatic) harvesting and stripping as well as more elaborate short circuit detection is also worth considering depending on the scale of the operation.

The recovery of copper from solutions involves electrowinning and in these cases gases are evolved at the anode and may produce an acid mist.

The tankhouse drainage systems are sealed and all solutions collected are recirculated. Anode slimes and electrolyte bleeds are recovered.

**Achieved environmental benefits**
The collection and removal of these mists.

**Cross-media effects**
None are reported.

**Operational data**
During electrorefining, oxygen is emitted and may entrain some of the electrolyte and produce an acid mist. This can be collected and returned to the process using cell hoods and a wet scrubber and demister. The levels of acid mist achieved are < 0.2 mg/Nm$^3$ as sulphuric acid [ 258, Finland input 2007 ].

**Applicability**
The processes and the techniques for control, fume collection and sulphur dioxide removal are suitable for use with new and existing installations.

**Economics**
None was provided but the processes are operating economically.

**Driving force for implementation**
The reduction of emissions and saving raw materials.

**Example plants**
Plants in DE, AT, FR, BE, PL and NL.

**Reference literature**
[ 238, ECI Copper Installations 2008 ], [ 90, Traulsen, H. 1998 ].

### 3.3.6.3 Slag treatment processes

There are various sources of slag produced in the processes to produce copper. Their techniques to consider depend on the source but essentially smelter slags and some converter slags can be treated in slag treatment furnaces (electric) when carbon is added and the slag is decopperised to produce matte and clean slag. Slags that are rich in copper such as smelter and converter slag are treated by different methods. They can be slow cooled, treated in an electric furnace or in a flotation unit to maximise cleaning and copper recovery. Slag cleaning by the injection of coal into the slag bath using a rotary furnace is also a technique to consider, slag fuming and slag recirculation into the first stage smelting furnace (reduction or matte smelting stage) are also techniques to consider.

Decopperised slag has a very low leachable metal content and has several useful properties that allow its use in sand blasting or in civil engineering (e.g. use as a drainage filling material) or as a filler in cement production. The use or the recycling of slags and the recycling of filter dusts is considered to be part of the process.

**Achieved environmental benefits**
The environmental benefits are the prevention of diffuse emissions of metals, dust and other compounds.

**Cross-media effects**
None are reported.

**Operational data**
None are available.

**Applicability**
The processes and the techniques are suitable for use with new and existing installations.

**Economics**
None was provided but the processes are operating economically.

**Driving force for implementation**

The reduction of emissions and saving raw materials.

**Example plants**
Plants in DE, AT, FR, BE, PL and NL.

**Reference literature**
[ 196, Finkeldei, L. 1999 ], [ 274, Farrell Mission in DE 2008 ].

### 3.3.6.4 Hydrometallurgical processes

~~The hydrometallurgical treatment of copper oxide and low grade sulphide ores is used where space is available for example at a mine site. The basic process outlined earlier and in Chapter 2 can have several variants depending on the characteristics of the ore. The background reports should be consulted [ 127, Chadwick, J. 1994 ], [ 134, Metallurgical Consulting Traulsen GmbH 1998 ], [ 261, Outokumpu ref 2002 ].~~

~~Because the hydrometallurgical processes involve leaching, solvent extraction and electrolytic stages, adequate disposal of leached material should be considered as well as the containment of the solvent extraction mixers and settlers. The techniques discussed in Chapter 2 to prevent emissions to water, for example by containing drainage systems, are relevant as are the techniques to recover VOCs and the use of benign solvents.~~
*Both paragraphs are not considered to be useful for the techniques to consider in the determination of BAT section. If needed relocate to 3.1.*

#### 3.3.6.4.1 Example of Reactor Leaching – Solvent Extraction – Electro Winning; Cobre las Cruces

**Description**
Open pit mining is used to extract copper ore which is roughly ground and then leached in sealed reactors using an atmosphere of oxygen. A dry residue is produced after leaching and the pregnant leach solution goes through a solvent extraction stage to purify and concentrate the copper solution which is the electrowon to produce copper cathodes. In the electrowinning stage modern hoods are used to cover the electrolysis cells in order to collect emissions to the atmosphere.

**Achieved environmental benefits**
The process avoids the use of a concentrator and transport of concentrate to smelters and other environmental aspects associated with producing copper such as the generation of $SO_2$. Recovery of the metal is higher compared to conventional flotation technology. The process selection eliminates traditional tailings dam by producing a dry residue. Modern SX technology is used which has low VOC emissions in the range of 5 to 15 mg/Nm$^3$ [ 103, Farrell, F. 1998 ].

**Cross-media effects**
Positive effect compared with other process options.

**Operational data**
Roughly ground ore is leached in 8 reactors having 350 m$^3$ effective volume at a feed rate of about 165 t/h each and leach retention time of 8 hours. The solid content in the leaching stage is 500-550 g/l. The reactors are agitated and the power needed is about1.4 kW/m$^3$ (with 98 % oxygen), motor size 500 kW. The leach temperature used is ~90 °C and the copper extraction efficiency is ~92 %. The flow sheet of the process is given in Figure 3.15 and an overview of the solvent extraction process is shown in Figure 3.16.

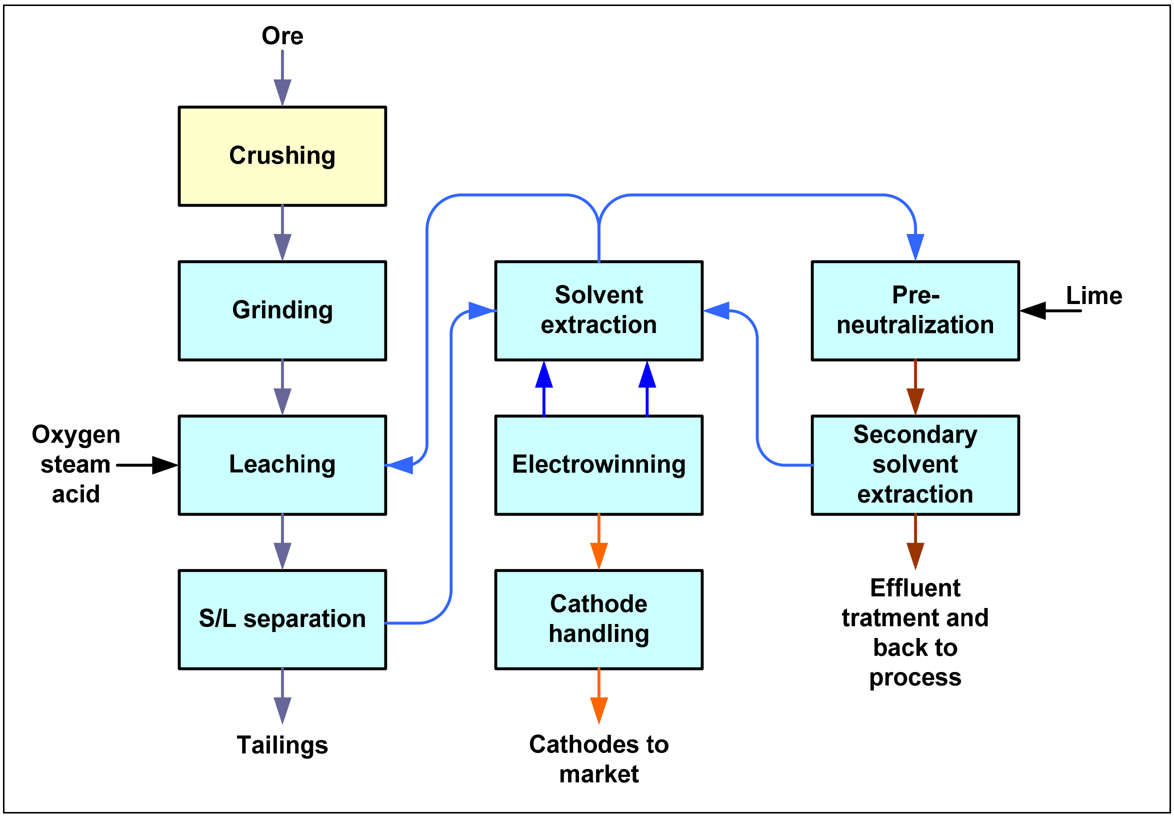


Figure 3.15: Block diagram of the hydrometallurgical process

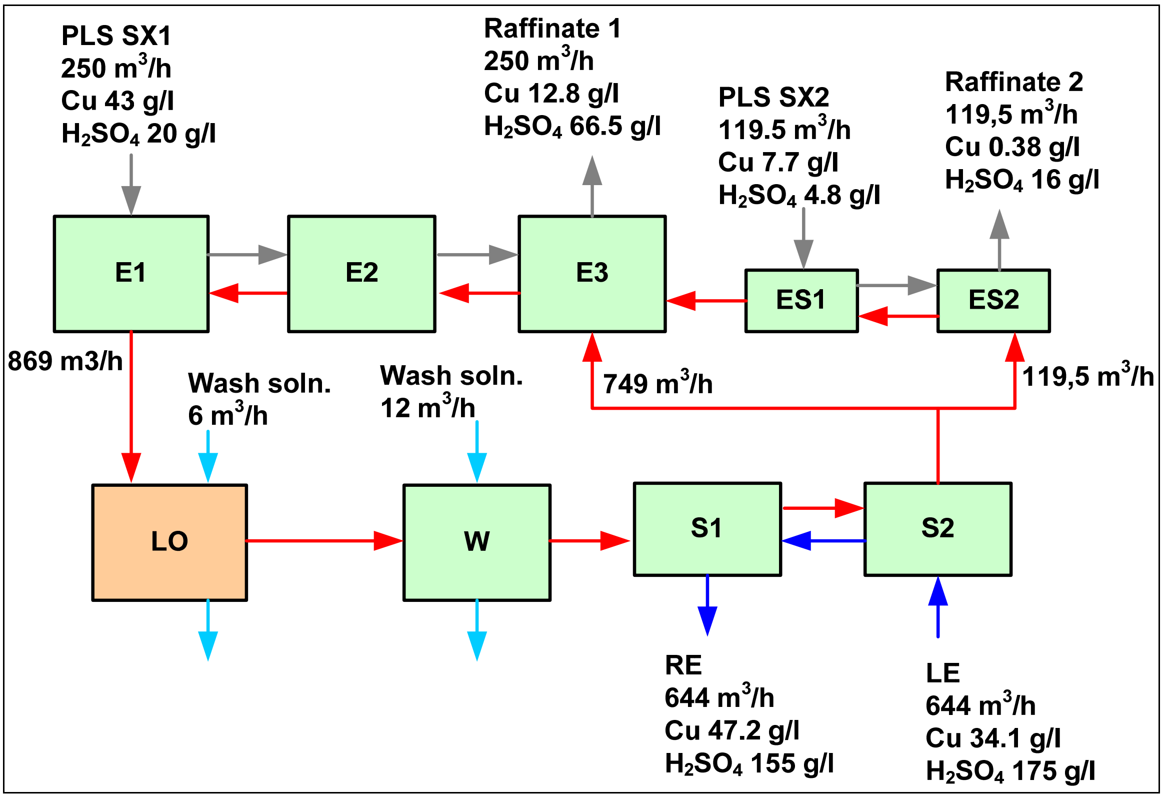


Figure 3.16: Overview of the SX phase of the Cobre Las Cruces plant.

*The abbreviations in this figure should be explained.*
*What about emissions to air? Emissions to water? Wastes? Water and chemical consumption? Energy consumption?*

In the electrowinning stage there are 144 cells with 84 cathodes per cell. Permanent cathodes are used with an area of 1.15 $m^2$ per side. The current density 301 $A/m^2$ and design 325 $A/m^2$. The tankhouse has automatic cranes and the electro winning cells have acid mist capture system. Cathodes are stripped in automatic stripping machines.

**Applicability**
The process was specially designed for the Cobre las Cruces plant. However, these techniques are applicable in other processes, too.

**Economics**
Estimated construction investment was EUR 463 million. The average annual production capacity is 72000 tonnes of copper. Operation costs are not available in 2009 but the techniques are all operating viably.

**Driving force for implementation**
Exploitation of the copper deposit near Gerena, Seville.

**Example plants**
Cobre las Cruces, ES.

**Reference literature**
http://www.cobrelascruces.com/index.php?option=com_content&task=view&id=5&Itemid=89

### 3.3.6.5 Tin and other metals

The processes that were discussed earlier as available techniques and are all considered being techniques to consider in the determination of BAT. The specific feed materials will influence the final process choice. Tin and lead can be separated from each other by vacuum distillation at high temperature. As a result of this, pure lead can be recovered. This technique is applied by some secondary copper installations in which ~~who also produce~~ lead and tin is produced also.

The techniques discussed in Chapter 2 should also be considered in conjunction with these processes.

**Achieved environmental benefits**
The environmental benefits are the prevention of diffuse emissions of metals, dust and other compounds.

**Cross-media effects**
None are reported.

**Operational data**
None are available.

**Applicability**
The processes and the techniques are suitable for use with new and existing installations.

**Economics**
None was provided but the processes are operating economically.

**Driving force for implementation**
The reduction of emissions and saving raw materials.

**Example plants**
Plants in DE, AT, FR, BE, PL and NL.

**Reference literature**
[ 229, Umicore etc 2007 ], [ 274, Farrell Mission in DE 2008 ].

### 3.3.6.6 Copper wire rod

The processes that were discussed earlier for copper wire rod production (Section 3.1.4) as available techniques are all considered to be techniques to consider in the determination of BAT. The use of advanced controls on the burners of a shaft furnace to optimise combustion and maintain minimum levels of CO while maintaining product quality should be considered.

**Achieved environmental benefits**
The environmental benefits are the prevention of diffuse emissions of metals, dust and other compounds.
*Data about dust and metal emissions should be included (see info in Section 3.2.2.3.2 about the relevance of these pollutants and Section 3.2.2.3.8 where some emissions factors for semis and wire rod production are given). What is needed are real measured data.*
**Cross-media effects**
None are reported.

**Operational data**
None are available.

**Applicability**
The processes and the techniques are suitable for use with new and existing installations.

**Economics**
None was provided but the processes are operating economically.

**Driving force for implementation**
The reduction of emissions and saving raw materials.

**Example plants**
Plants in DE, AT, FR, BE, PL and NL.

**Reference literature**
[ 238, ECI Copper Installations 2008 ], [ 274, Farrell Mission in DE 2008 ].

### 3.3.6.7 Ingots, tubes and semi-finished products

The specific feed materials and the final products will influence the choice of process and the factors discussed in Section 3.1.5 will apply. If copper alloys are used in the process the melting temperature should be controlled, any fume produced during melting and casting should be collected efficiently and treated in a fabric filter; ZnO can be recovered from the fume. The techniques for temperature and process control discussed in Chapter 2 should also be considered in conjunction with these processes.

**Achieved environmental benefits**
The environmental benefits are the prevention of diffuse emissions of metals, dust and other compounds.
*Data about dust and metal emissions should be included (see info in Section 3.2.2.3.2 about the relevance of these pollutants and Section 3.2.2.3.8 where some emissions factors for semis and wire rod production are given). What is needed are real measured data.*

**Cross-media effects**
None are reported.

**Operational data**
None are available.

**Applicability**
The processes and the techniques are suitable for use with new and existing installations.

**Economics**
None was provided but the processes are operating economically.

**Driving force for implementation**
The reduction of emissions and saving raw materials.

**Example plants**
Plants in DE, AT, FR, BE, PL and NL.

**Reference literature**
[ 238, ECI Copper Installations 2008 ], [ 274, Farrell Mission in DE 2008 ].

### 3.3.6.8 Fume/gas collection and abatement

The gas collection and abatement techniques discussed in Section 2.4.3 *(what about Section 2.4.5.1 and 2.4.5.2 (secondary fume collection)* and 2.9 of this document are techniques to be considered for the various process stages involved in the production of copper, etc. The identification of any organic contamination of secondary raw materials is particularly important to consider so that the most appropriate pretreatment, furnace and abatement combination can be used to prevent diffuse emissions and destroy PCDD/F and other organic components in the off-gas. Abatement methods are shown in Table 3.44.

The use of secondary hoods is also a technique to be considered. The use of intelligent systems for the targeting of fume collection can reduce the energy demand of these systems. There are several site-specific issues that will apply. The design of hooding systems should take account of access for charging and other furnace operations and the way the source of process gases change during the process cycle. Essentially the process technologies discussed in this chapter, combined with suitable-_abatement will meet the demands of stringent environmental protection.

| Source | Component in off-gas | Treatment Method |
|---|---|---|
| Poor combustion, organic material in feed | CO, VOC, PCDD/F | Process control, afterburner or RTO and activated carbon injection |
| Sulphur in fuel or raw material | Sulphur dioxide | Wet or semi-dry scrubber system, lime injection |
| Combustion conditions | $NO_X$ | Process control, correct use of oxygen and catalytic reduction |
| Furnace and handling molten materials | Dust and metal fumes | Scrubber and/or fabric filter |

**Table 3.44: Abatement methods**
[ 238, ECI Copper Installations 2008 ]

The use of hoods for tapping and casting is also a technique to consider. Tapping fume will consists of fumes from oxygen lancing, dust from drilling, fumes from the vaporised slugs if a tapping gun is used and fumes from all exposed metal and slag surfaces. These fumes will consist mainly of oxides of the metals that are involved in the smelting process.

The furnace gases that are collected are usually very hot and cooling or energy recovery is used to prevent damage to the abatement equipment. Conversion to sulphuric acid or the production of sulphur dioxide is the technique for primary copper. Fabric filters and/or scrubbers are used for secondary copper and for the drying and fire-refining stages, scrubbing or dry gas desulphurisation methods to remove lower concentrations of sulphur dioxide are techniques to consider.

**Achieved environmental benefits**
The environmental benefits are the prevention of diffuse emissions of metals, dust and other compounds.

**Cross-media effects**
None are reported.

**Operational data**
None are available.

**Applicability**
The processes and the techniques are suitable for use with new and existing installations.

**Economics**
None was provided but the processes are operating economically.

**Driving force for implementation**
The reduction of emissions and saving raw materials.

**Example plants**
Plants in DE, AT, FR, BE, PL and NL.

**Reference literature**
[ 238, ECI Copper Installations 2008 ], [ 274, Farrell Mission in DE 2008 ].

### 3.3.6.9 Process control and management

The principles of process control and management such as the use of ISO 9000 systems discussed in Chapter 2 are applicable to the production processes used in this group. Some of the furnaces and processes are capable of improvement by the adoption of many of these techniques. Temperature control of furnaces used for melting copper alloys is a technique to consider, in particular the oxygen coefficient of a furnace can be automatically controlled by a mathematical model that predicts the changes in the composition of the feed and furnace temperatures. The model is based on more than 50 process variables. Operator training, provision of operational instructions and management systems to implement these factors are vital. Systems for preventative maintenance should also be considered where justified or required.

**Achieved environmental benefits**
The capture of fumes and $SO_2$, the destruction of PCDD/F, the destruction of CO and other carbon compounds.

**Cross-media effects**
None were reported.

**Operational data**
Given in the descriptions of the process above.

**Applicability**

These techniques are applicable to most processes depending on the installation. Some techniques such as the change of furnace or process are only applicable for a new plant or a major upgrade or modernisation.

**Economics**
No economic data was reported but Annex 1 on costs has some general data.

**Driving force for implementation**
Compliance with permit conditions and improvement of efficiency.

**Reference literature**
[ 238, ECI Copper Installations 2008 ].

### 3.3.6.10 Techniques to reduce emission of metals

**Description**
Gas cooling system and fabric filters are used to treat the gases from a number of sources. They incorporate lime addition if sulphur dioxide is present in the gases.

**Achieved environmental benefits**
The treatment of gases from converter and fire-refining furnaces to remove dust and metals for further treatment and recovery.

**Cross-media effects**
No data has been reported.

**Operational data**
The following emission levels are achieved in the Austrian plant of Brixlegge.

Dust = <1 - 3 mg/Nm$^3$
Of which Cu+Pb+Zn = <0.2 mg/Nm$^3$.

The metal content of dust varies widely between processes. In addition, for similar furnaces there are significant variations in metal content due to the use of varying raw materials and the use of the furnaces to separate minor elements for subsequent collection and enrichment for further processing. It is therefore not possible to report specific achievable concentrations for all metals emitted to air in this document.

Table 3.45 gives some indication of the contents of metals in dust that will be encountered from various process stages of copper production.

| Component | Concentrate to matte smelting furnace ESP dust | Blast furnace dust | Scrap converter dust | Matte converter ESP dust | Electric slag cleaning furnace dust | Anode furnace dust | KRS Dust |
|---|---|---|---|---|---|---|---|
| Pb % | 0.1 - 5 | 5 - 50 | 5 - 30 | 2 - 25 | 2 - 15 | 2 - 20 | 15 - 20 |
| Zn % | 0.1 - 10 | 20 - 60 | 25 - 70 | 5 - 70 | 25 - 60 | 5 - 40 | 35 - 50 |
| Sn % | 0.1 - 1 | 0.2 - 5 | 1 - 20 | 0.1 - 4 | | | 2 - 4 |
| Cu % | 5 - 30 | 2 - 12 | 2 - 15 | 10 - 25 | 0.5 - 2.5 | 15 - 25 | 3 - 6 |
| As % | 0.1 - 4 | | | | | 0.5 - 10 | |
| Ni % | 0.1 - 1 | 0.1 - 1 | | 0.1 - 1 | | | |

**Table 3.45: Metal content of some dusts from various copper production processes**
[ 90, Traulsen, H. 1998 ]

Low concentrations of metals are associated with the use of high performance, modern abatement systems such as a membrane fabric filter provided the operating temperature is correct and the characteristics of the gas and dust are taken into account in the design.

**Applicability**
This technique is applicable to most converter and anode furnaces and is also applicable to dryers.

**Economics**
No economic data was reported but Annex 1 on costs has some general data.

**Driving force for implementation**
Compliance with permit conditions is the main driving force.

**Example plants**
AT, DE, PL, ES, SE.

**Reference literature**
[ 157, Winter, B. et al. 1999 ], [ 238, ECI Copper Installations 2008 ], [ 219, VDI (D) 1999 ].

## 3.3.7 Waste water

All waste water should be treated to remove dissolved metals and solids. The techniques listed in Section 2.12.2 are techniques to consider. In a number of installations cooling water and treated waste water including rainwater is re-used or recycled within the processes. Run-off water, if collected and kept separately, should be treated by settlement and/or pH adjustment before release.

### 3.3.7.1 Waste water treatment and treatment of waste water containing weak acids

**Description**
Treatment of waste water comprising weak acid from the sulphuric acid plant or various acidic wash-waters using lime and iron sulphate.

**Achieved environmental benefits**
Minimum waste water discharge, reduction in water consumption, production of clean gypsum are the achieved environmental benefits.

**Cross-media effects**
No cross-media effects were reported.

**Operational data**
The process outline is shown in Figure 3.17 and the results achieved are given in Table 3.46.

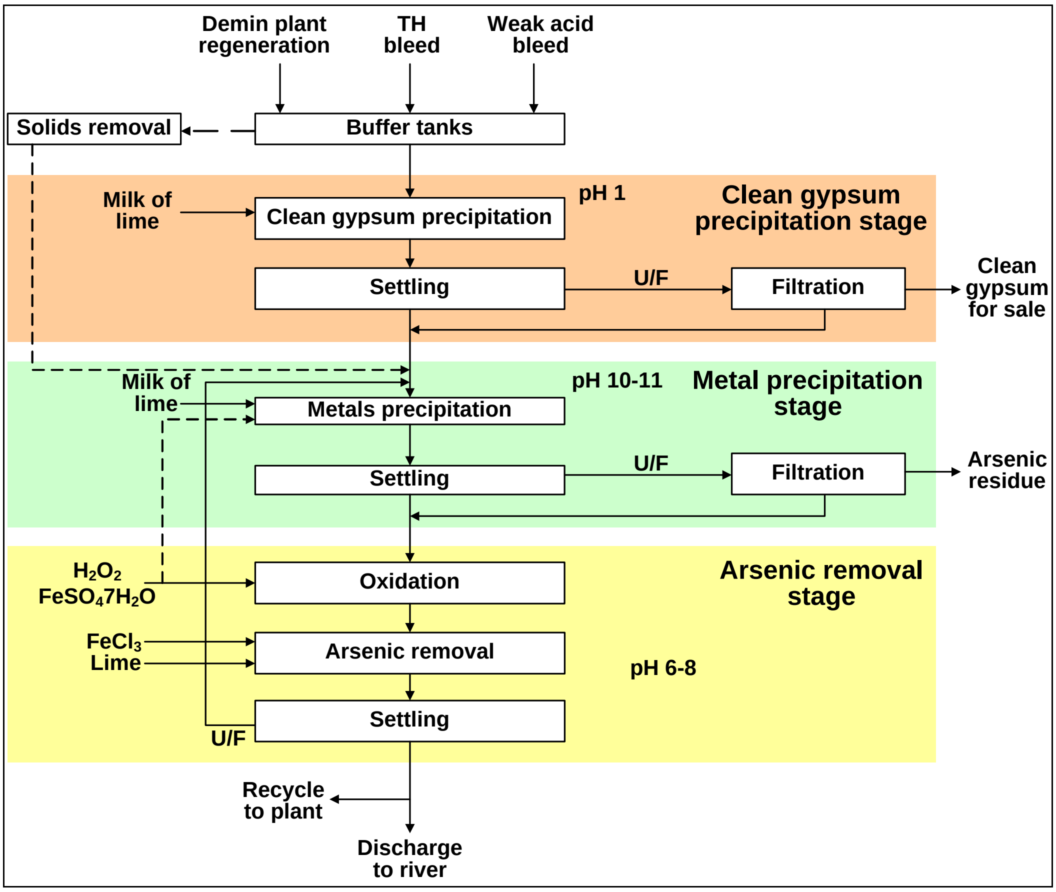


**Figure 3.17: Treatment of weak acid**
[ 238, ECI Copper Installations 2008 ].

The clean gypsum that is produced contains > 96 % Ca $SO_4.5H_2O$.

| Parameter | Range | Unit |
|---|---|---|
| | Inlet Conditions | |
| Flow | 35 | $m^3/h$ |
| Content | | |
| $H_2SO_4$ | 60 | g/l |
| Cu | 2100 | mg/l |
| Hg | 15 | mg/l |
| As | 2200 | mg/l |
| Pb | 2600 | mg/l |
| Ni | 7 | mg/l |
| Cd | 110 | mg/l |
| Suspended solids | 200 | mg/l |
| | Effluent water([1]) | |
| Flow | 31.2 | $m^3/h$ |
| pH | 9.5 | |
| Cu | 0.1 - 0.5 | mg/l |
| Hg | 0.05 | mg/l |
| As | 0.05 - 0.2 | mg/l |
| Pb | 0.1 – 0.5 | mg/l |
| Ni | 0.1 – 0.5 | mg/l |
| Cd | 0.01 – 0.2 | mg/l |
| | Gypsum sludge | |

| | | |
|---|---|---|
| Amount | 6 - 7 | t/h |
| Composition | 40 - 50 | %moisture |
| | ~ 30 - 35 | %$CaSO_4$ |
| | ~ 1 | %As |
| | ~ 1 | % Cu, |
| | ~ 1 - 2 | % Fe, |
| | ~ 0.01 | % Hg, |
| | ~ 1 | Pb, |
| | ~ <0.1 | % Ni, |
| | ~ <0.1 | % Cd. |
| (1) Design data taking variations in effluent into account.<br>The metal concentrations are daily averages based on qualified random samples or twenty four hour flow proportional samples. | | |

**Table 3.46: Performance data for the treatment of wastewater containing weak acid**
[ 238, ECI Copper Installations 2008 ].

**Applicability**
This technique is applicable to most process water systems.

**Economics**
Equipment costs were EUR 2.5 million, installation costs were EUR 4.5 to 5.2 million. Electricity: 200 kWh. Milk of lime: 10 %; 15 $m^3$/h. $H_2SO_4$: 10 %; 0.8 $m^3$/h. $FeSO_4.7H_2O$: 80 kg/h

**Driving force for implementation**
Effective treatment of weak acid to produce a saleable product is the driving force for implementation..

**Example plants**
Plants in Spain and Bulgaria.

**Reference literature**
[ 238, ECI Copper Installations 2008 ].

### 3.3.7.2 Waste water treatment and re-use in secondary copper production

**Description**
Process effluent, cooling water and potentially contaminated surface water are collected and treated together in the same waste water treatment plant. The purification comprises treatment with NaHS followed by settlement and sand filter. Water is re-used within the process and for stock yard watering.

**Achieved environmental benefits**
There is a minimisation of waste water discharge and a reduction in water consumption.

**Cross-media effects**
No cross-media effects were reported.

**Operational data**
Maximum water re-use achieved with this technique and 110000 $m^3$/yr of waste water is discharged. Performance data for a treatment system using NaHS at a secondary copper plant is given in Table 3.47.

| Component | Secondary copper process and surface water after treatment with NaHS, settlement and sand filtration |
|---|---|
| Cu (mg/l) | 0.05 – 0.2 |
| Pb (mg/l) | 0.05 – 0.2 |
| Ni (mg/l) | 0.05 – 0.2 |
| Zn (mg/l) | 0.1 – 0.5 |
| As (mg/l) | <0.01 |
| Cd (mg/l) | <0.01 |
| Hg (mg/l) | <0.01 |
| Suspended solids (mg/l) | 1.0 |
| The metal concentrations are daily averages based on qualified random samples or twenty four hour flow proportional samples. | |

**Table 3.47: Performance data for a treatment system using NaHS**
[ 238, ECI Copper Installations 2008 ].

**Applicability**
This technique is applicable to most installations.

**Economics**
No economic data was reported but Annex 1 on costs has some general data.

**Driving force for implementation**
The effective treatment of effluent to enable re-use or discharge is the driving force.

**Example plants**
BE.

**Reference literature**
[ 103, Farrell, F. 1998 ], [ 238, ECI Copper Installations 2008 ].

### 3.3.7.3 Direct c~~C~~ooling water treatment

**Description**
The treatment of direct cooling water bleed applied in an anode casting system using pH adjustment, precipitation and settling.

**Achieved environmental benefits**
Minimum waste water discharge and the reduction of water consumption are the achieved environmental benefits.

**Cross-media effects**
No cross-media effects were reported.

**Operational data**
Performance data for a cooling water bleed treatment system is given in Table 3.48.

| Main components | pH adjustment, precipitation and settling | |
|---|---|---|
| | Before treatment | In effluent |
| pH | | 8.5 - 9.5 |
| Cu (mg/l) | <30 | 0.01 - 0.25 |
| Pb (mg/l) | <2.5 | 0.001 - 0.1 |
| As (mg/l) | <2.0 | 0.001 - 0.1 |
| Ni (mg/l) | <0.5 | 0.002 - 0.06 |

| | | |
|---|---|---|
| Cd (mg/l) | <0.01 | 0.0001 - 0.003 |
| Zn (mg/l) | <1.0 | 0.02 - 0.5 |
| Raw water quantity: ~ 350000 $m^3$/yr. | | |

**Table 3.48: Performance data for a cooling water bleed treatment system**
[ 234, UBA Copper, lead, zinc and aluminium 2007 ]

*All values are the same as in section 2.12.2.3 but the upper one for Ni. Clarify.*

**Applicability**
This technique is applicable to most installations.

**Economics**
No economic data was reported but Annex 1 on costs has some general data.

**Driving force for implementation**
The minimisation of water use is the driving force.

**Example plants**
Hamburg, Germany.

**Reference literature**
[ 234, UBA Copper, lead, zinc and aluminium 2007 ].

### 3.3.8 Process residues and waste

The techniques reported in Section 3.2.2.5 comprising the recovery of metals from the residues and the minimisation of waste for final disposal are the techniques to consider in the determination of BAT.

## 3.4 Best Available Techniques

In understanding this section and its contents, the attention of the reader is drawn back to the Preface of this document and in particular the fifth section of the Preface: ‘How to understand and use this document’. The techniques and associated emission and/or consumption levels, or ranges of levels, presented in this section have been assessed through an iterative process involving the following steps:

- identification of the key environmental issues for the sector which for the production of copper are: $SO_2$, dust, metal oxide fumes, organic compounds, waste water, and residues (such as furnace linings), sludge, filter dust and slag. PCDD/F formation during the treatment of secondary copper materials is also an issue
- examination of the techniques most relevant to address these key issues
- identification of the best environmental performance levels, on the basis of the available data in the European Union and worldwide
- examination of the conditions under which these performance levels were achieved; such as costs, cross-media effects, and the main driving forces involved in implementation of the techniques
- selection of the best available techniques (BAT) and the associated emission and/or consumption levels for this sector in a general sense, all according to Article 2(12) and Annex IV to the Directive.

Expert judgement by the European IPPC Bureau and the relevant Technical Working Group (TWG) has played a key role in each of these steps and in the way in which the information is presented here.

On the basis of this assessment, best available techniques, and as far as possible emission and consumption levels associated with their use, are presented in this section that are considered to be appropriate to the sector as a whole and in many cases reflect the current performance of some installations within the sector. Where emission and consumption levels “associated with best available techniques” are presented, this is to be understood as meaning that those levels represent the environmental performance that could be anticipated as a result of the application, in this sector, of the techniques described, bearing in mind the balance of costs and advantages inherent within the definition of BAT. However, they are neither emission nor consumption limit values and should not be understood as such. In some cases, it may be technically possible to achieve better emission or consumption levels but due to the costs involved or cross-media considerations, they are not considered to be appropriate as BAT for the sector as a whole. However, such levels may be considered to be justified in more specific cases where there are special driving forces.

The emission and consumption levels associated with the use of BAT have to be seen together with any specified reference conditions (e.g. averaging periods).

The concept of ‘levels associated with BAT’ described above is to be distinguished from the term ‘achievable level’ used elsewhere in this document. Where a level is described as ‘achievable’ using a particular technique or combination of techniques, this should be understood to mean that the level may be expected to be achieved over a substantial period of time in a well maintained and operated installation or process using those techniques.

Where available, data concerning costs have been given together with the description of the techniques presented in the previous sections. These give a rough indication about the magnitude of the costs involved. However, the actual cost of applying a technique will depend strongly on the specific situation regarding, for example, taxes, fees, subsidies, and the technical characteristics of the installation concerned. It is not possible to evaluate such site-specific factors fully in this document. In the absence of data concerning costs, conclusions on economic viability of techniques are drawn from observations on existing installations.

The BAT (including the associated emission and consumption levels) given in this section are 'BAT in a general sense' (i.e. considered to be appropriate to the sector as a whole). It is intended that they are a reference point against which to judge the current performance of an existing installation or to judge a proposal for a new installation. In this way, they will assist in the determination of appropriate 'BAT-based' conditions for the installation or in the establishment of general binding rules under Article 9([8]) of the IPPC Directive. It is foreseen that new installations can be designed to perform at or even better than the BAT levels presented in this section. It is also considered that existing installations could move towards the BAT levels presented in this section or do better, subject to the technical and economic applicability of the techniques in each case.

While the BAT reference documents do not set legally binding standards, they are meant to give information for the guidance of industry, Member States and the public on achievable emission and consumption levels when using specified techniques. The appropriate permit conditions for any specific case will need to be determined taking into account the objectives of the IPPC Directive and the local considerations.

**Recommendation to help users/readers of this document:**

It is strongly recommended that this section on BAT be read in conjunction with the sections of this document that describe the techniques to consider in the determination of BAT. The applicability of the techniques and measures are reported in these sections and should be taken into account at a local level. To help the reader, references to the appropriate sections are included in the description of BAT.

If not otherwise mentioned, BAT associated emission and consumption levels given in this section are expressed as follows:

- for pollutants emitted to air (except dioxins): expressed on a daily average basis with standard conditions of 273 K, 101.3 kPa, measured oxygen content and dry gas with the plant operating normally under steady-state conditions and no dilution of the gases;
- for dioxins: expressed as the average over the sampling period which should preferably be a minimum of 6 hours;
- for waste water: based on qualified random samples or twenty four hour flow proportional composite samples.

As described in the Preface, this document does not propose emission limit values. The best available techniques and the ranges of emission or consumption levels associated with best available techniques (BAT-AEL ranges) are related to installations with different sizes, different kinds of operation and different raw materials. In this document, special local considerations cannot be taken fully into account. The determination of appropriate permit conditions will involve taking account of local, site-specific factors such as the technical characteristics of the installation concerned, its geographical location and the local environmental conditions. In the case of existing installations, the economic and technical viability of upgrading them also should be taken into account. Even the single objective of ensuring a high level of protection for the environment as a whole will often involve making trade-off judgements between different types of environmental impact, and these judgements will often be influenced by local considerations.

Although an attempt is made to address some of these issues, it is not possible for them to be considered fully in this document. The techniques and emission and consumption levels presented here will therefore not necessarily be appropriate for all installations. On the other hand, the obligation to ensure a high level of environmental protection including the minimisation of long-distance or transboundary pollution implies that permit conditions cannot be set on the basis of purely local considerations. It is therefore of the utmost importance that the information contained in this document is fully taken into account.

Section 2.20 to this document reports BAT for the following common processes and the following sections should be referred to for those techniques that are BAT:

- environmental management systems (EMS) (Section 2.20.1)
- material handling and storage (Section 2.20.2)
- process control (Section 2.20.3)
- fume and gas collection (Section 2.20.4)
- the prevention and the destruction of PCDD/F (Section2.20.5)
- sulphur dioxide removal (Section 2.20.6)
- the removal of mercury (Section 2.20.7)
- effluent treatment and water re-use (Section 2.20.8)
- energy efficiency (Section 2.20.9)
- intermediate products, process residues and wastes (Section 2.20.10)
- emission monitoring (Section 2.20.11)
- prevention of the formation of $NO_X$ (Section 2.20.12)
- removal of dust and particles (Section 2.20.13)

BAT for the production of copper is the combination of the generally applicable techniques reported in Section 2.20 and the specific techniques indicated in this section.

## 3.4.1 Prevention and control of emissions to air

### 3.4.1.1 Primary copper smelting and converting

**a) BAT is to prevent and control emissions to air from the production of copper from primary raw materials by using one of the techniques for smelting and conversion given in Table 3.49 (see Sections 2.8.2, 3.3.2 and 3.3.5.1).**

*I can not find any information about secondary fume collection. There should be a Technique to consider section for secondary fume collection and a BAT because in table 3.50 a BAT-AEL is given for secondary fume collection.*

| Technique | Raw materials | Comment |
|---|---|---|
| Outotec flash smelting/Pierce-Smith or Hoboken converter | Concentrate and copper scrap | Capacities proven up to 400000 t/yr copper. |
| Outotec direct blister flash smelting | Concentrate | Used with suitable (chalcocite) concentrates to produce blister copper directly without the converting stage. Capacities proven up to 200000 t/yr copper. |
| Partial roasting/electric furnace/Pierce-Smith converter | Normal and complex concentrates, lower grade secondary material, copper scrap | Proven process, capacity up to 220000 t/yr copper.<br>For zinc recovery the process is combined with slag fuming.<br>For lead recovery a Kaldo furnace is used. |
| Mitsubishi continuous process and converter | Concentrate and copper scrap | Capacities proven up to 240000 t/yr copper |
| Outotec and Kennecott flash smelting/flash converting process | Concentrate | Capacity (flash converter) ~ 300000 t/y copper |
| Ausmelt/ISA Smelt furnace | Concentrate and mixed primary, secondary and precious metals | Capacities proven up to 230000 t/yr copper |
| Noranda and El Teniente process/Pierce-Smith converter | Copper concentrate, copper scrap (Noranda) | Capacities proven up to 190000 t/yr copper |
| INCO flash/Peirce Smith converter | Copper concentrate | Capacities proven up to 200000 t/yr copper |
| shaft furnace/Hoboken converter | Low grade, low sulphur concentrates with high carbon content | Capacities proven up to 200000 t/yr copper |

**Table 3.49: BAT for primary copper smelting and converting techniques**

**b) BAT is to prevent and control emissions to air from the converter gases produced during primary copper production by converting the sulphur dioxide produced into sulphuric acid or by producing liquid sulphur dioxide using one or more of the techniques reported in Sections 2.11.3.1, 2.11.3.2 and 2.11.3.3.**

### 3.4.1.2 Primary copper slag treatment, fire-refining and anode casting

**a) BAT is to prevent and control the emissions to air from slag treatment by using an electric furnace, slag fuming furnace or a process of crushing/grinding and slag flotation (see Section 3.1.1.1.5).** *(The term fuming furnace is not included in 3.1.1.1.5. It is included in chapter 5 but not here)*

**b) BAT is to prevent and control the emissions to air from fire-refining during primary copper production by using a rotary or tilting reverberatory furnaces (see Sections 3.1.1.1.3 and 3.3.6.1).**

**c) BAT is to prevent and control the emissions to air from anode casting during primary copper production by using pre-formed moulds or a continuous caster (see Section 3.3.6.1).** *(pre-formed moulds are not included and described in this BREF)*

**d) BAT is to prevent and control emissions of dust, metals, sulphur dioxide, nitrogen oxides, total organic carbon and PCDD/F from the gases produced from fire-refining, slag treatment, anode casting and from secondary fume collection of converter gases during primary copper production using the techniques given in Table 3.50 (see also Sections 2.9.2.4.1 and 2.9.2.4.2) or a combination of them.**

**The emission levels given in Table 3.50 are the BAT-AELs.**

| Pollutant | Techniques | BAT-AELs | Comments |
|---|---|---|---|
| Dust | Fabric or ceramic filter | <1 to 5 mg/Nm$^3$ | A bag burst detection system is needed (see Sections 2.9.2.2.4 and 2.20.13). |
| Metals | Fabric or ceramic filter | See Section 3.3.6.10 | The concentration of metals is linked to the dust concentration and the proportion of the metals in the dust (see Section 3.3.6.10) |
| $SO_2$ | Alkali semi-dry scrubber and fabric filter or<br>wet alkali or double alkali scrubbers using lime, magnesium hydroxide, sodium hydroxide. | <50 to 400 mg/Nm$^3$ | Potential cross-media effects from energy use, waste water and solid residues together with the ability to re-use scrubber products will influence the choice of the technique used (see Section 2.11.3.4). |
| | Fabric filter with dry lime injection into cool gas. | 100 to 500 mg/Nm$^3$ | Part of the reacted lime can be used as a fluxing agent. (see Section 2.11.3.6) |
| $NO_X$ | Low-$NO_X$ burner<br>or<br>Oxy-fuel burner | <100 to 300 mg/Nm$^3$ | The higher values are associated with oxygen enrichment to reduce energy use. In these cases gas volume and mass emissions are reduced (see Sections 2.9.2.4.3, 2.20.12 and 3.2.2.3.7). |
| Total organic carbon as C | Afterburner<br>Optimised combustion | 1 – 10 mg/Nm$^3$ | Pretreatment of secondary material is needed to remove organic coatings (see Sections 2.9.2.6 and 3.2.2.3.3). |
| PCDD/F | High efficiency dust removal system (i.e. fabric filter) or<br>Afterburner followed by quenching or<br>Adsorption on activated carbon using a carbon filter or by injection with lime/carbon | <0.1 ng I-TEQ/Nm$^3$ | Treatment of a clean dedusted gas is required to achieve low levels (see Sections 2.10.2.1, 2.20.5 and 3.2.2.3.4) |
| NB: Collected emissions only. BAT-AELs are given as daily averages based on steady-state operation or, in cases where continuous monitoring is not practicable as the average over the sampling period. For PCDD/F, the BAT-AEL is the average over the sampling period which should preferably be a minimum of six hours. | | | |

**Table 3.50 BAT and BAT-AELs to prevent and control the emissions to air from fire-refining, slag treatment, anode casting and secondary fume collection, in the primary copper sector**

### 3.4.1.3 Secondary copper smelting, converting, fire-refining and anode casting

**a) BAT is to prevent and control the emissions to air from secondary copper smelting by using one of the techniques given in Table 3.51 (see Sections 2.8.2, 3.1.2.1 and 3.3.4).**

| Technique | Raw materials | Comments |
|---|---|---|
| Blast furnace | Low grade material | ~150 to 200 tonnes per day.<br>Production rate depends on type of feed and copper content |
| Submerged arc electric furnace | Electronic scrap;<br>Some raw material restrictions | CO formed burns in the furnace to provide heat.<br>Furnace rating 8 to 25 tonnes per hour |
| Mini Smelter | Iron material | Iron content provides the source of heat |
| TBRC | Range of material including particulate matter | 40 to 70 tonnes per batch |
| Ausmelt/ISA Smelt | Mixed primary and secondary | 30000 to 40000 tonnes per year |
| KRS smelter | Mixed secondary material;<br>Electronic scrap | |
| Converter | Black copper;<br>Copper alloys | Hooded, 15 to 35 tonnes per batch |
| Hearth shaft furnace | Higher grade scrap, anode and blister copper | Melting and refining of metal 250 t/d |
| Contimelt process | Higher grade scrap, anode and blister copper | Fire refining 50 to 100 t/h |
| Reverberatory hearth furnace | Higher grade scrap, and blister copper | Use for converting and fire-refining 250 to 400 t/d.<br>Semi-sealed and hooded |

**Table 3.51: BAT for secondary copper smelting techniques**

**b) BAT is to prevent and control emissions to air from secondary copper converting by using one of the secondary converters listed in Table 3.52 with total enclosure or efficient primary and secondary fume collection systems (see Section 3.3.5.2):**

| Converter technique | Raw materials | Comments |
|---|---|---|
| Pierce-Smith<br>(or similar, e.g. Hoboken) | Anodes and secondary scrap | Relies on ladle transfers.<br>15 to 35 tonnes per batch copper |
| TBRC | Secondary scrap | 40 to 70 Tonnes per batch of copper |
| Ausmelt/ISA Smelt and KRS | Mixed scrap | Primary and secondary production |

**Table 3.52: BAT for secondary copper converters**

**c) BAT is to prevent and control emissions to air from secondary copper fire-refining and anode casting by using rotary or tilting reverberatory furnaces (see Sections 3.1.1.1.3, 3.3.6.1 and 3.3.6.8).**

**d) BAT is to prevent and control emissions to air from secondary copper anode casting by using pre-formed moulds or a continuous caster (see Section 3.3.6.1).** *Why is here 3.3.6.1 included but not under 3.4.1.2 a?)*

**e) BAT is to prevent and control emissions of dust, metals, sulphur dioxide, nitrogen oxides, total organic carbon and PCDD/F from secondary copper smelting, converting and anode furnaces by using the techniques given in Table 3.53 (see Sections 2.8.2, 2.9.2.4.1, 2.9.2.4.2, 3.1.2, 3.3.4, 3.3.5.2 and 3.3.6) or a combination of them.**

**The emission levels given in Table 3.53 are the BAT-AELs.**

The variation in feedstock and the control of product quality will influence the combination of furnaces, pretreatment and the associated collection and abatement systems that are used.

| Pollutant | Techniques | BAT-AELs | Comments |
|---|---|---|---|
| Dust | Fabric or ceramic filter | <1 to 5 mg/Nm$^3$ | A bag burst detection system is needed (see Sections 2.9.2.2.4 and 2.20.13) |
| Metals | Fabric or ceramic filter | see Section 3.3.6.10 | The concentration of metals is linked to the dust concentration and the proportion of the metals in the dust (see Section 3.3.6.10) |
| $SO_2$ | Fabric filter with dry lime injection into cool gas. | 100 to 500 mg/Nm$^3$ | For oil fired processes.<br>Part of the reacted lime can be used as a fluxing agent.<br>(see Section 2.11.3.6). |
| $NO_X$ | Low-$NO_X$ burner or<br>Oxy-fuel burner | <100 to 300 mg/Nm$^3$ | The higher values are associated with oxygen enrichment to reduce energy use. In these cases, gas volume and mass emissions are reduced (see Sections 2.9.2.4.3, 2.20.12 and 3.2.2.3.7). |
| Total organic carbon as C | Afterburner<br>Optimised combustion | 1 – 10 mg/Nm$^3$ | Pretreatment of secondary material is needed to remove organic coatings (see Sections 2.9.2.6 and 3.2.2.3.3). |
| PCDD/F | High efficiency dust removal system (i.e. fabric filter) or<br>Afterburner followed by quenching or<br>Adsorption on activated carbon using a carbon filter or by injection with lime/carbon | <0.1 ng I-TEQ/Nm$^3$ | Treatment of a clean dedusted gas is required to achieve low levels (see Sections 2.10.2.1, 2.20.5 and 3.2.2.3.4). |
| NB: Collected emissions only. BAT-AELs are given as daily averages based on steady-state operation or, in cases where continuous monitoring is not practicable, as the average over the sampling period. For PCDD/F, the BAT-AEL is the average over the sampling period which should preferably be a minimum of six hours. $SO_2$ emissions depend on the fuel used. | | | |

**Table 3.53: BAT and BAT-AELs to prevent and control emissions to air from secondary copper smelting, converting, secondary fire-refining and melting**

*Why have all techniques mentioned in the previous draft for SO2 mitigation been cancled. Industry asked in their comment to* ***add*** *FF/dry lime injection only.*

### 3.4.1.4 Other process stages

*(Other process stages is not precise enough. Say exactly which processes are relevant)*

**a) BAT is to prevent and control emissions to air from the melting of copper cathodes or high grades of copper scrap without organic contamination by using the reverberatory hearth furnace, the hearth shaft furnace or Contimelt process (see Sections 3.1.5 and 3.3.6.1).**

**b) BAT is to prevent and control emissions to air from the production of wire rod, semis etc. by using the Southwire, Contirod, Properzi & Secor, Upcast, Dip Forming, continuous casting and similar processes (see Sections 3.3.6.6 and 3.3.6.7).** *(These sections contain almost no information on the environmental performance. BAT and BAT-AEL can not be derived)*

**c) BAT is to prevent and control emissions to air from the drying processes by drying raw materials in directly fired drum and flash dryers, in fluid bed dryers or in steam dryers (see Sections 2.7.1.2).** *(2.7.1.2 is not sufficient to conclude on any BAT or BAT-AEL for drying processes. Examples and data are needed and a Technique to consider section has to be introduced)*

**d) BAT is to prevent and control emissions to air from the production of tin by using the production processes that are described in Sections 3.1.3 and 3.3.6.5.** *(Cross referring to 3.1.3 and 3.3.6.5 is useless as long as no information is mincluded inthese sections. Examples and data are needed and the Technique to consider section 3.3.6.5 has to be improved)*

**e) BAT is to prevent and control emissions of dust, metals, nitrogen oxides, sulphur dioxide, total organic carbon and PCDD/F from the melting, casting and drying processes by using the techniques given in Table 3.54 or a combination of them (see Section 3.3.6.8).** *(It is necessary to distinguish between melting, casting drying because the emissions from these processes are totally different. Furthermore in section 3.3.6.8 smelting, tapping, casting, drying, firerefining are included. Try to get information and examples for these processes and data.*

**The emission levels given in Table 3.54 are the BAT-AELs.**

| Pollutant | Techniques | BAT-AELs | Comments |
|---|---|---|---|
| Dust | Fabric or ceramic filter. (ceramic filter are not described in the mentioned Sections. Ceramic filter are described in 2.9.2.2.5 but no examples are given and no achieved data are included. The one range given is not relevaqnt since its been taken from a VDI guidline and does not represent values achieved in the Non Ferrous metals industry. ). Maybe Ceramic filter are not relevant. | <1 to 5 mg/Nm$^3$ | Dust recirculation may be used for fabric protection/fine particle capture. A bag burst detection system is needed. Dust should be monitored continuously ( see Sections 2.9.2.2.4 and 2.20.13). 2.20.13 is just a plain repeatition of what is included here. For this it is not necessary to have the section in chapter 2. It has to be clearly indicated which information in table 2.14 belongs to Copper and which values could be used for prim and sec. production. Try to get more data. Check data in tables section 14.1.2 ff. |
| Metals | Fabric or ceramic filter (see above) | see Section 3.3.6.10 | The concentration of metals is linked to the dust concentration and the proportion of the metals in the dust (see Section 3.3.6.10). (backreferring to the section 3.3.6.10 does not help when no data are included in that section. Try to get more data. Check data in tables section 14.1.2 ff. |
| $NO_X$ | Low-$NO_X$ burner<br>Oxy-fuel burner | <100 - 300 mg/Nm$^3$ | Higher values are associated with oxygen enrichment to reduce energy use |

| | | | |
|---|---|---|---|
| | | | (consumption?). In these cases gas volume and mass emissions are reduced (See Sections 2.9.2.4.3 and 2.20.12) |
| $SO_2$ | Fabric filter with dry lime injection into a cool gas. | 100 to 500 mg/Nm³ | There are potentially significant cross-media effects using wet or semi-dry scrubbing systems with a cool gas (see Sections 2.11.3.4 and 2.11.3.6). |
| | Alkaline wet scrubber for $SO_2$ collection from hot gases (e.g. dryer gases after dust removal). | <50 to 400 mg/Nm³ | |
| Total organic carbon as C | Process control | 1 – 10 mg/Nm³ | (See Sections 2.9.2.6 and 3.2.2.3.3) |
| PCDD/F | High efficiency dust removal system (i.e. fabric filter with lime injection)<br>Afterburner followed by quenching<br>Adsorption on activated carbon using a carbon filter or by injection with lime/carbon. | <0.1 ng I-TEQ/Nm³ | Treatment of a clean dedusted gas is required to achieve low levels.<br>(See Sections Sections 2.10.2.1, 2.20.5 and 3.2.2.3.4) |
| NB: Collected emissions only. BAT-AELs are given as daily averages based on steady-state operation or, in cases where continuous monitoring is not practicable as the average over the sampling period. For PCDD/F, the BAT-AEL is the average over the sampling period which should preferably be a minimum of six hours. | | | |

**Table 3.54: BAT and BAT-AELs to prevent and control emissions to air from melting processes, casting processes and drying processes in the copper sector**

### 3.4.1.5 Electrorefining, electrowinning and hydrometallurgy

**a) BAT is to prevent and control the emissions to air and water from copper electrorefining, electrowinning or hydrometallurgical processes by using the following techniques (see Sections 3.3.6.2 and 3.3.6.4):**

- electrolytic copper refining by optimised conventional or mechanised permanent cathode technology
- the hydrometallurgical processes outlined in Section 3.1.1.2 for black copper, oxidic ores and low grade, complex copper sulphide ores.

**b) BAT is to prevent and control emissions of acid mist and VOC to air from hydrometallurgical and electrowinning processes by using the techniques presented in Table 3.55 (see Sections 3.3.6.2 and 3.3.6.4).**

**The emission levels given in Table 3.55 are the BAT-AELs.**

| Pollutant | Techniques | BAT-AELs | Comments |
|---|---|---|---|
| Sulphuric acid mists | Demister<br>Wet scrubber | < 0.2 mg/Nm³ as $H_2SO_4$ | A demister or water scrubber will allow the collected acid to be re-used (see Section 3.3.6.2) |
| VOC as C | Containment<br>Condenser<br>Carbon or bio-filter. | <5 – 15 mg/Nm³ | (See Sections 2.9.2.6 and 3.3.6.4.1) |
| NB: Collected emissions only. BAT-AELs are given as daily averages based on steady-state operation or, in cases where continuous monitoring is not practicable as the average over the sampling period. | | | |

**Table 3.55: BAT and BAT-AELs for the emissions to air from hydrometallurgical and electrowinning processes in the copper sector**

*Is it eletcrorefining included in this table and in 3.4.1.5 b)?*

### 3.4.2 Effluent treatment and water re-use

**a) BAT is to re-use all waste water if possible (see Section 2.12.2.1).**

**b) BAT for waste water treatment is to remove metals, solids and oils/tars and absorbed acid gases by using the techniques given in Sections 2.12.2, 2.20.8 and 3.3.7.**

**The emission levels given in Table 3.56 are the BAT-AELs.**

| Component | BAT-AELs (mg/l) |
|---|---|
| Cu | 0.2 to 0.5 |
| Pb | 0.2 to 0.5 |
| Ni | 0.2 to 0.5 |
| Zn | 0.2 to 1.0 |
| As | 0.1 to 0.2 |
| Cd | 0.1 to 0.2 |
| Hg | 0.01 to 0.05 |
| BAT-AELs are based on qualified random samples or twenty four hour flow proportional composite samples. | |

**Table 3.56: BAT-AELs for emissions to water from copper production**

*If you compare the data in the table with the ones provided by industry it is unclear how these values are drived.*

### 3.4.3 By-products, process residues and wastes

**a) BAT for the copper sector is to re-use or recycle intermediate products or process residues as far as possible in the processes or after leaching tests as construction material using the techniques listed in Table 3.57 (see Sections 2.20.10 and 3.2.2.5). If recycling or re-use is not economically possible, secure disposal should be used.**

| Source of residue | Intermediate product or process residue | Techniques |
|---|---|---|
| Abatement systems | Filter Dusts | Use as raw material for the recovery of Cu, Pb, Zn and other metals |
| | Mercury compounds([1]) | Use in the chemical industry([1]) |
| | Spent catalysts and acid | Recovery or regeneration |
| | Sulphuric acid sludges | Decomposition for $SO_2$ recovery, neutralisation (sludge for disposal), other uses, e.g. as leaching media. |
| | Weak acid | Production of clean gypsum |
| Smelter | Slag | Recycle in slag furnace or other separation/internal recycle system. |
| | Furnace linings | Recover as refractory |
| Converter | Slag | Internal recycle system |
| Slag furnace | Slag | Abrasive, construction material |
| Slag floatation | Slag | Filler in the cement industry |
| Refining (anode) furnace | Slag | Internal recycle system |
| Tankhouse | Electrolyte bleed | Recovery of Ni salts, Cu, acid |

| | | |
|---|---|---|
| Melting/smelting | Skimmings and slag | Metal recovery |
| General | Oils | Oil recovery |
| Waste water treatment | Clean gypsum | Sold as product.<br>Source of calcium in the smelter |
| Hydrometallurgy | Depleted electrolyte | Use as acid for leaching |
| Semis production | Acid pickling solutions and rinses | Recovery of the metal content |
| Rod production | Acid pickling solutions (if applied) | Recovery in separate electrolytic cell |
| (1) Regulation EC 1102/2008 should be complied with in any case. | | |

**Table 3.57: BAT for the recycling or re-use of intermediate products or process residues from the production of copper**

*3.4.4: Energy efficiency*
*So far there is nothing included about energy efficient techniques. Flash smelter have a 50% energy consumption compared with conventional smelters. Maybe they can be considered as BAT for new plants regarding the energy consumption.*

## 3.5 Emerging techniques

It has been reported [ 135, Gershel, T. 1998 ] that development activity is taking place in the development and improvement of bath smelting techniques. Bath smelting can offer low cost installations because of the potential high reaction rates in modern plants coupled with sealed or semi-sealed furnaces. Plant reliability should be proven in the long term and data from some of the Chinese and Russian installations using Baiyin or Vanyukov furnaces should be examined if data becomes available. These are shown in Table 3.58.

| Technique | Comments |
|---|---|
| Continuous smelting/converting: Combination Noranda reactor and Mitsubishi converter furnace | Results of commissioning in 1999 to be awaited for evaluation. |
| Noranda continuous converter | Results of commissioning to be awaited for evaluation. |

**Table 3.58: Emerging bath smelting techniques**

The use of hydrometallurgical processes such as bioleaching is also emerging and they are suitable for mixed oxidic/sulphidic ores that contain low concentrations of precious metals. Iron and sulphide oxidising bacteria may be used to assist leaching.

The Outotec Hydro Copper process that uses a chlorine-based leaching system is available at a demonstration plant scale. Some processes are being developed for concentrates and dust treatment based on leaching for example - leach: solvent extraction: electrowin (L:SX:EW) processes [ 309, A MODERN VSF™ SX PLANT 2007 ], [ 308, Hydrocopper 2007 ].

# 4 PROCESSES TO PRODUCE ALUMINIUM FROM PRIMARY RAW AND SECONDARY RAW MATERIALS INCLUDING THE PRODUCTION OF ALUMINA AND PREBAKED ANODES

*In the heading only prebaked is included, but under 4.1.1.2 Soederberg anodes are mentioned.*

## 4.1 Applied Processes and Techniques

### 4.1.1 Primary aluminium

Primary aluminium is produced from aluminium oxide (alumina) [ 6, McLellan and Partners Ltd 1993 ], [ 97, Lijftogt, J.A. et al 1998 ], [ 312, VDI 2286 Aluminium Part 1 and 2 2008 ] which is produced from bauxite. This process is often carried out at the mine and most primary aluminium installations do not have an alumina production process on site.

#### 4.1.1.1 Production of alumina

Alumina is usually produced from bauxite in the well-established Bayer process as shown in Figure 4.1. This process benefits from the different thermodynamic properties of the caustic soda - aluminium hydrate system. The solubility of the aluminium compound in the bauxite is much higher at elevated temperatures than at lower temperatures. Hence, the aluminium compound is dissolved in the Bayer process in the digestion area at temperatures of up to 280 °C and the dissolved aluminium hydrate is precipitated as solid material in the precipitation area at around 55 - 70 °C and thus, can be removed from the process.

Therefore, caustic soda flows in a circuit and is fed with ground bauxite and then heated up to digestion temperature. The alumina compound of the bauxite dissolves at these elevated temperatures in the digesters. Afterwards the non-dissolved material from the bauxite, the red mud, is removed from the process by means of thickeners. The supersaturated liquor is then cooled down to crystallisation conditions. The aluminium hydrate crystallises in the precipitation area and can be removed by either filters or thickeners from the Bayer circuit. The solid-free caustic soda is used to dissolve bauxite and the circuit starts again. In a last process step, the aluminium hydrate is converted to alumina by calcination.

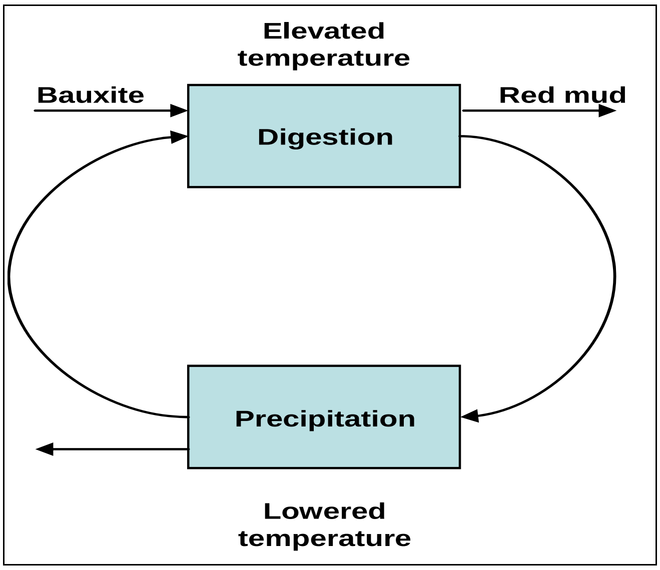


**Figure 4.1: General principle of the Bayer process**

Although the basic process is standard across the industry, there are variations in the equipment used in particular the digesters and calciners. These variations mainly affect the energy used in the process [ 75, Nordheim, E. (EEA) 1998 ].

**Digestion**

First of all the bauxite is ground in order to make it pumpable and to increase the surface for extraction. The bauxite is ground in ball or rod mills or a combination of both. In the grinding process, the first caustic soda (liquor) is added and the slurry is then usually stored in slurry tanks. The digesters are fed with this bauxite slurry and additional liquor in order to get the optimum dissolution properties.

The bauxite slurry is heated up to digestion temperature which varies from 143 to 280 °C depending on the bauxite quality, at which the aluminium compound dissolves. The hot slurry is cooled down in flash tanks. The evaporated steam is used to preheat the bauxite slurry and thus, the heat is recovered. In order to get the final digestion temperature, primary energy is used either indirectly or directly by injection of live steam. The condensate is used for various washing purposes i.e. removing the soluble caustic from the red mud and hydrate.

Due to the reaction during digestion of soda and silica, which are present in the bauxite, sodalithe precipitates and is removed from the process with the red mud. The amount of sodalithe depends on the silica content of the bauxite. Also depending on the bauxite quality, lime is added in order to remove vanadium and phosphate from the liquor and to improve the extraction yield.

**Red mud removal** (see also the reference document on the Management of Tailings and Waste-Rock in Mining Activities [ 295, European Commission 2004 ]).

The material that does not dissolve in the digestion process is known as red mud and is removed from the process liquors by means of thickeners. In these thickeners, the flow velocity of the liquor is reduced and the solid red mud settles out. Some refineries separate the coarse particles of the red mud, known as sand, prior the thickeners therefore avoiding erosion in the subsequent stages.

The separated red mud is then washed by condensate, which flows in a countercurrent direction through a washer train. Before each washer the red mud slurry from the previous washer and the overflow from the subsequent washer is mixed and settles out in the washer. In this way the alkali concentration is reduced in each stage of washing. The more washers that are installed, the lower the alkali concentration.

In some refineries the last step of recovering the alkali is the red mud filtration (this is the most efficient way regarding alkali recovery), in which the red mud is washed with condensate and the filter cake is stored in the red mud disposal area. In this manner the free alkali concentration can be reduced to a very low level. When a high pressure filtration is used, the solid red mud residue produced has a very low water content and can be stored as a solid or economically transported over long distances to be used in various applications.

**Precipitation and Calcination**

At first, the overflow of the red mud settlers should be filtered in order to remove the finest solid particles from the liquor. The liquor is then cooled down to the precipitation temperature and the precipitation is started by adding aluminium hydrate as a seed. The hydrate slurry flows through a tank cascade and hydrate is precipitated in each tank. At the end of the cascade, the solid hydrate is removed from the liquor by either a filtration or by thickeners. The separated hydrate is then washed with condensate and can afterwards be calcined. The solid-free liquor, after passing, in some cases, by an evaporation plant, is fed to the digestion area where it runs through the circuit again.

In the calcination stage the hydrate is heated to temperatures of around 1000 °C. Under these conditions the water of crystallisation is released and the hydrate is converted to alumina. This process can be carried in circulating fluidised beds, stationary or rotary calciners. Rotary calciners are less energy efficient than fluidised bed calciners but are used at higher temperatures (1200 – 1300 °C) to produce speciality alumina.

A typical process flow diagram for the Bayer process is shown in Figure 4.2, dashed lines indicate non-obligatory process steps.

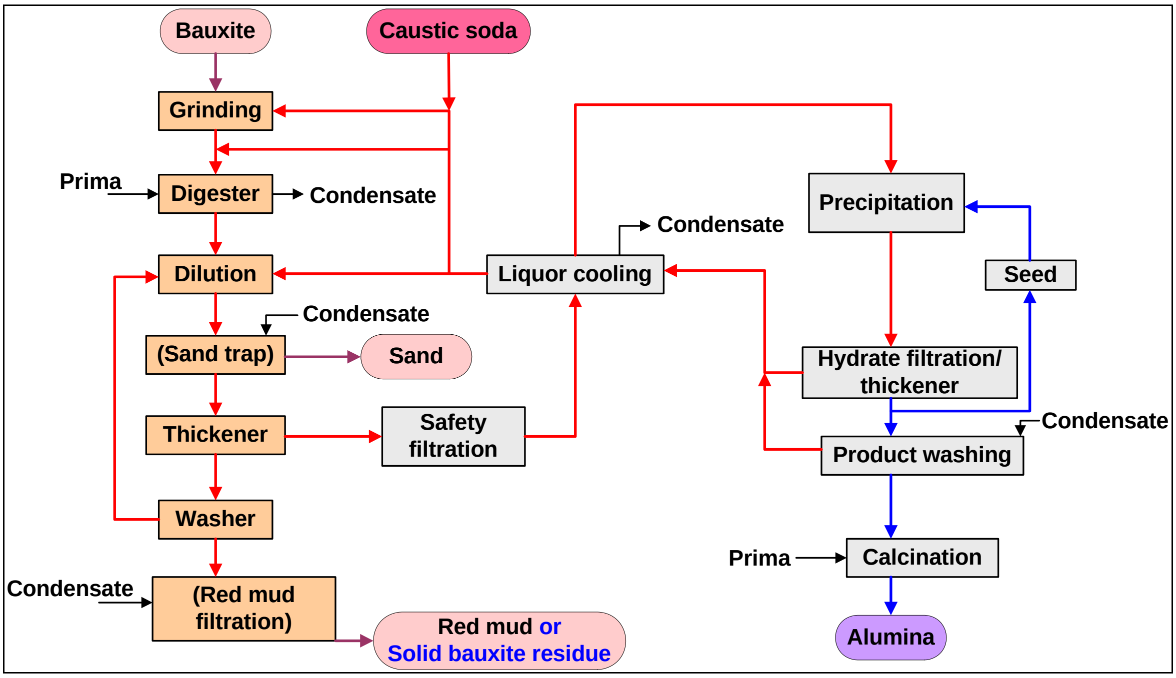


**Figure 4.2: Bayer process**
[ 272, Al input 2008 ]

Impurities such as oxalate and carbonate from the process are usually removed in side-streams by various techniques. Both salts originate from the digestion stage and come from the organic and carbonate content of the bauxite. The salt is generated as a residue or a by-product. If alumina production is based on bauxite that contains high levels of vanadium, the salt can further be used to obtain vanadium pentoxide. This process may have a waste water problem because the salt also contains arsenic that it transported into the leach liquor and then to the waste water.

#### 4.1.1.2 Aluminium production by electrolysis

Aluminium is produced by the electrolytic reduction of aluminium oxide (alumina) dissolved in a molten bath of mainly sodium aluminium fluoride (cryolite) at a temperature of approximately 960 °C. The electrolytic cells comprise a carbon cathode, insulated by refractory bricks inside a rectangular steel shell, and a carbon anode suspended from an electrically conductive anode beam [ 312, VDI 2286 Aluminium Part 1 and 2 2008 ]. The cells are connected in series to form an electrical reduction line (pot line). A direct current is passed from a carbon anode through the bath to the cathode and then, by a bus bar, to the next cell [ 6, McLellan and Partners Ltd 1993 ] [ 97, Lijftogt, J.A. et al 1998 ].

Alumina is added to the cells to maintain an alumina content of 2 - 6 % in the molten bath. ~~The point feeder prebake (PFPB) cells are most commonly used and allow better control of the process.~~ Additions are computer controlled in modern plants. Fluoride compounds are added to lower the bath melting point, enabling the cells to be operated at a lower temperature.

Aluminium fluoride ($AlF_3$), the most common additive, also neutralises the sodium oxide present as an impurity in the alumina feed. Aluminium fluoride can be added separately from alumina and additions can be controlled based on an algorithm of the cell flow pattern [ 233, Farrell Nordic Mission 2008 ]. Most cells are now operated with the $AlF_3$ content of the bath significantly in excess of the stoichiometric cryolite composition, however, fluoride emissions increase as the excess $AlF_3$ in the bath is increased [ 6, McLellan and Partners Ltd 1993 ], [ 97, Lijftogt, J.A. et al 1998 ].

Liquid aluminium is deposited at the cathode in the bottom of the cell. Molten aluminium is periodically withdrawn from the cells by vacuum siphons into crucibles. During electrolysis, oxygen from the alumina combines with the carbon anode, to form carbon dioxide. The carbon anodes are therefore continuously consumed during the process.

Cell systems vary according to the type of anode and the method used to feed alumina, as illustrated in Figure 4.3, [ 97, Lijftogt, J.A. et al 1998 ], [ 6, McLellan and Partners Ltd 1993 ], [ 16, HMIP (UK) 1994 ]. There are two main types of electrolytic cells, Søderberg and Prebake.

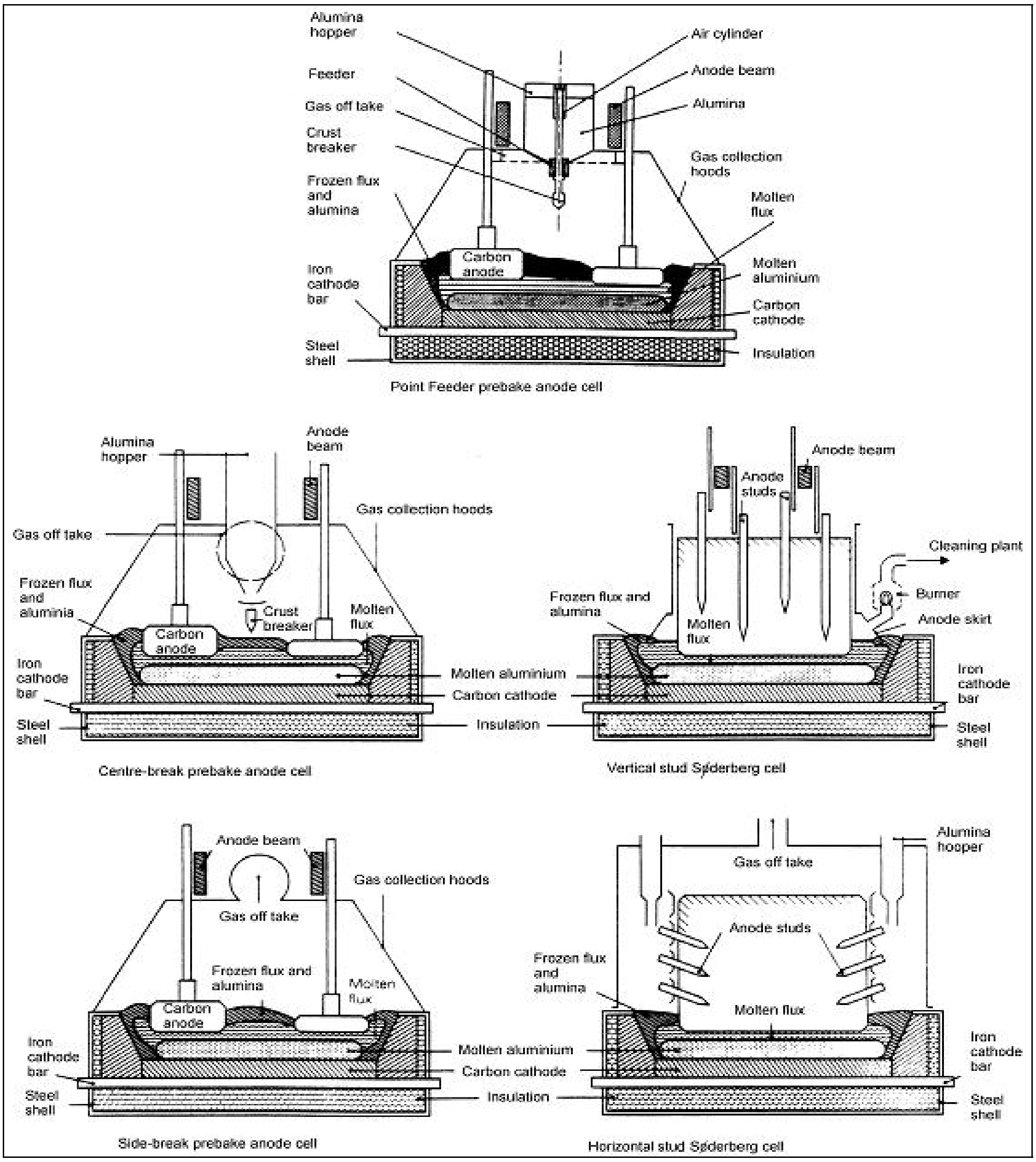


**Figure 4.3: Primary aluminium electrolytic cells**

**a) Søderberg cells**

Søderberg technology uses a continuous anodes which~~anodes~~ are made *in situ* from a paste of calcined petroleum coke and coal tar pitch, which is baked by the heat arising from the molten bath. The current is fed into the Søderberg anode through studs that have to be withdrawn and re-sited higher in the anode as the anode is consumed. As the anode is consumed, more paste descends through the anode shell, thus providing a process that does not require changing of the anodes. Alumina is added periodically to Søderberg cells through holes made by breaking the crust of alumina and frozen electrolyte which covers the molten bath. Automatic point feeding systems are used in upgraded plants, eliminating the need for regular breaking of the crust. A gas skirt is attached to the lower part of the anode casing for gas collection. Fumes are collected and combusted in burners to reduce the emission of tars and PAH. Pot room ventilation gases may also collected and treated.

Modernised Søderberg technology consists of equipping the cells with point feeders and improved burners so there is no need for regular crustbreaking. The use of dry paste with a lower pitch content, together with a reduction in the temperature on the anode top, through an increase of the anode height, reduces PAH emissions from the anode top. PAH emissions can be absorbed by the dry paste in the higher anode casing or, when necessary, collected by anode covers. The improvements are shown in Figure 4.4.

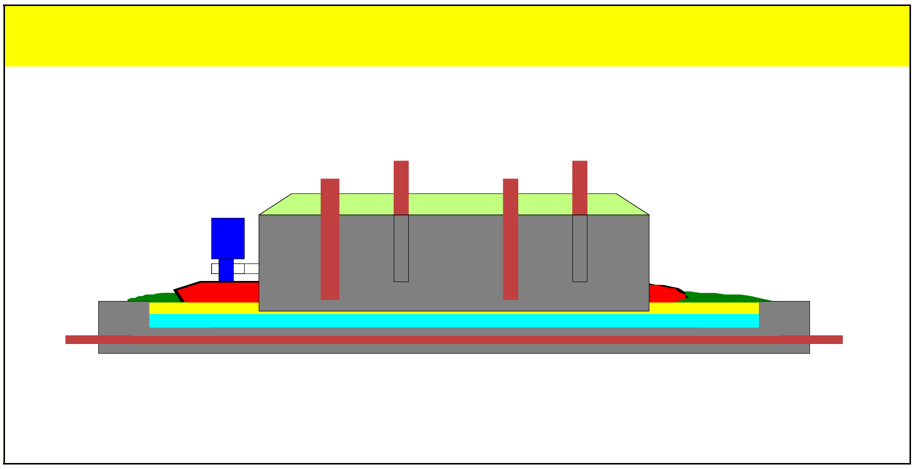


**Figure 4.4: Modernised Søderberg Cell**

[ 234, UBA Copper, lead, zinc and aluminium 2007 ]

*(This figure is not from [234]The description about how PAH emissions are absorbed by the dry paste in the higher anodes casting is unclear.The figure gives barly no information.*

**b) Prebaked cells**

Prebake technology uses multiple anodes which are manufactured from a mixture of calcined petroleum coke and coal tar pitch, which is formed into a block and baked in a separate anode plant. The anode production plant is often an integrated part of the primary aluminium plant.

The anodes are suspended in the cells by hanger rods attached to anode beams, which also serve as the electrical conductor. The anodes are gradually lowered as they are consumed and are replaced before the rods are attacked by the molten bath. The remnants of the anodes, which are known as anode butts, are cleaned of bath material and recycled through the anode plant.

Prebake cells normally have 12 to 40 individual anodes, which are changed at regular intervals. In a large pot room, anode changing is a frequent occurrence and involves the removal of the cell cover shields. This can result in an increase in diffuse emissions if several covers are removed at the same time. In some plants, an automatic system to increase the rate of air extraction is used for periods when hoods are open, there is usually little leakage from the cell being maintained (depending on the rating of the extraction system), the overall extraction rate from other cells is not reduced.

Prebake cells can be one of ~~two~~ three types depending on how alumina is added:

- Side worked prebaked anode cells (SWPB) where alumina is fed into the cells after the crust is broken around the circumference. The gas collection hoods over the length of the cells have to be opened during this operation.
- Centre worked prebaked anode cells (CWPB) where alumina is fed after the crust is broken along the centreline or at selected points on the centreline of the cell (PFPB~~point feeder~~). These feeding methods can be carried out without opening the gas collection hoods.

The point feeder prebake (PFPB) cells are most commonly used and allow better control of the process.

An overview of aluminium smelting technologies is given in Table 44.1.

| **Cell technology** | **Cell type** | **Anode configuation** | **Alumina feed configuration** | **Acronym** |
|---|---|---|---|---|
| Prebaked cell | Centre Worked | Vertical | Bar broken centre feed | CWPB |
| | | Vertical | Point centre feed | PFPB |
| | Side Worked | Vertical | Manual side feed | SWPB |
| Søderberg cell | Vertical Stud | Vertical | Manual side feed | VSS |
| | | | Point feed | |
| | Horizontal Stud | Horizontal | Manual side feed | HSS |
| | | | Bar broken feed | |
| | | | Point feed | |

**Table 4.1: Aluminium smelting categories**
[501]

A breakdown of the technology types is given in T~~t~~able 44.2.

| **Cell type** | **Acronym** | **Application (%)** |
|---|---|---|
| Centre Worked | CWPB | 80 |
| | PFPB | |
| Side Worked | SWPB | 3 |
| Vertical Stud | VSS | 13 |
| Horizontal Stud | HSS | 4 |

**Table 4.2: Cell type breakdown**
[501]

The gas collection system extracts the process gases to an abatement system that uses dry alumina scrubbers to remove and reclaim HF and fluorides. The scrubber also removes residual tars in the case of a Søderberg installation but does not remove sulphur dioxide. The alumina leaving the scrubbers is removed in fabric filters and is usually fed directly to the cells. Pot room ventilation gases may also be collected and treated in a wet scrubber system if the pot room concentration of pollutants are high [ 312, VDI 2286 Aluminium Part 1 and 2 2008 ].

The cathode is not consumed in the process but the cathodes deteriorate over time. Carbon blocks absorb electrolyte and after 5 to 8 years have to be replaced due to swelling and cracking which results in the penetration of molten electrolyte and aluminium to the cathode conductor bar and steel shell. Small amounts of cyanides are formed through a reaction between nitrogen and carbon. The cathode residue is known as spent pot lining and several disposal and recycling routes for this material are used [ 41, Ausmelt Ltd. 1996 ], [ 97, Lijftogt, J.A. et al 1998 ] and are described later in Section 4.2.3.4.

Molten aluminium is periodically withdrawn from the cells by vacuum siphon into crucibles. The crucibles with the siphoned aluminium for the reduction cells are transported to the casting plant and the aluminium is emptied into heated holding furnaces. These are usually induction or reverberatory furnaces. Reverberatory holding furnaces can be equipped with regenerative burners in order to preheat combustion air and so save energy. Alloying additions are made in these furnaces by the addition of the required metal (Si, Mg, Pb, Sn, Zn, Cu, Zr, Sr) or master alloy of the metal with aluminium (Ti, Cr, Fe, Mn, Ni). Other additions are also made to refine the grain of the metal, titanium or titanium boride are the most common. Homogenisation can be achieved by moving the melt with the help of stirrers or stirring machines. Electromagnetic or mechanical liquid metal pumps may also be used to achieve melt circulation and improve homogenisation of the alloyed metal in reverberatory furnaces.

The temperature for casting is controlled in the holding furnaces.

#### 4.1.1.3 Refining

The metal is refined to remove metallic impurities such as sodium, magnesium and calcium, non-metallic particles and hydrogen. This refining stage is performed by the injection of a gas into the molten metal usually in an in-line reactor. The treatment gas used varies depending on the impurities; argon or nitrogen are used to remove hydrogen while mixtures of chlorine and argon or nitrogen are used to remove metallic impurities of the alkali and alkaline earth group. Aluminium fluoride, magnesium chloride or potassium chloride are also used to remove metallic impurities. The metal is then filtered before casting.

Skimmings or dross are formed by the reaction products of the purging treatment and the oxidation of molten aluminium on the surface of the melt are skimmed off. Sealed containers or dross presses, nitrogen or argon blanketing or compaction can be used to minimise further oxidation of the skimmings or dross [ 103, Farrell, F. 1998 ]. Throughout this chapter both the terms skimmings and dross are used interchangeably. Both are recycled by the secondary aluminium industry.

#### 4.1.1.4 Casting

Slabs, T-bars or billets are cast in vertical direct chill casting machines that use water-cooled metal moulds and a holding table at the bottom part of the moulds. The table is lowered as the ingot is formed. Billets and slabs of smaller cross-sections can also be produced by horizontal direct chill casting. Other casting methods include the use of metal moulds (static or continuously moving) and the continuous casting of thin sheets as well as wire-rod [ 6, McLellan and Partners Ltd 1993 ]. Additional small quantities of skimmings or dross are also produced at this stage and are removed from the surface of the molten metal.

#### 4.1.1.5 Production of prebaked anodes for aluminium production

Carbon anodes produced for primary aluminium smelting are either produced in standalone anode production plants or in smelters with associated anode production. The production of anodes is similar to the production of carbon and graphite electrodes and shapes but there are significant differences in the percentage of coal tar pitch, the recycling of anode butts and also in the baking temperature and a comparison and is shown in Table 4.3.

| **Parameter** | **Anode production** | **Carbon electrode first baking stage** |
|---|---|---|
| Baking temperature °C | 800 - 1200 | 800 - 1100 |

| | | |
|---|---|---|
| Pitch content % | 13 - 18 | Up to 40 |
| Heating gradient °C/h | 10 - 14 | 1 - 2 |
| Specific gas volume m$^3$/h per tonne produced per year | 5000 | 50 – 110 |

**Table 4.3: Comparison of baking processes**
[ 318, Fume treatment from Baking Furnaces 2007 ]

The production of anodes for the primary aluminium industry is reported here and the production of carbon electrodes is reported in Chapter 12.

Processes use coke, pitch and cleaned anode butts to produce pastes which are then formed into anode blocks. Raw material storage and handling stages use enclosed coke delivery and handling systems and integral dust filters. Coal tar pitch delivery and storage systems use tank back venting and condensers for tank breathing when using liquid pitch and silos for solid pitch. In some cases the Regenerative Catalytic Oxidiser (RCO) or Regenerative Thermal Oxidiser (RTO) have been used to treat the gases.

Søderberg paste and prebaked anodes are formed and baked ready for use in appropriate facilities.

The basic process for green anode production is described in Figure 4.5.

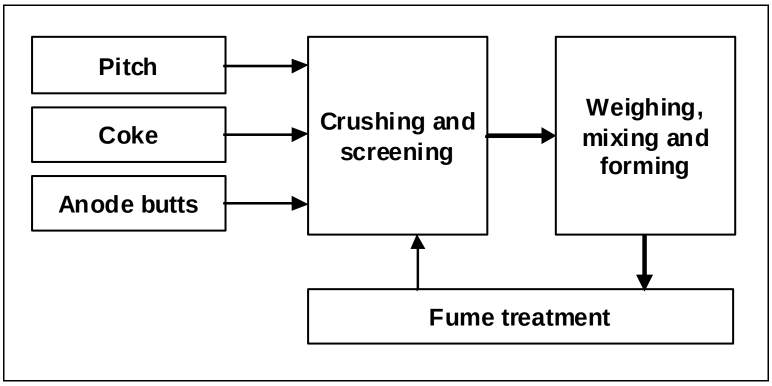


**Figure 4.5: Production of green anodes**

Green paste production is the starting point for the production of all carbon anodes. All green pastes are manufactured from a mixture of calcined petroleum coke and coal tar pitch, which acts as a binder. The petroleum cokes are a residue from the distillation of crude oils and can therefore be contaminated with substances like metals (e.g. nickel) and sulphur compounds. Cleaned anode butts, recycled from aluminium production, are often part of the aggregate mix.

Coke and solid pitch are normally transferred by sealed conveyors or dense phase pneumatic systems and are stored in silos. Liquid pitch is transported in the molten state and is transferred by pumping and is stored in heated tanks. The tank ventilation gases contain hydrocarbon fume and are usually cleaned. Condensers or oil scrubbers are used [ 75, Nordheim, E. (EEA) 1998 ] and back venting of the tank gases is also used. Petroleum coke and anode butts are ground and then mixed with pitch in heated mixers. The ratio of coke and pitch is adjusted according to the application and to allow the paste to be handled and formed into blocks.

In the case of Søderberg paste, the blend is produced to allow it to be added to the anode shell. Dry anode paste (low pitch content) is preferred to minimise the amount of hydrocarbon released during use [ 6, McLellan and Partners Ltd 1993 ]. Dry paste or cast iron rods are used for electrical connections. Green shapes are formed by pressing the green paste in moulds.

**Prebaked anodes**
These anodes are manufactured from a mixture of petroleum coke and 13 to 18 % coal tar pitch and residual material from anode butts [ 75, Nordheim, E. (EEA) 1998 ] [ 116, VDI (D) 1998 ].

Anode production involves crushing, grinding and mixing of the raw materials. The mixed materials are then formed into green anodes. The green anodes are then baked in ring furnaces comprising a large number of pits which contain the anodes. Refractory brick walls separate the pits and ducts are formed for the flue-gases. Green anodes are stacked in the anode furnace in rows and the heating ducts are formed. Layers of packing coke separate the anodes and prevent oxidation. This coke is consumed during the heating and cooling cycle at a rate of 12 to 18 kg per tonne of anodes and the remaining coke is re-used. At any one time, pits in separate sections of the furnace are being filled, heated, cooled or emptied [ 91, OSPARCOM 1992 ].

Hot air is passed through the ducts using movable gas-fired burners and the anodes are baked at 1100 °C in the absence of air. The ducts are kept under negative pressure to contain the fumes. At the end of the heating cycle the ducts are then connected to blowers to cool the section. Hot air passing from the furnace section being cooled is then recycled through the burners or through other furnace sections to preheat that part of the system.

The layout of baking furnaces can be seen in Section 12.1.

Two types of furnace are used for anode baking; open and closed ring furnaces. Open furnaces use a horizontal duct and closed furnaces use a vertical flue. Open furnaces account for more than 60 % of capacity and are used in new plants. The horizontal ducts of the open furnace are separate and parallel, this allows the heating cycle to be optimised for each duct and so reduces fuel consumption [ 91, OSPARCOM 1992 ]. The use of multiple chambers in the furnace allows heat from one section to be used in other sections.

During the baking process, the coal tar pitch is converted into coke making the material electrically conductive, there is approximately a 5 % loss in weight during baking [ 75, Nordheim, E. (EEA) 1998 ]. The baking process takes approximately 18 to 21 days. A regenerative afterburner (or regenerative thermal oxidiser) has been used in a standalone anode production plant to treat the process gases from these processes the techniques is described in Section 4.3.3.3. In cases where anode production takes place at the site of a primary smelter, alumina is used to absorb PAH and VOC from the gases the techniques is described in Section 4.3.3.1.

In the aluminium industry, the prebaked anodes are connected to the anode studs using rods. These are fixed into the anode in a rodding plant, allowing the anodes to be placed in the top of the electrolysis pot using hangers. The anodes are consumed during electrolysis and have to be replaced after about 80 % of the anode is consumed [ 6, McLellan and Partners Ltd 1993 ], [ 28, OSPARCOM 1997 ]. The anode residues (20 % of the original anode weight) are re-used for anode production after residual electrolyte has been removed. The steel rods are reconditioned for further use although a small proportion is scrapped if corroded.

## 4.1.2 Secondary aluminium

### 4.1.2.1 Production processes

The main feature of secondary aluminium production is the diversity of raw materials encountered and the variety of furnaces used [ 113, ALFED 1998 ]. Various scrap grades are defined in EN 13920 and the standards are numbered 1 to 16 depending on the scrap. Other categories might also be encountered which comply with the relevant environmental legislation. The type of raw material and its pretreatment is therefore used to judge the best type of furnace to be used for a particular type of scrap with its size, oxide content and degree of contamination among other factors [ 142, Boin, U. et al. 1998 ] [ 312, VDI 2286 Aluminium Part 1 and 2 2008

]. These factors also influence the choice of fluxes associated with the process to maximise the recovery of aluminium [ 2, McLellan et al. 1993 ], [ 113, ALFED 1998 ]. The choice of the process technique used will vary from plant to plant. The number of factors that influence the choice of process mean that there is the potential for many viable strategies which can address similar circumstances. The secondary aluminium generic process is shown in Figure 4.6.

Rotary or reverberatory furnaces (also known as closed-well, chamber or hearth furnaces) are used for melting a wide range of secondary raw materials. Rotary furnaces can incorporate a tilting mechanism. The tilting mechanism in some cases, allows increases in efficiency for raw materials that contain low amounts of aluminium including skimmings and dross and therefore the amount of salt cover needed for these materials can be reduced [ 142, Boin, U. et al. 1998 ], [ 256, Plant visit report AMAG 20071114.doc 2007 ]. Induction furnaces and shaft furnaces (the Meltower) are used to melt the cleaner aluminium grades. Reverberatory furnaces often include a side-well. A pumping system (mechanical or electromagnetic) is sometimes used to convey molten metal through the side-well and a charging well to assist the melting of small particles. Electromagnetic pumps have no moving parts and rely on an external coil to induce the electromagnetic force; stirring is induced in the charging well and in the furnace. Other pumps, which have heat resistant internal parts and metal spinners are also used [ 142, Boin, U. et al. 1998 ].

Reverberatory furnaces (closed-well, chamber or hearth furnaces) may also use a sloping hearth in the metal feed area where items containing large pieces of iron can be placed. Aluminium is melted off the iron substrate, which remains on the hearth. Contamination of the melt by iron is therefore minimised [ 75, Nordheim, E. (EEA) 1998 ], [ 113, ALFED 1998 ]. Details of some of the furnaces are given in Section 2.8.4.

Typical sources of aluminium scrap are process scrap, used beverage cans, foils, extrusions, commercial scraps, turnings, and old rolled or cast metal. In addition to this, aluminium is also recovered from skimmings or dross and salt slags. Various contaminants may be present and this is taken into account in the choice of pretreatment or in the design of the furnace [ 75, Nordheim, E. (EEA) 1998 ]. Scrap is sometimes sorted first into alloy types to produce the desired alloy with the minimum reprocessing [ 113, ALFED 1998 ], [ 118, Laheye, R. et al. 1998 ].

Scraps such as UBCs and turnings are major sources of material feedstock and may be contaminated. These sometimes need to be de-coated or de-oiled prior to melting to improve the melting rate (and thermal efficiency) and to reduce the potential for emissions [ 118, Laheye, R. et al. 1998 ], [ 119, McLellan 1998 ]. The melting of cleaned material can save energy and reduce the generation of skimmings or dross. The pretreatment processes are outlined in Figure 4.6 and Figure 4.7.

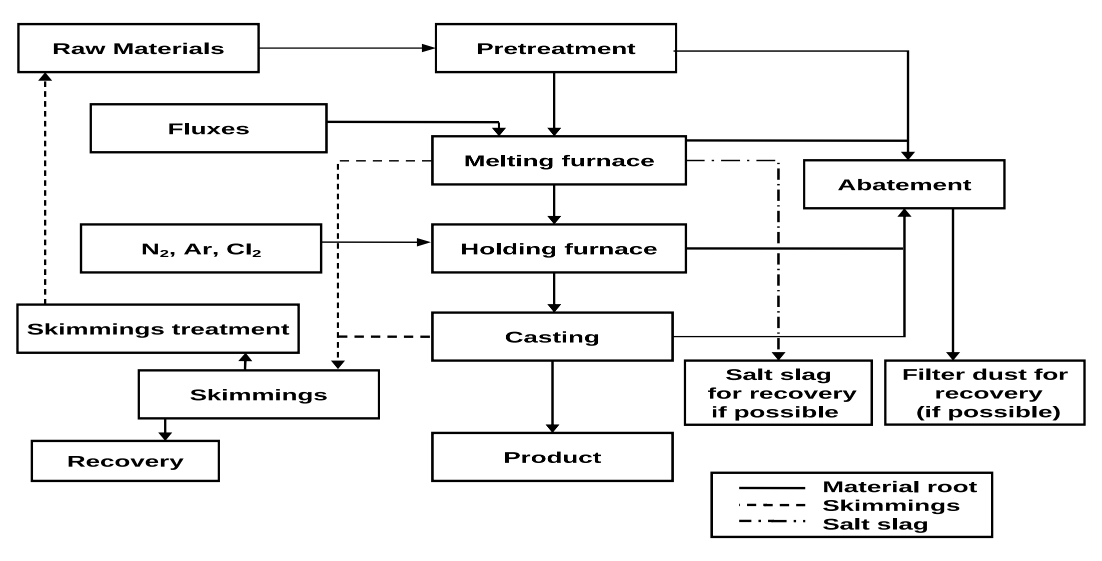


**Figure 4.6: Secondary aluminium generic process**
[ 272, Al input 2008 ]

A range of different fluxes which are normally mixtures of salts, is used within the secondary aluminium industry to assist in the processing of the metal in a number of ways. An example is the use of fused salt (a mixture of sodium and potassium chlorides and some fluorides) to reduce oxidation, to absorb impurities and to increase thermal efficiency. Furnace gases contain chlorides and hydrogen chloride produced from the salt. Refractory fluxes and fluorinated fluxes are also used. Salt slag is tapped separately from the metal. There are variations in the quantity of salt cover used and this depends on the furnace used and the oxide content of the raw material. Pretreatment of the feed material can reduce the salt usage. It has also been reported that up to 1.1 kg of salt per kg non-metallic constituents is used for a static rotary furnace and <0.5 kg per kg for a tilting rotary furnace [ 142, Boin, U. et al. 1998 ] [ 312, VDI 2286 Aluminium Part 1 and 2 2008 ].

The use of a side-well reverberatory or chamber furnace with a charging well and pumping system can increase the number of grades of scrap, including foil and small turnings that can be melted in these furnaces. It can also reduce the loss of metal by oxidation without using large quantities of salt or other cover [ 118, Laheye, R. et al. 1998 ], [ 119, McLellan 1998 ], [ 120, McLellan 1998 ].

### 4.1.2.2 Refining and casting processes

Metal may be tapped from the melting furnace where alloy additions are made either directly to a casting system or via a transfer system into a holding furnace (where other alloying additions can be made). The metal is then refined either in the holding furnace or in an in-line reactor, to remove gases and other metals in the same manner as primary aluminium. Magnesium and other impurities can be present in secondary aluminium and may need to be reduced. Treatment of molten aluminium with chlorine gas mixtures is used to remove magnesium although sodium aluminium fluoride and potassium aluminium fluoride are also used [ 113, ALFED 1998 ]. The latter material is a by-product of the production of some master alloys.

Large ingots, billets and slabs are cast in the same way as primary aluminium and a range of smaller ingots (e.g. for supplying the casting industry) may also be produced in a large variety of alloys depending on the final application. It is also possible to transport molten aluminium by road in special thermally-insulated containers to end-users.

### 4.1.2.3 Skimmings and dross

Aluminium is easily oxidised and this is a significant factor in the production processes. The melting of aluminium produces an oxide layer known as skimmings or dross. This is skimmed from the metal surface before casting. Skimmings or dross that have been removed from a furnace contain between 20 - 80 % aluminium. Skimmings or dross are sometimes treated as soon as they are removed from the furnace to reduce emissions and further oxidation of the metal present. Methods include inert gas cooling, hot pressing to remove molten aluminium and cooling in purpose built coolers [ 312, VDI 2286 Aluminium Part 1 and 2 2008 ].

Cold skimmings or dross are treated by a number of processes to recover aluminium. For example by smelting in rotary or tilting rotary furnace under a salt cover or by using separation techniques such as milling and processing to separate oxide from the metal [ 113, ALFED 1998 ]. In the latter case, the metal can be remelted in relevant furnaces and the fine fraction can be further processed, e.g. recycled in the steel industry or in the salt slag recovery process. It has been reported that the ultimate generation of salt slag and waste is reduced and the use of energy is lower due to a lower burden of inert material in the furnace. Skimmings or dross recovery processes are shown in Figure 4.7.

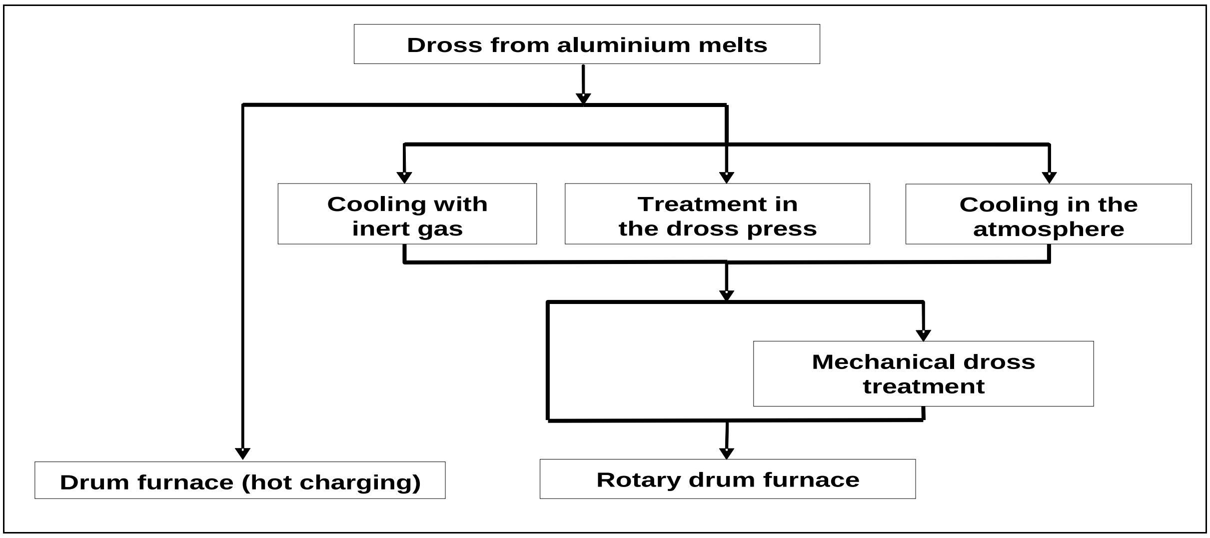


**Figure 4.7: Skimmings or dross recovery processes**
[ 272, Al input 2008 ]

### 4.1.2.4 Salt slag

Rotary or tilting rotary furnaces [ 256, Plant visit report AMAG 20071114.doc 2007 ] are used to recover aluminium from skimmings or dross and the metallic fraction produced from it. A salt cover is usually used to facilitate this process, as it reduces oxidation and promotes the removal of some impurities (e.g. Mg, Ca, Li). Several installations exist where salt slag can be recovered using a washing and crystallisation process and it is reported [ 272, Al input 2008 ] that sufficient capacity exists to recover salt slag from the secondary aluminium processes that are operated in the EU. The processes can produce recycled aluminium granules and salt. It is reported [ 88, Nordheim, E. 1998 ] that the metal oxide fraction (mainly oxides of aluminium, calcium and magnesium) can be further processed and washed to produce fine aluminium oxide that has been sold to the cement industry.

### 4.1.2.5 Salt slag recovery

Aluminium salt slags are hazardous wastes and are not suitable for landfill. In the full recycling process, they are completely recovered to produce marketable products and it is also possible to avoid the production of waste water. A partial recycling process exists (K+S Rekal) as part of a fertiliser production plant that only recovers KCl and aluminium granules while the remainder is disposed of [ 312, VDI 2286 Aluminium Part 1 and 2 2008 ].

The full recycling process is a combination of different physicochemical process steps for the recovery of salt slags and the full recycling process is shown in Figure 4.8. In each process step, the different material characteristics of the three main salt slag components used to separate the material fractions are:

- metallic aluminium (5 - 20 % in typical salt slag) is nearly insoluble in water; during crushing the ductile nature of aluminium means that small particles are pressed into flakes with a larger surface area which can be removed by sieving;
- oxidic components (35 - 55 % in typical salt slag) are insoluble in water and are brittle, crushing tends to break them into finer particles;
- alkaline chlorides (35 - 55 % in typical salt slag) are very soluble in water and are also brittle.

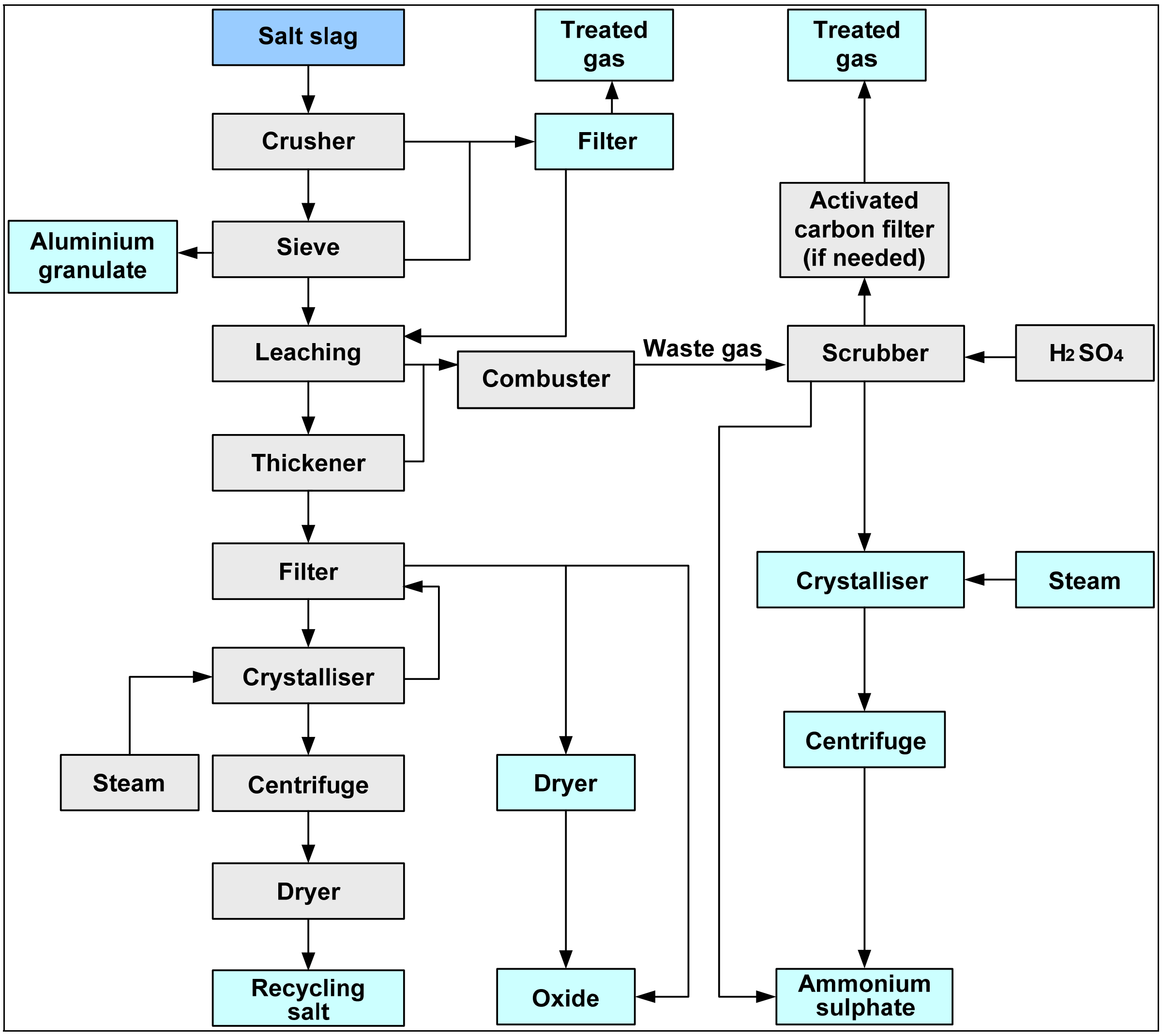


**Figure 4.8: Salt slag full recycling process**
[ 272, Al input 2008 ]

The large blocks of salt slag are crushed to manageable sizes and sieved to recover metallic aluminium granules (typically up to 10 %). There is the potential for major dust emissions during the crushing stages and the grinding is carried out under totally sealed conditions. The gaseous emissions are treated in fabric filters and the collected dust is sent directly to the dissolvers. In some plants all grinding stages are carried out under dry conditions and in others the final stage is carried out using water [ 267, BEFESA 2008 ]. The finely crushed material is then dissolved in water. The alkaline chloride fraction goes into solution and produces a brine. The coarse aluminium flakes are separated from the insoluble fraction consisting of metal oxides (predominantly alumina) and the finest metallic particles of aluminium in a wet sieving system. Gases are evolved from this stage of the process and mainly contain ammonia, methane, hydrogen, phosphine and hydrogen sulphide as well as dust generated in different plant sections. These are collected and cleaned either by a thermal or a wet system. In the case of a wet scrubber, ammonia can be separated and ammonium sulphate (solution or salt) produced for sale. It is also possible to use some of these gases as a fuel for other parts of the process [ 113, ALFED 1998 ]. The brine is filtered removing the insoluble oxides and the solution is then sent for evaporation and crystallisation from which the original sodium and potassium chlorides can be recovered. These chlorides are re-used as cover in the melting process.

The residual metal oxides comprise calcium, magnesium and aluminium oxides (up to 65 % $Al_2O_3$). Sulphates, chlorides and nitrates are also present [ 202, Fundación Entorno, Empresa y Medio Ambiente 1999 ]. The oxide fraction has markets in the brick, ceramics, clay, cement and mineral wool industries and further washing can be used to reduce these anions to manageable levels. The brine solution from the washing can be returned to the dissolution stage. With the full recycling process the salt slag is completely recovered to produce marketable products [ 88, Nordheim, E. 1998 ]. In the case of full recycling processes the generation of waste and waste water is avoided.

The partial recycling process is used in a process that forms part of a fertiliser production process and is specific to that industry. The process principally uses the same main steps as the full recycling process (mechanical pretreatment, leaching with waste gas treatment, solid/liquid separation, crystallisation). In this case, only the KCl content (18 - 30 % KCl in typical salt slag) is recycled as salt product. After further processing in an internal salt-refining step of the potash plant, it is sold to the fertiliser industry. The water-soluble NaCl content (30 - 50 % NaCl in typical salt slag) remains in the leaching (oxide) residue and NaCl will be leached out after the material is deposited on land [ 234, UBA Copper, lead, zinc and aluminium 2007 ].

In another case the separation process is similar to that in the full recycling process but salt is not recovered and the salt solution is discharged below the biotopical zone of a fjord.

It is also technically possible to recover the dust produced during the pretreatment processes of the aluminium slags and scrap, as well as the dust from the filtration of the furnaces and this is already carried out in some plants. This means that all the solid wastes generated by the secondary aluminium industry are capable of being recycled. Wash water is normally returned to the dissolvers to make up for the water evaporated in the process. Typical contents of the insoluble, non-metallic portion of salt slag are shown in Table 4.4.

| Component | % by weight | Component | % by weight(1) |
|---|---|---|---|
| $Al_2O_3$ | 60 - 75 | $TiO_2$ | 1.0 - 1.5 |
| MgO | 5 - 10 | MnO | <0.3 |
| $SiO_2$ | 8 - 12 | $Na_2O$ | <1.0 |
| CaO | 2 - 5 | $K_2O$ | <1.2 |
| $Fe_2O_3$ | 1.5 - 3.0 | $Cl^-$ | <0.8 |
| Moisture | 15 - 30 | | |
| (1) Refers to dry substances. | | | |

**Table 4.4: Typical contents of the insoluble, non-metallic portion of salt slag**

[ 272, Al input 2008 ]

## 4.2 Current emission and consumption levels

### 4.2.1 Alumina production

The material and energy inputs to the process are significant. Approximately two tonnes of bauxite are required to produce one tonne of alumina, which in turn produces about 0.53 tonnes of aluminium. The carbon anodes are consumed and approximately 0.4 to 0.45 tonnes of carbon are used per tonne of aluminium produced. The energy costs are also high and could account for approximately 30 % of the production costs. Input ranges for alumina production are shown in Table 4.5.

| Parameter | Typical range kg/t alumina |
|---|---|
| Bauxite | 2065 - 2275 |
| NaOH (50 %) | 30 - 70 |
| CaO | 30 - 80 |
| Water | 1000 - 5000 |
| Energy GJ/t | 7.6 - 11.7 |

**Table 4.5: Input ranges for alumina production**
[ 272, Al input 2008 ]

The production of alumina requires energy for digestion and calcination. The energy used is influenced mainly by the origin and chemical composition of the bauxite, the type of digesters used and the type of calciners used. The quantities of NaOH and CaO used are also linked to the composition of the bauxite.

The reduction of energy demand is mainly influenced by using tube digesters, which are able to operate at higher temperatures using a fused salt heat transfer medium and these plants have an energy consumption of less than 10 GJ per tonne. Tube digesters may not be compatible with the layout of existing plants.

#### 4.2.1.1 Red Mud

One major output of the Bayer process is the red mud, which is the remaining solid material after the extraction of the bauxite and does not dissolve in the liquor. The specific amount and composition of the red mud depends strongly on the bauxite quality. The quantity produced varies between 600 to 1500 kg red mud/t $Al_2O_3$ and, therefore, has a major disposal requirement. Current practice is to deposit red mud on or near the site in specially designed, sealed ponds. Excess water from the ponds is normally returned to the process.

Some refineries use high pressure filtration as the last step of the red mud treatment. The output from this operation is a solid bauxite residue, which can be easily and safely transported over long distances so that it can be used in various applications, such as in cement for the production of clinker, and the ceramic industry as an alternative raw material, or in road construction, etc. [ 247, New possible uses of Red Mud, French Report 2008 ]. The production of saleable products from this process is reported in Emerging techniques.

At one site, the red mud is resuspended to 20 - 25 % solids using fresh seawater and free water from the tailings pond, and is then pumped to the tailings pond. The neutralisation of the mud is performed by the flue-gas desulphurisation in the wet scrubbing operation, and with the magnesium chloride content of the fresh seawater in to the system [ 295, Theben, S. 2004 ].

Despite repeated washings, the solution entrained within the red mud still contains small amounts of caustic (sodium hydroxide), which causes the elevated pH characteristics, and alumina. Most of the caustic converts to sodium carbonate and sodium bicarbonate on the tailings stack.

## 4.2.2 Production of carbon anodes for aluminium production

### 4.2.2.1 Mass stream overview and input/output data

The energy used in anode production is 2000 – 2400 MJ per tonne of anode and is accounted for by the fuel used. Packing coke is consumed at a rate of ~12 to 18 kg per tonne of anodes [ 116, VDI (D) 1998 ].

### 4.2.2.2 Environmental issues for the production of carbon anodes

The production of carbon anodes for the aluminium production is primarily a source of particulate matter and emissions to air. When abatement techniques are applied to reduce emissions, cross media effects occur. Sections 4.2.2.2.1 to 4.2.2.2.3 below describe the most relevant environmental issues for the production of carbon anodes for primary aluminium production.

#### 4.2.2.2.1 Emissions to air for the anode production

There are potential emissions to air of hydrocarbons and PAH, sulphur dioxide, dust, fluorides (only for anode production if anode butts form a source of carbon). The formation of $SO_2$ is influenced by the fuel and raw materials used, whereas the formation of $NO_X$ is determined by the combustion temperature.

The emissions can escape the process either as stack emissions or as diffuse emissions depending on the age of the plant and the technology used. Stack emissions are normally monitored continuously or periodically and reported by on-site staff or off-site consultants to the competent authorities. Provisions are made for fume treatment plants to be bypassed in the event of scrubber failure or during maintenance periods.

The furnace gases are treated by afterburning, RTO or wet ESPs. When an anode plant is associated with a primary aluminium smelter, the process gases from a new plant can be combined with the electrolysis cell gases for scrubbing using alumina. In an existing plant, the gases are treated separately in a dry scrubber using alumina. A fabric filter serves the scrubber and the alumina collected is used in the electrolysis cells. Dust from handling and mechanical processes such as grinding, mixing and forming is collected in fabric filters [ 272, Al input 2008 ], [ 75, Nordheim, E. (EEA) 1998 ], [ 88, Nordheim, E. 1998 ].

The basic anode baking process and associated fume treatment for aluminium smelters producing primary aluminium by electrolysis is shown in **Error! Reference source not found.**.

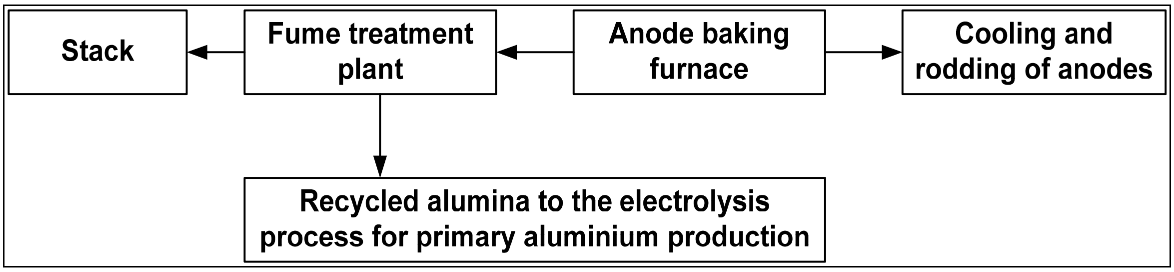


**Figure 4.9: Anode baking process and fume treatment**
[ 272, Al input 2008 ]

*(The expression fume treatment plant is a bit strange. Abatement system, unit, device is probably better)*

Emissions for the various abatement systems employed are as shown in Table 4.6 and Table 4.7.

| Source | Abatement type | Pollutant | Concentration range ($mg/Nm^3$) |
|---|---|---|---|

| | | | |
|---|---|---|---|
| Material storage and handling of coke | Cyclone | Dust | 20 - 60 |
| | Fabric filter | Dust | 1 - 20 |
| Material storage and handling of pitch | Pitch fume dry scrubber<br>or<br>RCO or RTO (if dust is not present)<br>or<br>Cooling and condenser | Hydrocarbon | <25 |
| Grinding, mixing and forming | Fabric filter | Dust | <5 |
| Baking | Open furnaces: Dry scrubbing with alumina and dust removal in a fabric filter. | Dust | <10 |
| | | HF<br>Total F | <0.5<br><0.8 |
| | | PAH (OSPAR 11) | 0.2 – 0.5 |
| | | B(a)P | <0.5 µg/Nm$^3$ |
| | Closed furnaces: ESP and scrubber Regenerative thermal oxidiser (RTO) with HF adsorption *(no FF?? Why is HF 10 times higher? Relevance of HF?)* | Dust | <5 |
| | | Hydrocarbon | <2 (total)(1) |
| | | PAH | 0.05 - 2.5 |
| | | HF | <5 |
| | | $SO_2$ | <250 |
| | | $NO_X$ | <150 |

The regenerative afterburner (RTO) is now classed as an available technique when used with pre and post treatment of the gases.

(1) Condensable and volatile hydrocarbons (state approved method reference). Can also be reported as TOC, measured by FID with a limit of 50 mg/m$^3$

PAH sampling is carried out in accordance with BS ISO 11338 and the subsequent analysis reports 16 PAH

**Table 4.6: Emission concentration ranges for anode production processes**
[ 272, Al input 2008 ], [ 345, Additional Data from UBA DE 2009 ], [ 349, ECGA data for emissions 2009 ].

| **Component** | **Typical range** |
|---|---|
| Fluoride kg/t | 0.01 - 0.1 |
| Dust kg/t | 0.01 - 1.0 |
| BaP g/t | 0.0015 - 3.0 |
| $SO_2$ kg/t | 0.1 - 6.0 |
| $NO_X$ kg/t | 0.1 - 0.4 |

**Table 4.7: Emission factors from the production of prebaked anodes**
[ 272, Al input 2008 ]

###### 4.2.2.2.1.1 VOCs, Hydrocarbons and PAH

Paste for anodes are produced from petroleum coke, cleaned anode butts and coal tar pitch. Emissions of hydrocarbons as tars can occur during delivery, transfer, mixing and baking. Coal tar pitch also contains PAH, which will also be emitted. PAH are potentially hazardous in the environment as well as inside industrial plants. Emissions are therefore controlled by the various forms of abatement equipment described. The preferred reporting convention for PAH is the EPA 16 as this is compatible with the PRTR reporting requirements.

###### 4.2.2.2.1.2 Dust

During production dust emissions occur during all process stages (storage, transfer, crushing, mixing and baking). The emissions are mainly caused by dust generated during crushing and from the carbonisation gases. The mechanical handling and treatment stages are usually enclosed and extracted [ 116, VDI (D) 1998 ]. The source of dust and its characteristics influence the abatement method used to remove it, carbon dust can be very fine and abrasive.

##### 4.2.2.2.1.3 Combustion gases

Gases produced from the combustion of gas or fuel oil will be emitted from the process. There are potential emissions of carbon oxides and the oxides of sulphur and nitrogen. Optimisation of combustion conditions and the use of low-$NO_X$ burners is commonly practised and fuel choice is made according to site conditions.

##### 4.2.2.2.1.4 Sulphur dioxide

The raw materials from which the anodes are made contain sulphur and the fuel used for heating can also contain sulphur. This results in a small emission of sulphur dioxide during baking [ 6, McLellan and Partners Ltd 1993 ]. The emissions of $SO_2$ are in the range of 0.5 (gas) to 2 kg (fuel oil) per tonne aluminium depending on the fuel used. This is far less than the emissions of sulphur dioxide produced during electrolysis as the anode is consumed.

##### 4.2.2.2.1.5 Fluorides (anode production if anode butts are used)

Fluorides are emitted when anode butts from the aluminium electrolysis process are used in the blend for anode production. The anode butts are slightly contaminated with fluorides from the electrolyte. Emissions of particulate fluoride from anode baking plants are negligible. The HF emissions from the anode baking (if scrubbed) equal about 1 % of the emissions generated by aluminium electrolysis [ 97, Lijftogt, J.A. et al 1998 ].

##### 4.2.2.2.1.6 PCDD/F

At the time of writing (2009), test results on emission sources and abatement units in this sector indicate that PCDD/F are not relevant for the conventional carbon manufacturing processes. This will need to be examined if chlorine compounds or additives are used.
*(remark in the concluding remarks…)*

#### 4.2.2.2.2 Emissions to water

The production of carbon anodes is an inherently dry process although small quantities of water may be added to increase the homogeneous nature of the mix (Eirich mixer). The discharge of process waste water is usually limited to cooling water but most processes use a sealed cooling system. Rainwater run-off from surfaces and roofs may contain carbon dust and associated material. Open storage of raw materials and deposited solid emissions are the source of potential contamination. Typical values for processes associated with primary aluminium production for this contamination are <0.03 kg/tonne for suspended solids and <0.02 kg/tonne for dissolved fluoride [ 97, Lijftogt, J.A. et al 1998 ]. Best practice is to use vacuum systems for material transfer and closed silos for storage. Contamination of run-off is therefore reduced. *(These figures are not helpful because they can barely be associated to a concentration in the waste water. )*

Indirect water systems can also be used to cool the flue-gases, to make them suitable for abatement with regular techniques (fabric filters, electrostatic precipitators) [ 97, Lijftogt, J.A. et al 1998 ].

#### 4.2.2.2.3 By-products, process residues and waste

The production of carbon and graphite is related to the generation of several by-products, residues and wastes, which are also listed in the European Waste Catalogue (Council Decision 2001/118/EEC).

Refractory bricks from the baking furnaces. These bricks can be re-used in other applications after cleaning or can be disposed of as waste. Typical furnace lining life for prebaked anodes is about 100 cycles and this represents approximately 10 kilograms of bricks per tonne of anode produced.

Other residues include the material removed during the forming process together with tar or pitch fractions. Depending on the material, they are usually suitable for recycling within the process as raw materials or in other processes as fuel or carburant.

### 4.2.3 Primary aluminium

Besides $CO_2$, which is inherently linked to the process, there are emissions to the pot cell air of HF and particulate fluorides, $SO_2$, dust, and CO. The latter are emitted constantly inside the cell, while PFCs and PAH can occur be emitted intermittently, depending on the state of the process [ 6, McLellan and Partners Ltd 1993 ], [ 97, Lijftogt, J.A. et al 1998 ] [ 312, VDI 2286 Aluminium Part 1 and 2 2008 ]. Input and output from primary aluminium production is shown in Figure 4.10.

There are emissions of dust, $SO_2$, fluorides and PAH from wet scrubbers and potential emissions from storm water run-off. *(Where comes this extension from? What does is mean potential emissions from storm water run-off??)*

The main sources of waste are spent pot lining materials (SPL).

PAH emitted to water should be reported as the six compounds in the Borneff list and those emitted to air as the 16 PAH reported in the EU protocol [ 28, OSPARCOM 1997 ], [ 125, Euro Alliages (B) 1998 ].

The use of anode butts from the production of aluminium as part of the raw material input to this process contributes fluorides. *(I thought that the fluoride from the anode butts leads to HF emissions in the anode production process (see 4.2.2.2.6) and the HF from the electrolysis results from the residual hydrocarbons on the anodes and trace water in the alumina and air humidity reacting with the fluoride bath.)*

*The following Table 1 from VDI 2286 part 1 [357] should be introduced inparticular to give the specific off gas flows from the cell operation and from the pot room ventilation. Roof emissions can be up to 90% of the total emissions. This Table shows the raw gas concentration of different pollutants.*
*Introduce also from the Canadian report[303] the measured dust values (emission factors) and calculate the emissions concentrations. What can be seen is that the emissions cancentration for the cell room only, is often higher than 5 mg dust/Nm3.*

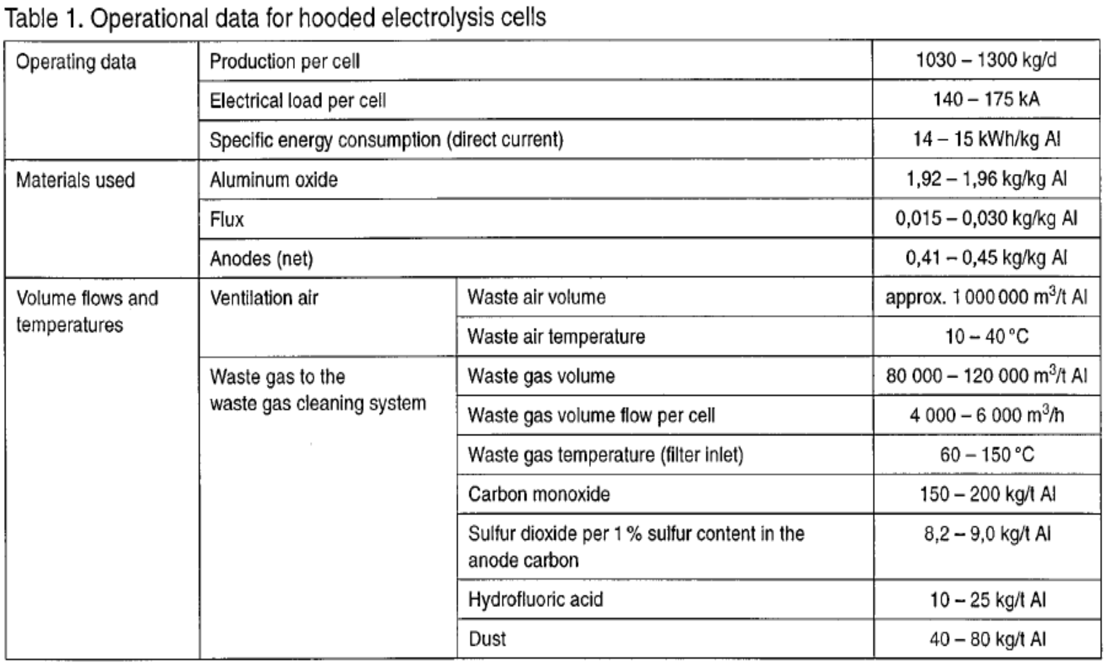


Table 1. Operational data for hooded electrolysis cells

| | | | |
|---|---|---|---|
| Operating data | Production per cell | | 1030 – 1300 kg/d |
| | Electrical load per cell | | 140 – 175 kA |
| | Specific energy consumption (direct current) | | 14 – 15 kWh/kg Al |
| Materials used | Aluminum oxide | | 1,92 – 1,96 kg/kg Al |
| | Flux | | 0,015 – 0,030 kg/kg Al |
| | Anodes (net) | | 0,41 – 0,45 kg/kg Al |
| Volume flows and temperatures | Ventilation air | Waste air volume | approx. 1 000 000 m³/t Al |
| | | Waste air temperature | 10 – 40 °C |
| | Waste gas to the waste gas cleaning system | Waste gas volume | 80 000 – 120 000 m³/t Al |
| | | Waste gas volume flow per cell | 4 000 – 6 000 m³/h |
| | | Waste gas temperature (filter inlet) | 60 – 150 °C |
| | | Carbon monoxide | 150 – 200 kg/t Al |
| | | Sulfur dioxide per 1 % sulfur content in the anode carbon | 8,2 – 9,0 kg/t Al |
| | | Hydrofluoric acid | 10 – 25 kg/t Al |
| | | Dust | 40 – 80 kg/t Al |

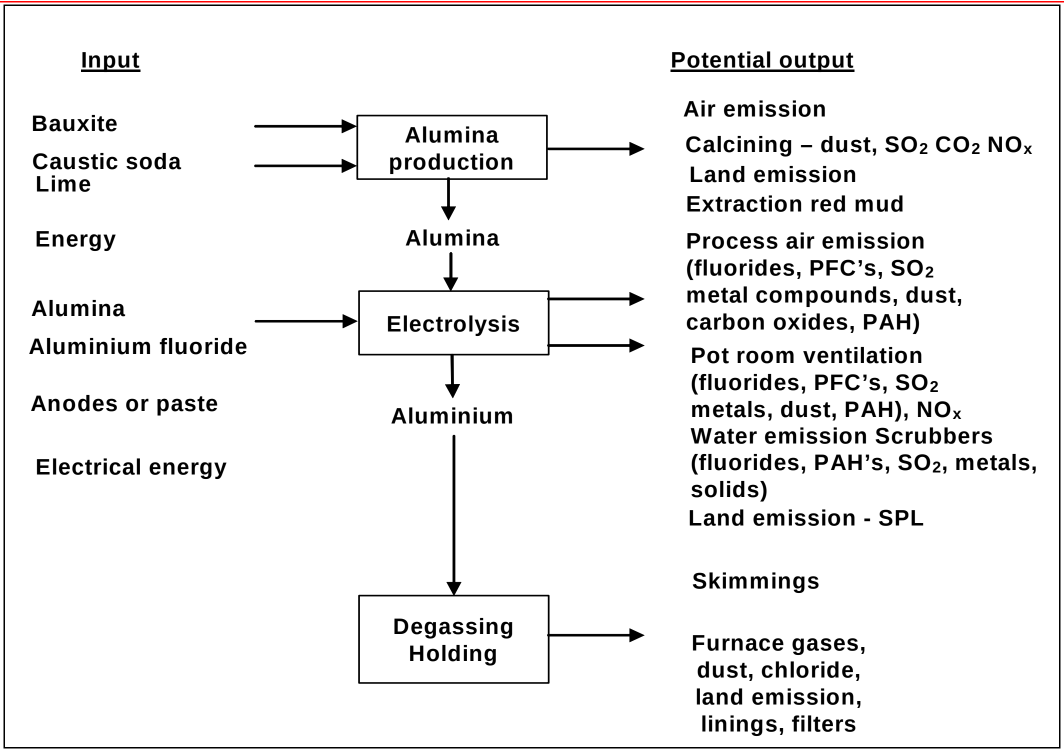


**Figure 4.10: Input and output from primary aluminium production**

[ 272, Al input 2008 ]

*(Land emissions?) Crosscheck with figure 4.11. There these are called waste!CO2 and CO is missing, crosscheck with UBA report*

#### 4.2.3.1 Energy and other inputs

*(In the tables 4.8 and 4.9 many other inputs are included. Modify the heading or relocate the tables to a more appropriate place to increase tracability.) Shift the whole section to the end of 4.2.3 to keep the order air-water-waste-energy)*

The reduction of energy demand is mainly influenced by using tube digesters, which are able to operate at higher temperatures using a fused-salt heat-transfer medium and the use of fluidised bed calciners. These plants have an energy consumption of well below 10 GJ per tonne of alumina produced.

The aluminium electrolysis stage has a high energy use ranging from 53 GJ per tonne for the best operated CWPB cells (including anode production) to 61 GJ per tonne for some traditional Søderberg cells. Input ranges for electrolysis and energy consumption are shown in Table 4.8. The energy costs are also high and can account for up to 40 % of production costs. Energy requirements are also influenced by cell geometry, bus bar configuration and other factors influencing magnetic upheaval of the liquid metal pad.

| Parameter | Prebake | Søderberg |
|---|---|---|
| Alumina - kg/t Al | 1900 - 1930 | 1900 - 1930 |
| Anodes nett - kg/t Al | 390 - 440 | |
| Anode Paste - kg/t Al | | 470 - 530 |
| Al $F_3$ - kg/t Al | 13 - 30 | 18 - 25 |
| Cathode Life - years | 5 - 8 | 4 - 6 |
| Power for alumina production GJ/tonne AL | <10 | <10 |
| Power for electrolysis - kWh/kg Al | 12.9 - 15.5 | 14.5 - 17.0 |
| Total electrical power - kWh/kg Al ([1]) | 13.6 - 15.7 | 15.1 - 17.5 |
| ([1]) Including rectifier loss, pollution control and auxiliary consumption.<br>Energy data is produced based on the conventions used by the Industry.<br>Anode production accounts for 5500 MJ/t. | | |

**Table 4.8: Input ranges for electrolysis**
[ 272, Al input 2008 ] *Check German contribution [234], at least ad the reference here. It seems that all the data from Germany are within the above mentioned range.*

The production of aluminium from recycled metal uses down to 5 % of the energy of primary production [ 28, OSPARCOM 1997 ]. The consumption data for the casthouse are shown in Table 4.9

| Parameter | Range |
|---|---|
| Skimmings/dross produced - kg/t Al | 10 - 50 |
| Fluxes - kg/t Al | 0 - 1.5 |
| Gases – kg/t Al | 0 – 0.04 |
| Swarf, etc. - kg/t Al | 0 - 3 |
| Water - kg/t Al | 200 - 10000 |
| Homogenisation energy MJ/t Al | 500 - 1200 |
| Casthouse Energy - MJ/t Al | 300 - 2500 ([1]) |
| ([1]) Not including remelting of cold metal. | |

**Table 4.9: Casthouse consumption data**
[ 272, Al input 2008 ]

### 4.2.3.2 Emissions to air

There are five distinct sources of emissions to air within the process:

- gases from calcining and heating for the production of alumina
- process gases from anode baking
- process gases from electrolytic cells
- pot room ventilation
- degassing and casting.

The potential emissions from the electrolysis stage are:

- fluorides
- polyfluorocarbons (PFCs) in connection with anode effects

- tars and poly-aromatic hydrocarbons (PAH) in the case of Søderberg electrodes
- sulphur dioxide ($SO_2$) and other sulphur compounds
- dust
- metal compounds
- oxides of nitrogen ($NO_X$)
- carbon monoxide (CO)
- carbonyl sulphide (COS) which can account for up to 20 % of the sulphur output from a smelter
- carbon dioxide ($CO_2$).

The emissions that take place from the electrolytic cells and via the pot room ventilation are related to each other by the efficiency in which the flue-gases from the cells are captured [ 28, OSPARCOM 1997 ], [ 97, Lijftogt, J.A. et al 1998 ], [ 226, Nordic Report 2008 ] [ 357, VDI 2286 Part 1 1998 ]. The specific gas emission rate from the electrolytic cells due to the cell extraction system is reported to be 80000 to ~~100000~~ 120000 $Nm^3$ per tonne of aluminium [ 348, French input for Aluminium 2010 ].

#### 4.2.3.2.1 Capture of gases

Prebake cells can be either side worked prebake cells (SWPB) or centre worked prebaked cells (CWPB) depending on how the crust is broken and the alumina is added.

Side worked prebaked anode cells (SWPB) where alumina is fed into the cells after the crust is broken around the circumference. The gas collection hoods over the length of the cells have to be opened during this operation.

**a) Prebake cells**

In CWPB the alumina is fed after the crust is broken along the centreline or at selected points on the centreline of the cell. This latter is called point feeder prebake (PFPB) and can be considered as the most advanced technology now used in the majority of plants. These feeding methods can be carried out without opening the gas collection hoods. The cells are totally enclosed and have a fume extraction system. A typical value for CWPB or PFCB cells for the efficiency of capturing the flue-gases within the process air is 95 to >99 % depending on the design of the extraction system, the effectiveness of the cell covers and the arrangement of the extraction and filter systems. [ 357, VDI 2286 Part 1 1998 ]

Side worked prebaked anode cells (SWPB) where alumina is fed into the cells after the crust is broken around the circumference. The gas collection hoods over the length of the cells have to be opened during this operation. SWPB cells are usually partially enclosed and a capture efficiency of about 85 to 95 % is achieved. This is due to the poor hooding arrangements and the reliance on the frozen alumina layer to contain the gases. Some SWPB cells are fully hooded but need to be opened more frequently for alumina additions, anode change and maintenance. The SWPB cells are gradually being replaced by PFPB cells.

**b) Søderberg cells**

For conventional VSS Søderberg electrodes, the situation is similar to SWPB cells. The crust breaker and the alumina feeder are mounted on vehicles and the cells are only partly hooded. There is a low degree of automation and there are consequent problems with controlling accurate alumina feeding to the bath with this pot system.

During crust breaking and alumina feeding, emissions of air pollutants to the pot room atmosphere increase. The steel contact bolts (studs) that support the anodes and conduct the electricity must be pulled out at regular intervals and replaced in a higher position. During this operation, higher levels of PAH are emitted. The gas collection skirt surrounding the anode casing is connected to a simple gas burner leading to a gas exhaust tube. This burner aims to burn CO and hydrocarbons that are emitted [ 6, McLellan and Partners Ltd 1993 ].

Several improvements have been made to the conventional Søderberg electrode system. The objectives were to reduce anode effects and emissions from the pots to a level comparable with the total emission from prebaked pots, including anode baking. The main features are:

- automatic alumina point feeding and control of electrolysis
- improved coverage of the bath crust
- the use of dry paste with a lower pitch content
- improved burner for incineration of PAH and other hydrocarbons in pot exhaust gas
- complete hood coverage of the anode top, which is connected to a separate gas exhaust and dry alumina scrubber
- dry anode top in combination with stud hole paste and increased anode height depending on effectiveness.

These improvements result in a significant increase in the capture of gases [ 28, OSPARCOM 1997 ], [ 226, Nordic Report 2008 ]. The range that is encountered in improved Søderberg plants is up to 95 % capture efficiency based on the HF depending on the degree of modification. It also depends on the extent of evaporation of HF from the bath which cannot be captured [ 75, Nordheim, E. (EEA) 1998 ], [ 233, Farrell Nordic Mission 2008 ]. The HF concentration in the cell room atmosphere can be monitored continuously using an open path continuous monitoring system.

The pot room emissions from SWPB and Søderberg cells are therefore significant and these processes often have wet scrubbing systems such as seawater scrubbers to remove fluoride and PAH from pot room ventilation air. *(Check whether this is the case and try to find examples. Can PAH be abated by wet scrubbing with seawater???)* CWPB cells are inherently more efficient at capturing process gases but rely on good design, maintenance and operating procedures.

#### 4.2.3.2.2 Fluorides

*Throughout the whole section it should be accurately be distinguished between cell off-gas and cell room off-gas. Decide wheter to use 'cell' or 'pot'. Don't change this all the time.*

Airborne gaseous and solid fluorides are emitted from the pots during electrolysis. 50 to 80 % of the fluoride is gaseous HF, whilst the rest is solid fluorides (mainly aluminium fluoride and cryolite). HF is formed by reaction of aluminium fluoride and cryolite with hydrogen, introduced to the pot as fixed water in aluminium oxide, as residual hydrogen in anodes and as moisture in the air. As modern pots are often operated with a high stoichiometric excess of $AlF_3$ (12 - 13 %), the fluoride generation has increased over the years and fume capture has become more important [ 97, Lijftogt, J.A. et al 1998 ].

The total fluoride emissions from the pots varies between 20 and 40 kg fluoride per tonne aluminium. With a capture efficiency of >98 % and a cleaning efficiency of 99.8 to 99.9 % in the dry scrubbing installations, the stack emission can be 0.06 to 0.3 kg total fluoride per tonne aluminium. Alumina is used as the scrubbing medium. The alumina is normally collected in a fabric filter, and is then used directly in the electrolysis cells. The fluorides collected in the alumina form aluminium fluoride and sodium fluoride (after reaction with any sodium oxide present in the alumina) and contribute to the amount of cryolite in the cell bath. Several plants that operate alumina scrubbers produce excess cryolite from the reaction of fluorides with the sodium content of the alumina and this is sold as excess bath. This is not produced all of the time, as its formation depends on sodium contents in the alumina, which might change over time or when suppliers are changed [ 348, French input for Aluminium 2010 ].

Uncaptured emissions are discharged to the pot room atmosphere and emitted through the ventilation system. This can represent 0.4 - 0.8 kg *(of what?)* per tonne of aluminium giving a total fluoride emission in the range of 0.4 - 1.0 kg per tonne aluminium [ 28, OSPARCOM 1997 ]. *(How is this calculation be made: 0.4 – 0.8 → 0.4 – 1.0 kg total fluoride/t Al??)*

Most of the Søderberg plants operating in Scandinavia use wet scrubbers (using seawater or caustic soda) in addition to the dry scrubber to remove sulphur dioxide ($SO_2$) from the cell exhaust gases. [ 28, OSPARCOM 1997 ] [ 97, Lijftogt, J.A. et al 1998 ]. Some plants also use seawater scrubbers ~~for ventilation air~~ to remove fluorides, sulphur dioxide and dust from the pot room ventilation air ~~in addition to the dry scrubber to remove $SO_2$ and remaining PAH from the cell gases~~ but their use should assessed to consider potential cross-media effects.

Fluorides and chlorides are also emitted during the degassing and refining stages. The quantity and components of the emissions depend on the degassing and refining agents used.

#### 4.2.3.2.3 PFCs (polyfluorocarbons)

The PFCs, tetrafluoromethane ($CF_4$) and hexafluoroethane ($C_2F_6$) are formed during the anode effects. They are emitted in the ratio $CF_4$:$C_2F_6$ of approximately 10:1. They cannot be removed from the gas stream with existing technology once they are formed [ 28, OSPARCOM 1997 ].

An anode effect occurs when the alumina content of the electrolyte falls below 1 - 2 %. Consequently, instead of decomposing alumina, the cryolite bath is decomposed into metal and fluoride ions, the latter forming gaseous PFCs when reacting with the anode carbon. The amount of PFCs generated is therefore directly linked to the frequency and duration of anode effects. The gases form an electrically isolating layer below the anode. This isolating film stops the production of the metal and increases the cell voltage from 4 - 5 to 8 - 50 volts and causes the current to suddenly jump from a normal 4 - 5 volts to above 25 volts. The control of cell voltage and alumina additions is a major factor in controlling anode effects [ 6, McLellan and Partners Ltd 1993 ].

The PFC emission from modern plants can be minimised by using semi-continuous point feeding of alumina and improved process control. These plants can be operated with an anode effect frequency of <0.1 to 0.5 per pot per day, resulting in emissions ranging from 0.01 to 0.1 kg PFCs per tonne Al [ 75, Nordheim, E. (EEA) 1998 ] [ 97, Lijftogt, J.A. et al 1998 ]. Many older plants used anode effects as a control for bath alumina content and consequently PFC emissions can be much higher. The use of modern control systems and automatic point feeding of alumina in both Prebaked and Søderberg cells minimises the number and duration of anode effects [ 28, OSPARCOM 1997 ], [ 75, Nordheim, E. (EEA) 1998 ]. An automated anode effect killing system can also be used in conjunction with the control system for example, the use of anode height differential or compressed air.

In the late 1990s, considerable efforts to lower PFC emissions have been made by the European aluminium industry. Advanced process control measures have been implemented in order to control cell voltage and alumina content in the cell closely, and therefore avoid anode effects and limit the duration of any that do occur.

#### 4.2.3.2.4 Tar and PAH

The emissions of tar and PAH during electrolysis in prebake plants are negligible due to the fact that the anodes are baked in a separate operation. Very small amounts of tar and PAH may be emitted from a limited number of prebake plants using carbon paste for anode pin connection and for protection collars. Measurements at startup of new cells and from plants using collar paste indicate that emissions are negligible [ 97, Lijftogt, J.A. et al 1998 ].

Installations that include an anode production plant will have a source of tars and PAH from this part of the process. There are examples where the process gases from an anode plant share the same alumina scrubber and fabric filter as the electrolysis process. The results from these plants show no difference in performance of the abatement plant when anode process gases are included. It can be concluded that the alumina scrubber is efficient at removing PAH and tars from an anode plant or from Søderberg cells. Spent alumina from the scrubbers is used as feed to the cells (but not for covering the bath). ESPs are also used to remove tar (see Chapter 12). Wet scrubbers for the ventilation gases will also remove some PAH, particularly the dust fraction.

| Component | Raw gas content (kg/t aluminium(1)) | Remarks |
|---|---|---|
| Fluorides (gaseous) | 0.05 - 0.6 | Emission of solid fluoride is usually negligible |
| PAH<br>Hydrocarbons | 0.15 - 0.5<br>25 - 40 | Estimated value based on a weight loss of about 5 % during baking |
| Dust | 5 - 10 | Estimated value |
| For a process associated with primary aluminium production. Raw gas masses of various pollutants. Captured emissions are treated in the alumina scrubber/fabric filter that is used for the electrolysis gases. | | |

**Table 4.10: Raw gas from anode production in a plant associated with a primary aluminium smelter**
[ 272, Al input 2008 ]

At Søderberg plants, tar and PAH are emitted during the electrolysis due to the self-baking anode. Emissions occur by evaporation from the carbonisation of the paste. Stud pulling is the operation giving the most significant emissions. Emissions depend on the anode design, the paste quality, and the operating practises. Generally, the use of dry scrubbers removes tar and PAH effectively from the pot gases [ 28, OSPARCOM 1997 ], [ 75, Nordheim, E. (EEA) 1998 ]. The use of dry anode paste and colder anode tops help to reduce the PAH emissions from the anode.

#### 4.2.3.2.5 Sulphur dioxide and sulphur compounds

*What about sulphur in the alumina. Check reference [503]. $SO_3$ in the alumina can account for up to 15 % of the $SO_2$ emissions. Check email from Island, 11.8.2010.*

The anodes used have a sulphur content ranging from 1 to over 3.5 %. The sulphur is emitted as carbonyl sulphide (COS) which reacts with oxygen resulting in the emissions of sulphur dioxide and carbon monoxide. Due to the differences in the sulphur content of the anodes, the emission of sulphur dioxide can range from about 8 to over 30 kg per tonne Al, based on an anode consumption of 0.43 tonne per tonne Al. For COS it has been reported that ~ 10 - 20 % of sulphur in the anode is formed into carbonyl sulphide equivalent to 2 kg/t of Al for anodes that contain 2.5 % S [ 348, French input for Aluminium 2010 ].

The emissions of $SO_2$ via the pot room ventilation will range from 0.2 to 0.6 kg per tonne (concentration: 0.1 to 3 mg/Nm$^3$). The emissions via the process air from the cells have a typical concentration ranging from 50 to 400 mg/Nm$^3$ [ 28, OSPARCOM 1997 ] [ 97, Lijftogt, J.A. et al 1998 ]. Where the process gas is wet scrubbed, the concentration range in the emissions to air will typically be 5 - 40 mg/Nm$^3$. Cross-media effects must be considered on a case by case basis if seawater scrubbers are used.

It has been reported that sulphur in the anodes may have a beneficial effect in suppressing the adverse effects of sodium contained in the anode butts for recycling [ 75, Nordheim, E. (EEA) 1998 ], [ 88, Nordheim, E. 1998 ].

European cokes, while being of consistent quality and good density, have the disadvantage that anodes made exclusively from these cokes have a shorter life and may cause smelter operational problems through excessive reaction with carbon dioxide, a phenomenon called dusting. In a modern computer controlled smelter where stable operation and maximum power and cost efficiencies are the norm, this is unacceptable.

Low sulphur cokes from Latin America and China show the same phenomena and are also low in density. The $CO_2$ reactivity is suppressed by the presence of sulphur in increased quantities, so it is judged desirable and beneficial to blend European calcined petroleum coke with higher sulphur calcined coke from US.

This is a recognised and commonplace practice in European smelters, and limits the lower level of sulphur content of anodes used in Europe. Meanwhile some smelters are testing calcined pitch coke in combination with calcined petroleum cokes which increase density and lower the sulphur content. The high sulphur value reduces dusting, so for some, this coke is considered preferable to all others. However, because of the higher sulphur content, US West Coast coke has not made major inroads into European markets. ~~[ 272, Al input 2008 ].~~
*Do we need the last 3 highlighted paragraphs. Where are they from?Could not find this in [272]*

### 4.2.3.2.6 Dust

Alumina and cryolite are the principal dusts emitted during electrolysis. Alumina that is used to remove fluorides from the exhaust gases is called secondary alumina and is also emitted if the dust collection system is not efficient. This secondary alumina will contain some HF adsorbed on the surface.

Total dust generation varies and depends on the type of process applied and the type of alumina, but ranges from 0.6 to 10 kg per tonne Al. Typical dust concentrations for pot room ventilation are 0.5 to 5 mg/Nm$^3$ whereas the dust concentration in the process air ranges from 150 to 500 mg/Nm$^3$ before abatement and from 1 to 20 mg/Nm$^3$ after abatement [ 97, Lijftogt, J.A. et al 1998 ].

Casting is another source of dust (and metals) and casthouse fumes are usually collected and treated in a fabric filter. Some studies have been carried on the presence of PCDD/F in fumes from the casting process as the use of chlorine for degassing and the presence of carbon from combustion gases may lead to their formation. All measurements from primary smelter casthouses show levels significantly below 1 g/year ~~[ 312, VDI 2286 Aluminium Part 1 and 2 2008 ].~~ *(This information is not from these references)*

### 4.2.3.2.7 Metals

Metals are known to occur in trace concentrations in alumina and aluminium fluoride and can therefore be emitted during electrolysis. Tellurium is extracted from alumina produced at one installation and is therefore a potential contaminant. Other volatile metals are also present and can be emitted from the pot room and the casthouse. A limited amount of information is available about the environmental impact but trace metals are not considered to be a significant release [ 97, Lijftogt, J.A. et al 1998 ].

### 4.2.3.2.8 Oxides of nitrogen

Oxides of nitrogen ($NO_X$) are produced during electrolysis due to the presence of nitrogen in the anode, which can be oxidised to $NO_X$. The nitrogen content in the anodes generally ranges from 0.2 to 0.4 %. When the nitrogen is completely converted into $NO_X$, the emission may be 0.5 to 2 kg $NO_2$ per tonne Al (concentrations of 5 to 20 mg/Nm$^3$ in the stack). The actual amount of $NO_X$ released is still subject to discussion. Control measurements at two prebake plants in Norway showed emission levels of 0.1 to 0.2 kg $NO_2$ per tonne Al [ 97, Lijftogt, J.A. et al 1998 ]. The combustion gases from the burners used in holding and melting furnaces in the casthouse will contain oxides of nitrogen.

### 4.2.3.2.9 Carbon monoxide

Carbon monoxide (CO) is produced during electrolysis by the back reaction of aluminium metal dissolved in the electrolyte with the $CO_2$ produced at the anode (2 Al + 3 $CO_2$ -->$Al_2O_3$ + 3 CO), this lowers the cell efficiency. In a modern smelter, the generation of CO before any re-oxidation to $CO_2$ is in the order of 100 to 150 kg per tonne Al. The production of CO also increases during an anode effect [ 6, McLellan and Partners Ltd 1993 ], [ 97, Lijftogt, J.A. et al 1998 ].

### 4.2.3.2.10 Carbon dioxide

Carbon dioxide ($CO_2$) is formed during electrolysis by the reaction of the carbon anode with the oxygen formed by electrolysis and by a secondary reaction with air. An efficient prebake plant consumes about 0.4 tonnes of carbon anodes per tonne aluminium, corresponding to 1.4 to 1.7 *(in the table below is stated 1.6 to 1.7)* tonnes of $CO_2$ per tonne aluminium. These emissions are however far lower than the emissions of $CO_2$ by combustion of fossil fuels when used for the generation of the electrical power required for electrolysis [ 75, Nordheim, E. (EEA) 1998 ]. Carbon dioxide is also emitted from burners used in the holding and melting furnaces.

### 4.2.3.2.11 Summary of main air pollutants

A summary of the relevance of the main air pollutants and their emission sources, as discussed above and based on literature findings, is given in Table 4.11 and Table 4.12.

| Component | Flue-gases from electrolysis cells | Pot room ventilation | Degassing and holding |
|---|---|---|---|
| Fluorides gaseous and total F | • | ••• | •<br>(chlorides) |
| PFCs | ••• | • | |
| Tars and PAH ($^2$) | • | •• | |
| $SO_2$ (without scrubbers)($^1$) and COS | ••($^1$) | | • |
| Carbon dioxide | •• | | |
| Dust | • | • | |

($^1$)Wet scrubbers are generally used after dry scrubbing in Scandinavia to remove $SO_2$ and are usually associated with the use of seawater as the scrubbing medium.

($^2$)Tars and PAH are relevant to Søderberg processes and prebake processes that have an integrated electrode production process. They can also be relevant for the small number of plants using paste for anode pin connection protection collars.

••• More significant – • less significant

**Table 4.11: Significance of potential emissions from primary aluminium**

| Parameter | Pre bake | Modified Søderberg | Vertical stud |
|---|---|---|---|
| HF kg/t Al | 0.15 - 1.0 | 0.4 - 1.6 | 0.2($^1$) - 1.7 |
| HF kg/t Al if wet scrubbing is used | | 0.15 - 0.25 | |
| Total fluoride kg/t Al | 0.25 - 1.5 | 0.5 - 1.5 | |
| Total fluoride kg/t Al if wet scrubbing is used | | 0.30 - 0.5 | 0.5($^1$) - 3.0 |
| Dust kg/t Al | 0.5 - 3.0 | 0.9 - 4.0 | |
| Dust kg/t Al if wet scrubbing is used | | 0.8 - 1.2 | 1.0 - 8.0 |
| $SO_2$ kg/t Al | 10 - 30 | 10 - 30 | 10 - 30 |
| $SO_2$ kg/t Al if wet scrubbing is used | 0.88 - 3.5 | 0.8 - 1.5 | 1.0 - 3.5 |
| $CF_4/C_2F_6$ kg/t Al | 0.01 - 0.38 | <0.05 calculated | 0.05 - 0.5 |
| Carbon dioxide t/t Al | 1.~~6~~4 - 1.7 | 1.6 - 1.9 | 1.6 - 1.9 |
| BaP g/t Al | - | 5 - 15 | |
| BaP g/t Al if wet scrubbing is used | | 5 - 8 | 5 - 25 |

($^1$) With wet scrubbing for ventilation. *(Unclear: If wet scrubbing is used only for the lower range of vertical stud it should not appear in the right column)*

**Table 4.12: Total air emissions from primary aluminium smelters**

[ 25, OSPARCOM 1996 ] [ 272, Al input 2008 ]
*The data for CF4/C2F6 can not be confirmed by [501] which is the IAI survey about anode effects. There the Soederberg plants have much higher values for CF4/C2F6.*
*Try to get real measured data.*
*Check German contribution [234], at least ad the reference here. It seems that all the data from Germany are within the above mentioned range.*

The relevance of the uncontrolled emissions by the pot room ventilation is based on 98 % fume capture from the cells. Regular CWPB cells can achieve this efficiency but when a lower efficiency is achieved, for example in SWPB or Søderberg cells, the relevance of the pot room ventilation increases [ 75, Nordheim, E. (EEA) 1998 ], [ 97, Lijftogt, J.A. et al 1998 ].

Gases emitted from the casthouse in primary smelters have been calculated and are shown in Table 4.13 [ 28, OSPARCOM 1997 ]. The calculation was based on the concentration of the components in the cell gases and the capture efficiency of the hood and extraction system. This calculation is relevant in establishing the significance of uncaptured emissions but draws the same conclusion as the importance of the efficiency of the fume capture system and this factor is deemed to the most relevant for this work. Most smelters will also have a regular monitoring of this.

| Parameter | Emission kg/tonne of Al |
|---|---|
| Dust | 0.01 - 0.1(1), (2) |
| $NO_X$ | <0.1 - 0.4 |
| $SO_2$ | 0 - 1.8(2) |
| (1)Depending on filter system.<br>(2) Depending on fuel used. | |

**Table 4.13: Primary aluminium casthouse - emissions to air**
[ 272, Al input 2008 ]

Table 4.14 and Table 4.15 show the untreated and treated mass emissions from anode production when it is associated with a primary aluminium smelter.

| Component | Raw gas content (kg/t aluminium(1)) | Remarks |
|---|---|---|
| Fluorides (gaseous) | 0.05 - 0.6 | Emission of solid fluoride is usually negligible |
| PAH<br>Hydrocarbons | 0.15 - 0.5<br>25 - 40 | Estimated value based on a weight loss of about 5 % during baking |
| Dust | 5 - 10 | Estimated value |
| NB: For a process associated with primary aluminium production. Raw gas masses of various pollutants. Captured emissions are treated in the alumina scrubber/fabric filter that is used for the electrolysis gases. | | |

**Table 4.14: Raw gas from anode production in a plant associated with a primary aluminium smelter**
~~[ 272, Al input 2008 ]~~*This is from the old BREF and not from [272]*

| Component | Typical range per tonne of aluminium |
|---|---|
| Fluoride kg/t | 0.01 - 0.1 |
| Dust kg/t | 0.01 - 1.0 |
| BaP g/t | 0.0015 - 3.0 |
| $SO_2$ kg/t | 0.02 - 6.0 |
| $NO_X$ kg/t | 0.1 - 0.4 |

**Table 4.15: Mass emissions from the production of prebaked anodes**
*This is from the old BREF and not from [272]*
~~[ 272, Al input 2008 ]~~

#### 4.2.3.2.12 Greenhouse gases

The production of primary aluminium results in emissions of $CO_2$ as an inherent product of the electrolytic process (from carbon-based anodes) and from the combustion of fuel to produce alumina and the generation of electricity where this is based on fossil fuels ~~[ 312, VDI 2286 Aluminium Part 1 and 2 2008 ].~~ *This is from the old BREF and not from [312]*~~-~~In addition to this, polyfluorinated hydrocarbons (PFCs) like $CF_4$ and $C_2F_6$ are produced during the anode effect in the electrolysis cells. Both gases are powerful climate gases with 100 year global warming potentials of 6500 and 9200 respectively.

Calculations for European primary aluminium smelters show that the total quantity of PFC gases emitted, calculated as $CO_2$ equivalent emissions were about 15 million tonnes in 1990. Improvements in controlling the electrolysis process have significantly reduced the number of anode effects and the duration of the each anode effect. The PFC emissions have therefore been considerably reduced and calculations show that the $CO_2$ equivalent emission below 6 million tonnes in the year 2000 were achieved. *(This is outdated and should either be reviewed and updated ot deleted)*

Efficiency improvements in other parts of the process have also contributed to a reduction in direct $CO_2$ emissions, reducing the total emissions of climate gases. The specific PFC emissions from different technologies are given in Table 4.12. The improvements and further reductions are discussed under techniques to consider in the determination of BAT.

Work is still progressing at a pilot stage, to develop an inert anode material so that carbon dioxide would not be produced during electrolysis. The elimination of a carbon anode would also prevent the formation of PFCs ~~[ 303, Canadian Al Rapport final in French.pdf 2008 ].~~ *This is from the old BREF and not from [303]*

### 4.2.3.3 Emissions to water

The production of primary aluminium is inherently a dry process. The discharge of waste water is usually limited to cooling water, rainwater run-off from surfaces and roofs, and seawater scrubbers for pot room ventilation gases. The rainwater run-off can be contaminated by the open storage of raw materials and deposited solids. Typical values for this contamination are <0.03 kg/tonne Al for suspended solids and <0.02 kg/tonne Al for dissolved fluoride. In addition, considerable amounts of waste water can be discharged when wet systems are used for air pollution control [ 97, Lijftogt, J.A. et al 1998 ].

Anode production can account for a production of waste water consisting of cooling water used to cool the green anodes or the flue-gases. The cooling process can be performed using indirect water systems, resulting in a discharge of cooling water. Indirect water systems can also be used to cool the flue-gases, to make them suitable for abatement with regular techniques (fabric filters, electrostatic precipitators) [ 97, Lijftogt, J.A. et al 1998 ].

The production of alumina from bauxite operates on a closed system to eliminate water emissions. Water that is contained in the red mud or is used to transport it to the disposal site is highly alkaline and is pumped back to the plant and re-used [ 75, Nordheim, E. (EEA) 1998 ].

The electrolysis stage is a dry process and no waste water is produced directly. Rainwater contamination is prevented by the techniques outlined in Section 2.12.

Emissions to water from the primary aluminium electrolysis plants using ventilation air water scrubbers or $SO_2$ water scrubbers are shown in Table 4.16.

| Parameter | Preb~~-B~~aked | Søderber |
|---|---|---|

| | | g |
|---|---|---|
| Fluoride kg/t Al | 0.06 - 1.0 | 0.5 - 1.5 |
| Suspended solids kg/t Al | 0.1 - 0.5 | 0.5 - 2.0 |
| PAH (Boneff 6) g/t Al | | 6 - 15 |

**Table 4.16: Process emissions to water from the primary aluminium electrolysis plants using ventilation air water scrubbers or $SO_2$ water scrubbers**
[ 272, Al input 2008 ] *[0.06 is from another reference]*

### 4.2.3.4 By-products, process residues and waste

The production of metals is related to the generation of several by-products, residues and wastes, which are also listed in the European Waste Catalogue (Council Decision 94/3/EEC). *This has been replaced by a new directive 75/442/EEC (see Section 5.2.4)* The most important process-specific residues are described in Sections 4.2.3.4.1 to 4.2.3.4.3 below.

#### 4.2.3.4.1 Red mud

Red mud produced during the extraction of alumina from bauxite is a significant waste material and has a major disposal requirement. The mud is generally alkaline from the extraction process and contains 3 to 12 kg of NaOH per tonne of alumina produced. It therefore requires careful handling. Current practice is to deposit red mud on or near the site in specially designed, sealed ponds. Excess water from the ponds is normally returned to the process ~~[ 295, Theben, S. 2004 ].~~ *This is from the old BREF and not from [295]*

A salt that contains vanadium may also be produced during the removal of impurities from the liquor produced during digestion. This salt is a major source of other metals such as vanadium and tellurium.

#### 4.2.3.4.2 Spent pot lining

With a cathode lifetime of 5 - 8 years, which is common for modern plants, the quantity of spent pot lining (SPL) generated is 20 - 40 kg/t aluminium produced. The SPL normally consists of two distinct fractions plus steel which is recycled. The two wastes are the carbon part and the refractory material. The carbon part is the actual cathode from the electrolysis cell and the remainder is varying types of insulating material~~.~~ [ 272, Al input 2008 ].

The two fractions are often separated when dismantling the cathode. The spent cathode also contains some bath material, steel bars used to conduct electricity to the carbon cathode, and often flakes of aluminium metal from metal penetration into the cathode. These parts are either re-used directly at the plant or, in the case of steel bars, sent outside the plant for recycling. The carbon part is relatively homogeneous, while the refractory part can be composed of a number of different types of refractory materials or other types of insulation ~~[ 272, Al input 2008 ]~~.

Table 4.17 gives a typical analysis of SPL.

| **Compound** | **Carbon lining (1st cut)** | **Insulation (2nd cut)** |
|---|---|---|
| | **Range wt-%** | |
| $A1_2O_3$ | 0 - 10 | 10 - 50 |
| C | 40 - 75 | 0 - 20 |
| Na | 8 - 17 | 6 - 14 |
| F | 10 - 20 | 4 - 10 |
| CaO | 1 - 6 | 1 - 8 |
| $SiO_2$ | 0 - 6 | 10 - 50 |

| | | |
|---|---|---|
| Metallic A1 | 0 - 5 | 0 |
| CN total | 0.01 - 0.5 | 0 - 0.1 |
| CN free | 0 - 0.2 | 0 - 0.05 |
| Others | | |

**Table 4.17: Composition of spent pot lining**
[ 131, Nordheim 1998 ]

The problem constituents linked to this material are soluble fluoride and soluble cyanide. In addition, any wetting of this material will produce an alkaline leachate and liberate minor quantities of $NH_3$ and flammable gases. PAH is not considered to be a problem since the carbon lining has already been carbonised at temperatures above 1250 °C and any ramming paste has been heated to above 900 °C in the electrolytic cell. The problem constituents mentioned are mainly linked to the carbon part of the SPL and the refractory parts in immediate contact with this. As can be seen from Table 4.17, the content of these constituents is lower in the refractory part.

SPL can be re-used, treated, partially treated or disposed of [ 131, Nordheim 1998 ].

**Re-use**
The preferred recovery route for most European smelters is one of the following:

- re-use in the cement, ceramics or brick industries
- re-use as a fuel
- re-use as a carburiser (steel industry).

**Treatment processes**

- Comalco Comtor process
- Alcan low caustic leaching and liming (LCLL)
- Ausmelt/ISA Smelt furnace
- Elkem ferro alloy process [ 226, Nordic Report 2008 ].

**Disposal**
Pretreat followed by disposal in a disposal site that is compliant with EC Directive 1999/31/EC.

#### 4.2.3.4.3 Other materials

*Inappropriate heading. SPL is included in the previous section thus it should not be included here again.*

Skimmings or dross from the holding and treatment processes represent 15 to 30 kg per tonne of aluminium produced. This material contains 30 to 80 % aluminium and cooling under an inert gas blanket prevents oxidation. Skimmings and dross are used as a raw material in the secondary aluminium industry. Spent filters from metal treatment are usually disposed of. Solid wastes produced by gas-cleaning installations (dust and sludge) can be re-used [ 75, Nordheim, E. (EEA) 1998 ].

Anode butts from some plants are also disposed of if they fail to meet quality standards. If there is no anode plant on site, anode butts can be used in the steel industry as a coke substitute therefore lowering primary coke demand. Furnace linings from the casting process and anode baking process may be recovered or disposed of.

Good waste management practice and the use of recovery methods makes it possible to reduce waste for disposal. Options and quantities are shown in Table 4.18 and Table 4.19.

| Source | Use/treatment options |
|---|---|
| Aluminium | Recovery |

| | |
|---|---|
| Filter dust | Re-use in process |
| SPL | Carburant, flux and furnace linings, cement industry |
| Bricks | From anode furnaces, re-use |
| Steel | Recovery |
| Carbon dust (anode plant) | Re-use |

**Table 4.18: Options to reduce waste for a primary aluminium smelter**
[ 272, Al input 2008 ]

| Source | kg per tonne Al |
|---|---|
| Al skimmings or dross | 15 - 30 |
| SPL | 20 - 40 |
| Other hazardous waste | 7 - 15 |
| Non-hazardous waste | 12 - 14 |
| Provided no external scrap is melted | |

**Table 4.19: Specific waste quantities from primary aluminium production**
[ 272, Al input 2008 ]

Steel from the anode plant is normally remelted in an induction furnace and recast for use in the process. The melting of steel that is contaminated with fluorides is a further potential source of these emissions and appropriate collection and abatement is required.

## 4.2.4 Secondary aluminium

There are potential emissions to air of dust, metal compounds, $Cl_2$, HCl, $NO_X$, $SO_2$ and HF and products of poor combustion such as PCDD/F and other organic compounds from the melting and treatment furnaces. The formation of PCDD/F in the combustion zone and in the cooling part of the off-gas treatment system (de novo synthesis) may be possible. The emissions can escape the process either as stack emissions or as diffuse emissions depending on the age of the plant and the technology used. Stack emissions are normally[rr33] monitored continuously or periodically and reported by on-site staff or off-site consultants to the competent authorities [ 312, VDI 2286 Aluminium Part 1 and 2 2008 ].

*(VDI 2286 Part one is not for secondary aluminium. Delete!)*

Input and output from secondary aluminium production is shown in Figure 4.11. Organic compounds such as VOC and PCDD/F can be associated with dust.

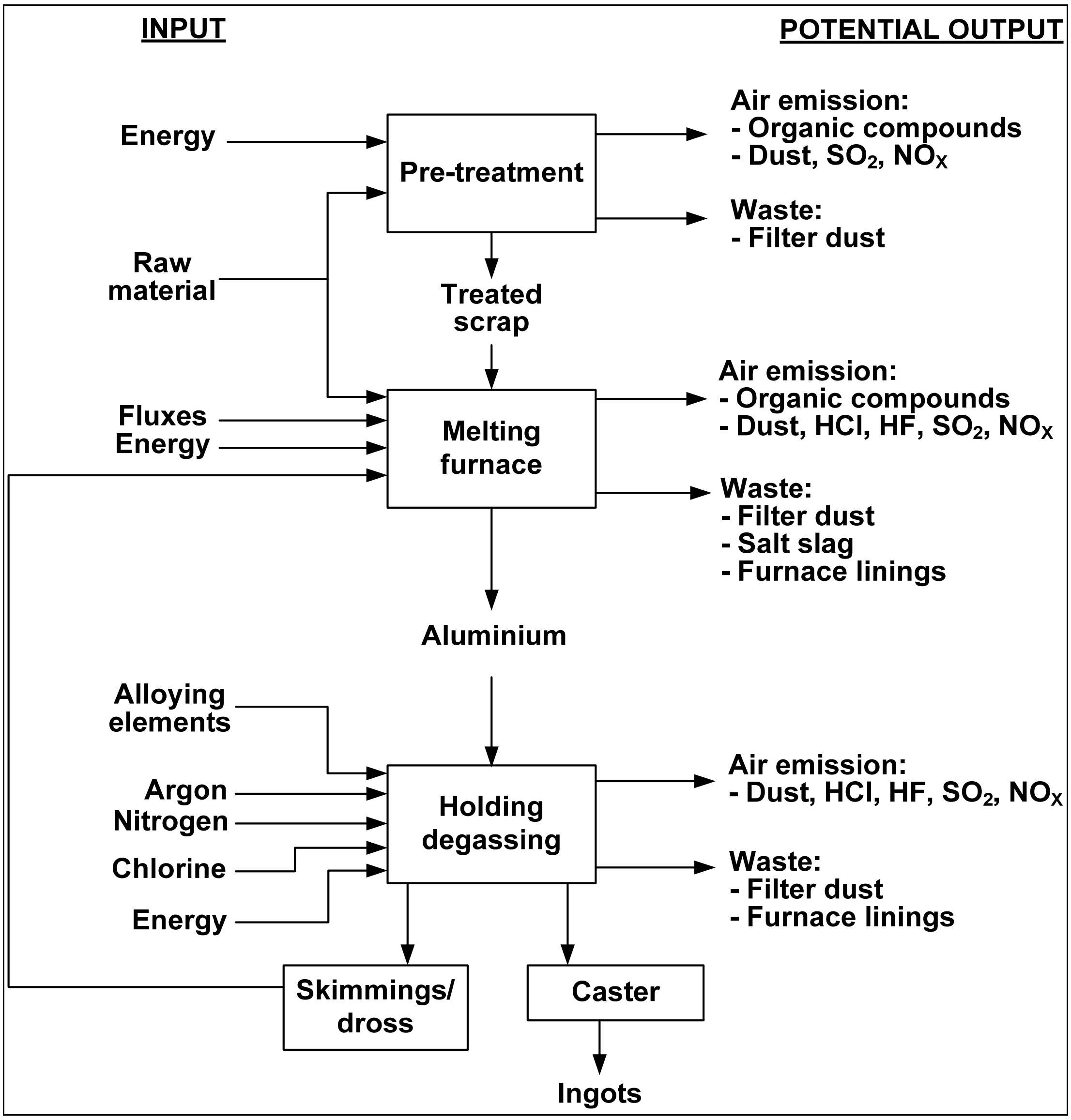


**Figure 4.11: Input and output from secondary aluminium production**

[ 272, Al input 2008 ] *There are some outputs missing. Better say 'Melt treatment'than 'Holding degassing'. Melt treatment includes holding and degassing. See new figure in new AL folder. See also Table 4.22 which gives further information which pollutants arise at what stage.*

Ammonia and other gases can be emitted from the reaction with humidity in the air, improper storage, treatment and transport of skimmings or dross [ 32, Mantle et al. 1998 ]. Dust will also arise from the handling and treatment of the skimmings or dross. There are potential emissions to water of suspended solids, metals and oils from the improper product and material storage.

The type and quality of scrap has a major influence on the significance of the emissions. This is discussed in detail in the section dealing with techniques to consider [ 312, VDI 2286 Aluminium Part 1 and 2 2008 ]. *(VDI 2286 Part one is not for secondary aluminium. Delete!)*

There are potential sources of emissions from the pretreatment, melting, degassing and holding stages.

Pretreatment processes are covered in Section 2.7, the secondary aluminium industry mainly uses swarf drying and thermal de-coating to pretreat scrap and millings and other mechanical process and concentration methods for skimmings or dross and salt slags. Some examples of process data from different treatment processes are shown in Table 4.20, Table 4.21 and

Table 4.22 below. [ 256, Plant visit report AMAG 20071114.doc 2007 ], [ 234, UBA Copper, lead, zinc and aluminium 2007 ]

| **Operating parameters** | **Unit** | **Range of typical values and remarks** | | |
|---|---|---|---|---|
| Throughput | (t swarf/h) | 0.8 - 5 | | |
| Energy consumption | (MJ/t swarf) | 3500 - 5200 | | |
| Type of heating | - | Indirect as well as direct, fuel-heated | | |
| Type of fuel | - | Natural gas | | |
| Drying temperature | (°C) | <500 | | |
| Emission controls | - | Thermal afterburning, sorption stage, fabric filters | | |
| Afterburning temperature | (°C) | >700 | | |
| **Emission data(1)** | **-** | **Raw gas** | **Clean gas** | |
| | | **Concentration** | **Concentration** | **Emission factor** |
| Dust | (mg/$Nm^3$) | 1500 | 1 - 10 | 0.03 kg/t |
| $SO_2$ | (mg/$Nm^3$) | - | <100 | |
| $NO_X$ | (mg/$Nm^3$) | - | 69 - 350 | 0.17 kg/t |
| CO | (mg/$Nm^3$) | | 3 – 97 | 0.06 kg/t |
| Total C | (mg/$Nm^3$) | - | <0.3 - 50 | 0.02 kg/t |
| PCDD/F | (ng ITEQ/$Nm^3$) | - | <0.1 - 0.5 | |
| (1) Half-hourly averages. | | | | |

**Table 4.20: Plant and process data for a swarf dryer**
[ 234, UBA Copper, lead, zinc and aluminium 2007 ] *(This table is from VDI 2286 Part 2, page 12)*

| **Operating parameters** | **Unit** | **Range of typical values and remarks** |
|---|---|---|
| Purpose | | Washing off oil and emulsion adhering to Al swarf |
| Throughput | t swarf/h | 1 - 4 |
| Specific energy requirement | MJ/t swarf | 400 - 600 |
| Wash solution temperature | °C | 60 - 90 |
| Wash solution | | Recirculation |
| Drying temperature | °C | Approximately 120 |
| Waste gas rate | $Nm^3$/t swarf | 250 - 350 |
| Emission control | | Dust filter with direct dryer heating |
| **Emission data(1)** | | |
| Dust | mg/$Nm^3$ | <5 - 20 |
| $SO_2$ | g/$Nm^3$ | 0.35 |
| $NO_X$ | g/$Nm^3$ | 0.35 |
| Total C | mg/$Nm^3$ | <10 - 50 |
| **Residues** | | |
| Sludge | kg/t swarf | approximately 2 - 5 |
| Al grease | kg/t swarf | approximately 2 - 5 |
| (1) Half-hourly averages (clean gas). | | |

**Table 4.21: Performance data for a swarf washing process**
[ 234, UBA Copper, lead, zinc and aluminium 2007 ] *(This table is from VDI 2286 Part 2, page 11)*

| **Operating parameters** | **Unit** | **Range of typical values** |
|---|---|---|
| Screening unit throughput | t dross/h | approximately 10 |
| Ball mill throughput | t dross/h | approximately 2.5 |
| Fractions:<br>Lumps >60 mm | <br>% | Share (average values)<br>13 |

| | | |
|---|---|---|
| Oversize 1 >10 mm - 60 mm | % | 11 |
| Oversize 2 >0.5 mm - 10 mm | % | 58 |
| Remainder (dead material, ball mill, screen and filter dust) | % | 18 |
| **Emission data(1)** | | |
| Waste gas temperature | °C | Room temperature |
| Waste gas rate | $m^3$/t dross | approximately 12000 |
| Dust | mg/$Nm^3$ | <10 mg/$Nm^3$ |
| (1) Half-hourly averages | | |

**Table 4.22: Example of plant and process data from mechanical processing of dross**
[ 234, UBA Copper, lead, zinc and aluminium 2007 ]
*(This table is from VDI 2286 Part 2, page 9)*

The production of aluminium from recycled metal uses as low as 5 % of the energy of primary production. The metals are first sorted into cast alloys and wrought alloys. The choice of suitable treatment processes, the furnace types themselves and the other necessary process steps (holding, alloying, melt treatment) depend primarily on the type and composition of the raw materials employed and on the demanded product quality. Direct comparisons between the performances of different smelters, for instance, are not helpful, as the processes are optimised for their specific application. However, industrial experience has yielded typical fields of application that permit the practical selection of smelters for the specific application. Typical process steps include heating-up, charging, smelting[rr34], skimming, holding, treating the molten metal and casting. As a result, the process parameters of relevance to the emissions of a plant (e.g. waste gas temperature, raw gas contamination) are subject to strong fluctuations. The comparability of data is also hampered by different measuring locations.

Salt slags arise when mixtures of sodium and potassium chloride are used to cover the molten metal to prevent oxidation, increase yield and increase thermal efficiency. These slags are generally produced in rotary furnaces and have an adverse environmental impact if they are deposited on land. The quantity of salt slag produced varies considerably and is dependent on the type of material, the furnace and the degree of contamination of the aluminium, etc. There are options available for salt-free melting in some furnaces using many types of feed materials and there are options for recycling all of the components of salt slag [ 312, VDI 2286 Aluminium Part 1 and 2 2008 ].

The range of the typical plant, process and emission parameters (raw gas) of aluminium smelting plants is shown in Table 4.23 [ 312, VDI 2286 Aluminium 2008 ].

| Parameter | Unit | Rotary drum furnace | Tilting rotary furnace | Closed-well or Hearth furnaces | | | Shaft furnaces | Crucible furnaces (a) fuel-heated, (b) resistance-heated, (c) inductively heated | Channel induction furnace |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Single chamber | | Multiple-chamber, hearth furnace with melting bridge | | | |
| Preferred application | | Generation of secondary aluminium | Generation of secondary aluminium | Generation of secondary aluminium, foundries | | Generation of secondary aluminium | Moulding shops | Moulding shops | secondary aluminium |
| Purpose | | Melting | Melting | Melting | Holding, casting | Melting | Melting, holding | Melting (M), holding (H) | Melting (M), Holding (H) |
| Preferred feedstock | | New scrap (thin-walled, in small pieces), old scrap, dross | Old scraps, dross | Ingots, old scrap, new scrap | Molten metal | Thin-walled new/old scraps (painted/coated) | Ingots, new scraps, (recycled material) | Ingots, new scrap | Ingots, new scraps, old scraps |
| Preferred melt treatment | | Salt cover | Reduced salt cover compared to rotary drum | No salt cover, chlorination | | No salt cover | No salt cover | No salt cover | No salt cover, chlorination |
| Capacity | (t) | Up to 150 | Up to 30 | Up to 180 | | Up to 180 | 0.5 - 4 (possibly up to 15) | 0.1 - 0.6 (b),<br>0.5 - 6 (c),<br>0.1 - 1.2 (a) | Approximately 50 |
| Melting efficiency | (t feedstock/h) | Up to 20 | Up to 7 | Up to 30 | - | 3 - 28 | Up to 2.5 (typically 1.5) | 0.075 - 0.26 (b),<br>0.25 - 3 (c),<br>0.1 - 0.43 (a) | Approximately 7 (melting efficiency) |
| Preferred fuels | | Natural gas, LPG, light fuel oil, medium/heavy fuel oil | Natural gas, LPG, extra-light fuel oil | Natural gas, LPG, extra-light fuel oil | | Natural gas, LPG, extra-light fuel oil | Natural gas, LPG, extra-light fuel oil | Natural gas, LPG, extra-light fuel oil or electrically heated | Electrically heated |
| Energy use d) | (GJ/t metal) | 2 - 4.7 | 2 - 2.5 | 2.5 - 4.4 | No details | 2.4 - 4.3 | 2.1 - 3.3 (depending on the mode of operation) | 5.1 - 7.4 (M, a),<br>1.7 - 3.5 (H, a),<br>2.7/1.9 - 2.1 (M, b/c),<br>0.4/0.9 - 1.2 (H, b/c) | Approximately 3.6 (M/H) |
| Waste gas rate e) | ($m^3$/t metal) | 9000 - 18000, | 9000 - 13000, | 5000 - 13000 | No details | 10000 - 15000 | 2000 - 4000 | 2000 - 4000 (M, a) | Max. 14500 |
| Dust generation a) | | +++ | +++ | ++ | + | ++ | NR | NR | + |

| **Parameter** | **Unit** | **Rotary drum furnace** | **Tilting rotary furnace** | **Closed-well or Hearth furnaces** | | | **Shaft furnaces** | **Crucible furnaces (a) fuel-heated, (b) resistance-heated, (c) inductively heated** | **Channel induction furnace** |
|---|---|---|---|---|---|---|---|---|---|
| | | | | **Single chamber** | | **Multiple-chamber, hearth furnace with melting bridge** | | | |
| Nitrogen oxides [a, c]) | | + (Assuming optimised combustion conditions) or ++ (For fuel/oxygen-heated furnaces) | | | | | | NR | NR |
| Sulphur dioxides [a, c]) | | NR | | | | | | | |
| Chlorine [a, d]) | | ++ (Chlorination) | | | | | | | |
| Hydrogen chloride [a, d]) | | +++ | ++ | +, ++ (Chlorination) | +, ++ (Chlorination) | ++ | NR | ++ (Chlorination) | ++ (Chlorination) |
| Hydrogen fluoride [a]) | | +++ | ++ | + | + | + | NR | ++ | + |
| Total carbon [a, e]) | | ++ | ++ | + | + | + | NR | NR | NR |
| PCDD/F [a, b]) | | +++ | ++ | ++ | NR | + | NR | NR. | NR |

a) Relevance of process emissions: +++ high, ++ moderate, + low, NR Not Relevant (e.g. because of very low melting rate).
b) Primarily dependent on type and composition of feedstock.
c) Primarily dependent on firing (choice of fuel, flame control).
d) Primarily dependent on type and extent of melt treatment, inter alia dependent on such variables as metal yield, air preheating, plant capacity utilisation, etc.
e) Overall plant (sum of energy needs for treatment, smelting and holding, inclusive of auxiliary energy).
f) Dependent on the appropriate treatment of the feedstock or on suitable process-integrated measures

**Table 4.23: Range of the typical plant, process and emission parameters (raw gas) of aluminium smelting plants**
[ 312, VDI 2286 Aluminium Part 1 and 2 2008 ] *The data capacity and melting efficiency have been partly changed. What was the reference for this?*

### 4.2.4.1 Emissions to air

The potential emissions to air are shown Table 4.24 and are:

- dust, $PM_{10}$ and $PM_{2.5}$
- metal compounds
- organic components (VOC, and PCDD/F) and CO
- oxides of nitrogen ($NO_X$)
- sulphur dioxide
- chlorine, hydrogen chloride and hydrogen fluoride ($Cl_2$, HCl and HF).

A significant proportion of the emission of these substances is produced by the fuel used and by contamination of the feed material. Some dust is produced by fine dusty scrap and by salt fume [ 75, Nordheim, E. (EEA) 1998 ].

| Component | Pretreatment | Melting | Refining and degassing |
|---|---|---|---|
| HCl, HF and ~~chlorine~~$Cl_2$ | •• | •• | ••• |
| Metals and compounds | •• | •• | •• |
| Oxides of nitrogen | • | •• | • (combustion gases) |
| $SO_2$ | • (with suitable fuel) | • (with suitable fuel) | • (combustion gases) |
| Organic compounds (CO, VOC, PCDD/F) | ••• | ••• | |
| Dust | ••• | ••• | •• |
| NB: ••• More significant – • less significant | | | |

**Table 4.24: Significance of potential emissions to air**

In addition, there are potential emissions of ammonia, dust, hydrogen sulphide and phosphine from the treatment of salt slag that may need to be considered as a cross-media effect.

#### 4.2.4.1.1 Capture of gases

In aluminium remelting/recycling plants, diffuse emissions mainly arise during the storage, handling and loading/unloading of dust-emitting materials (e.g. slag), as well as a result of the insufficient capture of furnace off-gases, particularly when the furnace is open (charging, melt treatment, slag tapping, skimming and casting). The diffuse emissions occurring in the process during charging, melt treatment, slag tapping, skimming and casting are subsequently emitted from the buildings, e.g. via open doors or ventilation openings in the roof (roof lights), if no extraction devices of sufficient capacity are available. [ 234, UBA Copper, lead, zinc and aluminium 2007 ].

~~Section 2.8 covers the techniques used.~~ Fume extraction is an important element in secondary aluminium production as dust and smoke can be formed from contaminants on the feed as well as from the combustion and melting stages [ 32, Mantle et al. 1998 ]. The presence of several possible emission points on a furnace is also significant, and the collection of the emissions from such points should be addressed. In addition, various systems may be employed to reduce diffuse emissions during the charging phase of the process. For example, docking cars that seal against the charging door can be used to prevent emissions during charging.

The other important factor is the combustion of organic coatings in the pretreatment or melting furnace and the extraction and abatement systems can all be designed to cope with the treatment of these emissions. Diffuse emissions can be significant unless the fume collection systems are well designed.

#### 4.2.4.1.2 Dust and metals

*This section can be improved. It should be explained more comprehensive from which sources dust emissions are emitted. The highlighted parts should be relocated to 4.2.4.1.3.*

Dust and metals are associated together and are produced from the combustion gases or from the scrap or fluxes used. Some metals, which are present as contaminants, will be fumed off during melting and will form dusts. The production of smoke due to the presence of organic carbon and the presence of chloride may lead to the formation of PCDD/F that will also be associated with the particles [ 312, VDI 2286 Aluminium Part 1 and 2 2008 ]. Afterburning is used to destroy organic components that escape the combustion zone. Injection of treatment materials such as lime, sodium bicarbonate and carbon is also practised. Most installations then use (high-efficiency) fabric filters or ceramic filters to remove dust, and emissions are below 0.6 to 15 mg/Nm$^3$. A spark arrester or cooling chamber often precedes them to provide filter protection.

The typical composition of filter dust from secondary aluminium is shown in Table 4.25

*The composition of dust is more related to the section about residues 4.2.4.3.*

| Contents | Typical value (%) | Range (%) |
|---|---|---|
| CaO | 25 | 0 - 50 |
| $Al_2O_3$ | 15 | 6 - 25 |
| NaCl, KCl | 35 | 20 - 50 |
| Carbon | 6 | 1 - 6 |
| Metals ($^1$) | - | 0.01 - 10 |
| Al metal | 3 | 2 - 7 |
| PCDD/F as ITEQ | 5 µg/kg | 3 - 10 µg/kg |
| ($^1$) Zn, Pb, Cu, Mn, V, Cr, Ni, Sn, (in traces Co, As, Tl, Be, Sb) | | |

**Table 4.25: Typical composition of filter dust from secondary aluminium**
[ 250, UBA AT study "Stand der technik in der Sekundarkupfererzeugung im Hinblick auf die IPPC Richtlinie" 199 1999 ].

Although salt slag processing may not be a process that is included in a permit for aluminium production, the potentially significant emissions of dust from the crushing stages of an off-site process is an issue that can be taken into account locally.

*That is important: Are salt slag recovery plants included in the scope of this BREF?*

The emissions of metals depends on the raw materials used and the dust levels achieved.

Diffuse emissions of dust from the crushing of salt slag can be highly significant, grinding installations should be sealed in order to avoid dust leaking out. Emission summaries are given in [ 234, UBA Copper, lead, zinc and aluminium 2007 ].

| Emissions | Range |
|---|---|
| Dust mg/Nm$^3$ | 2 – 10 |
| $NH_3$ Ammonia mg/Nm$^3$ | 1 – 20 |
| $PH_3$ Phosphine mg/Nm$^3$ | 0.2 – 0.5 |
| $H_2S$ Hydrogen sulphide mg/Nm$^3$ | 1.1 – 4.2 |
| TOC Total organic carbon (TOC) mg/Nm$^3$ | 10 - 50 |
| Energy consumption MJ/t | 1800 - 2600 |

**Table 4.26: Typical collected air emissions from salt slag recycling plants**
[ 234, UBA Copper, lead, zinc and aluminium 2007 ]

#### 4.2.4.1.3 Organic components (VOC, PCDD/F) and CO

Poor combustion of fuel or the organic content of the feed material can result in the emission of organic components. The provision of effective burner and furnace controls is used to optimise combustion. Peak combustion rates due to included organic components need to be taken into account if they are fed to the furnace. It is reported that the precleaning of scrap removes much of the organic material and improves the melting rate [ 119, McLellan 1998 ]. The use of chlorine mixtures and the use of chlorides (salt cover) will provide a source of chlorine for the potential formation of PCDD/F.

Afterburners for off-gases can be used to destroy organic components produced in the furnace or pretreatment stages. Carbon may be added and efficient dust filtration used to remove organic components and PCDD/F that are associated with dust.
*Data for PCDD/F from different sources if available can be included here!*

#### 4.2.4.1.4 Sulphur dioxide and oxides of nitrogen

Both of these compounds are produced as a result of the sulphur and nitrogen contents of the raw materials, fuels and combustion systems used in the furnaces. For example, salt fluxes can contain sulphate. Low-$NO_X$ burners and low sulphur fuels can be used to minimise emissions. The use of oxy fuel burners can reduce the formation of thermal $NO_X$ but there is a possibility that oxygen enrichment might have the opposite effect due to higher operating temperatures[rr35]. Similarly, preheating the combustion air will also increase $NO_X$ concentrations. Higher concentrations are associated with lower gas volumes and overall quantities. Preheating combustion air in regenerative or recuperative burners may also increase emissions of $NO_X$ [ 250, UBA AT study "Stand der Technik in der Sekundarkupfererzeugung im Hinblick auf die IPPC Richtlinie" 199 1999 ]. Reported emissions are in the range of 10 to 900 grams of $NO_X$ per tonne of metal depending on the furnace [ 113, ALFED 1998 ] [ 250, UBA AT study "Stand der Technik in der Sekundarkupfererzeugung im Hinblick auf die IPPC Richtlinie" 199 1999 ].

*The information about NOx is confuse. Why is this reference [250] quoted here? We are in the aluminium section and not in the copper section. Where are the figures from?*
*In this section there is no information about SOx.*

$SO_2$ emission in all cases depend on fuel used and availability, $NO_x$ is measured as $NO_2$.

#### 4.2.4.1.5 HF, HCl and chlorine

Chlorine may be used to treat the molten aluminium before casting to remove hydrogen, magnesium (demagging) and other impurities. One possible use of rotary furnaces is for magnesium removal without any further use of chlorine. If an excess of chlorine is used it could be emitted as chlorine or aluminium chloride. The latter can hydrolyse in contact with air (or water?) to produce HCl. Most sites use dry or semi-dry scrubbing to remove these compounds and only a few use wet scrubbers. Their formation can be minimised by good control and by using mixtures of chlorine and inert gases instead of pure chlorine. The use of salt cover in a melting furnace can also result in the emission of very fine fumes that contain metal chlorides. The use of fluorides for demagging or as a flux can result in the release of HF and fluorides in small quantities.

#### 4.2.4.1.6 Summary of emissions to air

A summary of emissions to air is shown in Table 4.27, Table 4.28, Table 4.29, Table 4.30 and Table 4.31 [ 234, UBA Copper, lead, zinc and aluminium 2007 ] [ 256, Plant visit report AMAG 20071114.doc 2007 ].

| Emissions | Range | Emission factor |
|---|---|---|

| | | (kg/t) |
|---|---|---|
| Dusts mg/Nm$^3$ | 1.3 - 15 | 0.03 |
| HF mg/Nm$^3$ | <3 | |
| Chlorine mg/Nm$^3$ | <3 | |
| HCl mg/Nm$^3$ | 3 - 30 | |
| $SO_2$ mg/Nm$^3$ | 15 - 350 | |
| $NO_x$ mg/Nm$^3$ | 40 - 350 | 0.17 |
| PCDD/F ng I-TEQ/Nm$^3$ | <0.1 - 0.5 | |
| VOCs mg/Nm$^3$ | <0.3 - 50 | 0.02 |
| CO mg/Nm$^3$ | 3 - 97 | 0.06 |
| Energy consumption MJ/t swarf | 3500 - 5200 | |

**Table 4.27: Swarf drying – emissions to air**
[ 234, UBA Copper, lead, zinc and aluminium 2007 ], [ 256, Plant visit report AMAG 20071114.doc 2007 ][rr36].

| Emissions | Range |
|---|---|
| Dusts mg/Nm$^3$ | <1 - 15 |
| HF mg/Nm$^3$ | 0.1 - 3 |
| Chlorine mg/Nm$^3$ | 1 - 3 |
| HCl mg/Nm$^3$ | 0.1 - 30 |
| PCDD/F ng I-TEQ/Nm$^3$ | <0.1 - 0.5 |
| Energy consumption MJ/t | 1900 - 3600 |

**Table 4.28: Induction furnace melting (abated) – emissions to air**
[ 234, UBA Copper, lead, zinc and aluminium 2007 ]

| Emissions | Range | Emission factor (kg/t) |
|---|---|---|
| Dusts mg/Nm$^3$ | 1 - 15 | 0.02 |
| HF mg/Nm$^3$ | 0.1 - 3 | 0.012 |
| Chlorine mg/Nm$^3$ | <1 - 3 | <0.01 |
| HCl mg/Nm$^3$ | 0.1 - 30 | 0.085 |
| $SO_2$ mg/Nm$^3$ | 1 - 350 | 0.37 |
| $NO_X$ mg/Nm$^3$ | 10 - 500 | 0.61 |
| PCDD/F ng I-TEQ/Nm$^3$ | <0.1 - 0.5 | |
| VOCs mg/Nm$^3$ | 5 - 50 | 0.19 |
| Pb, Zn, Cr, Cu, Mn, V, Sn | 0.045 - 0.0047 | 0.006 |
| As, Co, Ni, Cr(vi) Se, Te | <0.071 | <0.001 |
| Energy consumption MJ/t Al | 4000 - 4700 | |

**Table 4.29: Rotary furnace melting (abated) – emissions to air**
[ 234, UBA Copper, lead, zinc and aluminium 2007 ], [ 256, Plant visit report AMAG 20071114.doc 2007 ].

| Emissions | Range Closed and side -well | Range sloping hearth |
|---|---|---|
| Dusts mg/Nm$^3$ | <0.1 - 15 | <5 - 15 |
| HF mg/Nm$^3$ | 0.1 - 3 | <3 |
| Chlorine mg/Nm$^3$ | <1 - 3 | 1 - 3 |
| HCl mg/Nm$^3$ | 0.5 - 30 | <30 |
| $SO_2$ mg/Nm$^3$ | 0.5 - 355 | 10 - 350 |
| $NO_x$ mg/Nm$^3$ | 15 - 500 | 20 - 350 |
| PCDD/F ng I-TEQ/Nm$^3$ | <0.1 - 0.5 | <0.1 - 0.5 |
| VOCs mg/Nm$^3$ | 10 - 50 | 5 - 50 |
| Energy consumption MJ/t Al | 3300 - 4400 | 3300 - 4400 |

**Table 4.30: Reverberatory (closed-well and side-well ) and sloping hearth furnaces for melting (abated) – emissions to air**
[ 234, UBA Copper, lead, zinc and aluminium 2007 ], [ 256, Plant visit report AMAG 20071114.doc 2007 ].

| Emissions | Range | Emission factor (kg/t) |
|---|---|---|
| Dusts mg/Nm$^3$ | 0.7 - 1.1 | 0.016 |
| HF mg/Nm$^3$ | 0.06 - 0.8 | 0.006 |
| Chlorine mg/Nm$^3$ | 1 - 3 | <0.01 |
| HCl mg/Nm$^3$ | 1.6 - 1.8 | 0.03 |
| $SO_{2\ mg}$/Nm$^3$ | <1.8 | 0.22 |
| $NO_x$ mg/Nm$^3$ | 11 - 36 | 0.28 |
| PCDD/F ng I-TEQ/Nm$^3$ | <0.1 - 0.3 | <0.1 |
| VOCs mg/Nm$^3$ | <0.3 - 398 | 0.28 |
| Be | 0.0001 | 0.0000017 |
| Hg | 0.0005 | 0.00001 |
| Tl | 0.0001 | 0.0000017 |
| Zn | 0.002 - 0.017 | 0.00017 |
| Pb, Co, Ni, Se, Te | 0.003 - 0.005 | 0.00007 |
| Sb, Cr, Cu, Mn, V, Sn | 0.003 - 0.004 | 0.00006 |
| As, Cd, Cr(VI), B(a)P | 0.0003 - 0.002 | 0.00002 |

**Table 4.31: Tilting rotary furnace (abated)**
[ 234, UBA Copper, lead, zinc and aluminium 2007 ], [ 256, Plant visit report AMAG 20071114.doc 2007 ][r37].

~~$SO_2$ emission in all cases depend on fuel used and availability, $NO_x$ is measured as $NO_2$.~~

~~The emissions of metals depends on the raw materials used and the dust levels achieved.~~

### 4.2.4.2 Emissions to water

The production of aluminium from secondary raw materials is essentially a dry process. Discharge of waste water is usually limited to cooling water, which is often recirculated, and rainwater run-off from surfaces and roofs. The rainwater run-off can be contaminated by the open storage of raw materials such as oily scrap and deposited solids. Typical values for this contamination are <0.03 kg/tonne Al for suspended solids. In addition, considerable amounts of waste water can be discharged when wet systems are used for air pollution control.
*Waste water:*
- *surface water*
- *water from swarf washing (usually completely reused*
- *waste water from gas treatment*
- *cooling water from casting (0.15 to 0.3 m$^3$/ t Al)*

### 4.2.4.3 By-products, process residues and waste

Skimmings or dross from the holding and treatment processes represent 15 to 30 kg per tonne of aluminium produced. This material contains a significant amount of aluminium. The pretreatment of the skimmings or dross, e.g. by pressing or cooling under an inert gas blanket, reduces oxidation. During storage, skimmings or dross can react with moisture (from the air) to produce ammonia and other gases. Skimmings or dross are used as a raw material in other parts of the secondary aluminium industry. Sometimes they are pretreated by milling and air classification to separate aluminium from aluminium oxide.

Spent filters from metal treatment are usually disposed of. In some cases, when sodium bicarbonate is used for gas-cleaning , solid residues can be recovered with the salt cover [ 2, McLellan et al. 1993 ], [ 32, Mantle et al. 1998 ], [ 142, Boin, U. et al. 1998 ], [ 312, VDI 2286 Aluminium Part 1 and 2 2008 ].

Furnace linings and dust can be recovered in the salt slag treatment processes or disposed of. Typical residues from secondary aluminium production are shown in Table 4.32 and skimmings and dross treatment in Table 4.33.

| Residue | Origin | Volume | Treatment | Driving force |
|---|---|---|---|---|
| Salt slag | Melting in rotary furnaces | Up to 500 kg/t Al | Recovery via dissolution and crystallisation techniques.<br>Production of re-usable substances Al granulate, mixed salt, $Al_2O_3$ | Salt is not used in all furnaces.<br>Ban on landfill |
| Filter dust | Exhaust gas-cleaning | Up to 35 kg/t Al<br>(0.1 to 10 kg/t Al(²)) | Disposal with pretreatment or underground site, partly reconditioned with salt slag or used in the steel industry | Ban on surface disposal in some countries, thermal treatment possible (neutralisation with $NaHCO_3$ or $Na_2CO_3$ → use with salt slag) |
| Furnace lining | Melting furnace | Up to 4 kg/t Al | Potential for reconditioning with skimmings or dross, otherwise leaching + landfill | Aim to prevent landfill<br>Recycle to produce moulds |
| Skimmings or dross | Cleaning of smelter and foundries | Up to 80 kg/t Al(¹) | Smelting in rotary furnace.<br>Recovery, pellets used in rotary drum furnace, dross dust used in the recovery of salt slag | Ban on landfill |

(¹) using Closed-well furnace provided no external scrap is melted.
(²) Non metallic products (oxide proportions from Al scrap).

**Table 4.32: Typical residues from secondary aluminium production**
[ 234, UBA Copper, lead, zinc and aluminium 2007 ] [ 256, Plant visit report AMAG 20071114.doc 2007 ]
*What about grease/oil from swarf processing??*

| Emissions | Range |
|---|---|
| Dust mg/Nm³ | 10 - 40 |
| Dust kg/t (¹) | 300 - 700 |
| Energy consumption MJ/t | 300 - 800 |

(¹) The quantity of dust depends on the metallic content of the original skimmings or dross.

**Table 4.33: Emissions from s~~S~~kimmings or dross treatment**
[ 272, Al input 2008 ]
*This table should be relocated to the section about ' air emissions'.*

Proprietary salt flux is a mixture of sodium chloride (NaCl), potassium chloride (KCl) and ~~NaCl, KCl and~~ calcium fluoride ($CaF_2$). Some fluoride may also be added up to 5 %. When the

used flux is tapped from the furnace (at this stage called salt slag) it contains large amounts of aluminium oxide, which the flux has separated from the raw materials. 2 to 10 % of the total weight of salt slag is metallic aluminium. The sodium and potassium chlorides can be recovered for further use using separation and crystallisation processes. In most plants, the oxide portion is sold after a washing stage to the cement or mineral wool industry.
Typical outputs from slat slag recovery processes are given in table 4.3.1. A typical composition of salt slag is shown in Table 4.32.

~~Diffuse emissions of dust from the crushing of salt slag can be highly significant, grinding installations should be sealed in order to avoid dust leaking out. Emission summaries are given in Table 4.31, Table 4.32 and Table 4.33 [ 234, UBA Copper, lead, zinc and aluminium 2007 ].~~ *This paragraph and the associated table is included under dust emissions in section 4.2.4.1.2.*

| Process | Intermediate product or residue | Quantity (t/t of salt slag) | Use or treatment option |
|---|---|---|---|
| Full recycling (BEFESA) | Aluminium granulate | 0.09 | Sale to secondary Al smelter |
| | Salt (NaCl/KCl) | 0.53 | Sale to secondary Al smelter |
| | Aluminium oxides | 0.68 | Sale to brick, ceramics, clay, cement and mineral wool industry |
| | Ammonium sulphate | 0.08 | Sale to fertiliser industry |
| Partial recycling (REKAL) | Aluminium granulate | 0.08 | Sale to secondary Al smelter |
| | Salt (KCl 95 %) | 0.09 | Sale to fertiliser industry |
| | Leaching residue (including 20 % moisture, aluminium oxides, NaCl) | 0.97 | Cover layer for tailing piles, NaCl will be washed into groundwater |
| | Ammonium sulphate<br>Phosphate solution (waste gas treatment) | 0.03<br>0.07 m³/t salt slag | Sale to fertiliser industry<br>Sale to fertiliser industry |

**Table 4.34: Typical outputs from salt slag recovery**
[ 234, UBA Copper, lead, zinc and aluminium 2007 ]

| Contents | Typical value (%) | Range (%) |
|---|---|---|
| Al, metallic | 6 | 2 - 10 |
| Water soluble parts (1) | 37 | 20 - 40 |
| Water insoluble parts (2) | 55 | 45 - 75 |
| PCDD/F | 5 ng/kg | <0.1 - 0.5 ng/kg |
| NB: (1) Water soluble salts. (2) Metal oxides, non-recovered metal and insoluble salts. | | |

**Table 4.35: Typical composition of salt slag**
[ 234, UBA Copper, lead, zinc and aluminium 2007 ]

| ~~Emissions~~ | ~~Range~~ |
|---|---|
| ~~Dust mg/Nm$^3$~~ | ~~2 – 10~~ |
| ~~Ammonia mg/Nm$^3$~~ | ~~1 – 20~~ |
| ~~Phosphine mg/Nm$^3$~~ | ~~0.2 – 0.5~~ |
| ~~Hydrogen sulphide ppm~~ | ~~0.8 – 3.0~~ |
| ~~Total organic carbon (TOC) mg/Nm$^3$~~ | ~~10 - 50~~ |
| ~~Energy consumption MJ/t~~ | ~~1800 - 2600~~ |

~~**Table 4.33: Typical collected air emissions from salt slag recycling plants**~~
~~[ 234, UBA Copper, lead, zinc and aluminium 2007 ]~~

## 4.3 Techniques to consider in the determination of BAT

The sections of this document entitled 'Techniques to consider in the determination of BAT' set out techniques considered generally to have the potential for achieving a high level of environmental protection in the industries within the scope of the document. The background to the way the techniques are described is given in Section 2.1.2 and Table 2.2.

This section presents a number of techniques for the prevention or reduction of emissions and residues as well as techniques for reducing overall energy consumption. They are all commercially available. Examples are given in order to demonstrate techniques which illustrate a high environmental performance. The techniques that are given as examples depend on information provided by the industry, European Member States and the valuation of the European IPPC Bureau. The general techniques described in Chapter 2 'common processes' apply to a large extent, to the processes in this sector and influence the manner in which the main and associated processes are controlled and operated.

Techniques used by other sectors are also applicable particularly those relating to the removal of tar and PAH.

The techniques to consider on a site by site basis are strongly influenced by the raw materials that are available to a site, the processes in place and, in particular, the type and variability of secondary raw materials. For example, the metals they contain can be crucial to the choice of process. For $SO_2$ or total carbon removal, the variation in raw gas concentration during batch processes may affect the performance of the abatement system.

The applied remelting and refining processes described in Sections 4.1.2 and 4.2.2 are applied to a wide range of secondary raw materials of varying quantities and composition. These processes are used worldwide. In primary processes there has been much process optimisation in existing installations mainly in the fields of computer-based control of the operating conditions, feeding techniques, bus-bar optimisation and emission capture systems.

### 4.3.1 Material handling, storage and pretreatment processes

The storage of raw materials depends on the nature of the material. The storage of fine dusts in enclosed buildings, silos or in sealed packaging is used. The storage of non-dusty, non soluble material in open stockpiles and large items individually in the open is also used [ 312, VDI 2286 Aluminium Part 1 and 2 2008 ].

#### 4.3.1.1 Primary raw materials (PRIM. AL)

**Description**

The raw materials are bauxite, caustic soda, lime, chlorine mixtures, alumina, fluxes, anode material, secondary material and fuel. Other important materials are the products, skimmings or dross, slags and process residues. Important aspects are the prevention of leakage of dust and wet material, the collection and treatment of dust and liquids and the control of the input and operating parameters of the handling and feeding processes. The issues specific to this group are summarised in Table 4.36 and include the following:

- The potentially dusty nature of bauxite, alumina and fluxes meaning that enclosed storage, handling and treatment systems may be appropriate in these instances. Closed conveyors, pneumatic transfer systems and storage silos are techniques to be considered.
- The dust generated by some milling and separation operations meaning that collection and abatement may be applicable for this process.
- Fabric or ceramic filters achieve better dust removal efficiencies than ESPs.

| Material | Storage | Handling | Pretreatment | Comments |
|---|---|---|---|---|
| Coal or coke | Covered bays and silos | Covered conveyors, pneumatic. | | |
| Liquid fuels such as oils and pitch | Tanks or drums in bunded areas | Secure pipeline or manual system | Heated storage and pipelines | Back venting of displaced gases |
| Bauxite and alumina | Enclosed if dust-forming | Enclosed with dust collection. Covered conveyor. Dense phase conveyor | | |
| Chlorine gas or mixtures that contain chlorine | Approved pressure vessels | Approved methods | | |
| Products - Slab, billets, sheets and ingots | Open storage | | | |
| Process residues for recovery, e.g. skimmings or dross | Covered or enclosed depending on dust formation | Depends on conditions | | Salt slag and skimmings or dross kept dry. Appropriate drainage system |
| Wastes for disposal | Covered or enclosed bays or sealed (drums) depending on the material | Depends on conditions | | Appropriate drainage system |

**Table 4.36: Materials storage, handling and pretreatment methods for primary aluminium**

Skimmings or dross and other metallic residues that are destined for recovery off site should be cooled preferably under an inert atmosphere in order to avoid oxidation and stored in dry conditions or other suitable ways depending on the material, e.g. size reduction.

**Achieved environmental benefits**
The capture of dust is achieved allowing the reduction of main emissions and the recovery of other metals.

**Cross-media effects**
Use of energy.

**Operational data**
Given in the descriptions of the process above.

**Applicability**
These techniques are applicable to most processes depending on the installation.

**Economics**
None reported.

**Driving force for implementation**
Environmental impact and energy costs

**Example plants**
UK, ES, DE.

**Reference literature**
[ 290, EC 2006 ]

### 4.3.1.2 Secondary raw materials

**Description**

There are a variety of secondary raw materials and they range from fine dusts to large single items. The metal content varies for each type of material and so does the content of other metals and contaminants.

Secondary raw materials that contain oil or water-soluble components are stored under cover. Skimmings or dross can hydrolyse to produce ammonia gas. The techniques used for storage, handling and pretreatment will therefore vary according to the material size and the extent of any contamination.

Secondary materials storage, handling and pretreatment methods for aluminium are shown in Table 4.37.

| Material | Storage | Handling | Pretreatment | Comment |
|---|---|---|---|---|
| Liquid fuel such as oils | Tanks or drums in bunded areas | Secure pipeline or manual system | Heated storage and pipelines | Back venting of displaced gases |
| Fluxes and salt. | Enclosed (Silo) if dust-forming | Enclosed conveyors with dust collection | | |
| Fine dust (skimmings or dross), etc. | Enclosed if dust-forming | Enclosed with dust collection | Milling and density separation. | |
| Swarf | Covered bays if soluble or emulsified oil | Mechanical loader | Swarf dryer. Centrifuging | Oil collection |
| Coarse dust | Open or covered bays | Mechanical loader | Swarf dryer | Oil collection |
| Lump (raw material or slag). | Open | Mechanical loader | | Oil collection |
| Whole Items, foils and sheets. | Open or covered bays | Mechanical loader | | Oil collection |
| Chlorine gas or mixtures that contain chlorine | Approved pressure vessels | Approved methods | | |
| Products - Slab, billets, sheets and ingots | Open | | Preheating | |
| Process residues for recovery, e.g. skimmings or dross, salt slag and linings. | Covered or enclosed depending on dust formation | Depends on conditions | Separation by milling and/or dissolution. - Potentially very dusty. | Skimmings or dross and salt slag need to be kept dry. Appropriate drainage system. |
| Wastes for disposal. | Covered or enclosed bays or covered containers for transport depending on the material | Depends on conditions | | Appropriate drainage system. |

**Table 4.37: Secondary materials storage, handling and pretreatment methods for aluminium**
[ 290, EC 2006 ]

The raw materials vary from site to site and the techniques discussed in Section 2.5 will be applied on a site and material-specific basis. The specific issues that apply to this group include the following:

- Pretreatment stages are often used to remove oil or coatings or to separate aluminium from oxides. The removal of oil and coatings by thermal means, for example in a swarf drier is a technique to consider.
- Other pretreatment stages may also include granulation, media separation and magnetic separation to remove ferrous contamination. These are techniques to consider.
- Skimmings or dross treatment by milling and grinding techniques when used with good dust extraction and abatement is also a technique to consider. The fine dust that is produced may be treated to recover other metals.
- The use of pneumatic or other density separation techniques are technique to consider.
- Fine dusts storage and handling in a manner that prevents the emission of dust is a technique to consider.

**Achieved environmental benefits**
Capture of dust and oils.

**Cross-media effects**
No cross-media effects were reported.

**Operational data**
Given in the descriptions of the process above.

**Applicability**
These techniques are applicable to most processes depending on the installation. Some techniques such as the change of furnace or process are only applicable for a new plant or a major upgrade or modernisation.

**Economics**
No economics were reported.

**Driving force for implementation**
Environmental impact and energy cost savings are the driving forces.

**Example plants**
UK, ES, DE

**Reference literature**
[ 312, VDI 2286 Aluminium Part 1 and 2 2008 ]

### 4.3.2 The production of alumina from bauxite (PRIM. AL)

**Descriptions**
In the Bayer process, energy and the production of residues are significant issues. The major energy consumers are digestion, calcination and the production of steam for the process. The choice of the energy source has a big influence on the amount of $CO_2$ emissions. Where it is available, low sulphur natural gas should be used rather than coal or heavy oil, since the $CO_2$ emissions of natural gas is only about half of that of coal for the same amount of produced energy. Red mud is produced as a residue that poses a disposal problem and can be strongly alkaline.

One major factor in the design of an alumina refinery is the recovery of as much energy as possible.

Some possible proven examples regarding maximum heat recovery are the:

- application of tube digester technology

- application of plate heat exchangers instead of flash cooling in the liquor cooling area, if the condensate balance allows it
- application of circulating fluidised bed calciners instead of rotary kilns
- recovery of energy wherever possible and avoiding any losses.

The removal of impurities is also an important issue, since the impurity level influences the productivity of the process and hence, the specific energy consumption. The use of fresh caustic soda is minimised by the addition of lime which precipitates carbonate and caustic soda is recovered.

The techniques to consider for the various process stages are:

a. Tube digester

By using tube digesters the slurry is heated up in one circuit without using live steam and heating up to the digestion temperature is therefore without dilution of the slurry.

b. Liquor cooling

The amount of heat recovered from the liquor flowing to the precipitation is increased by using plate heat exchangers rather than a flash cooling plant. This reduces the amount of energy, which is wasted in a cooling tower when using a flash cooling plant. If the condensate balance and the liquor conditions allows it, plate heat exchangers should be used.

c. Calciners

Circulating fluid bed calciners have a much higher energy efficiency, since the heat recovery from the alumina and the flue-gas is at a higher level.

d. Bauxite quality

The bauxite ore quality has influence over the energy consumption. Bauxite with a higher moisture content carries more water into the process which should be evaporated.

A high silica content in the bauxite leads to a higher loss of caustic soda due to the reaction of silica, sodium and aluminium causing dilution of the liquor.

By optimising the bauxite quality, the specific energy consumption can be reduced to below 7.0 GJ/t $Al_2O_3$ when using tube digesters. For other plants with traditional digestion, technology-specific energy consumption can be reduced to below 10 GJ/$Al_2O_3$.

Alumina refineries also demand electrical power and a cogeneration plant using a turbine fired with natural gas is an optimum solution. The hot flue gas of the turbine is used to generate steam, which can be used in the Bayer process.

e. Red mud

Red mud is generally alkaline from the extraction process and contains 3 to 40 kg of water-soluble NaOH per tonne of alumina produced. The water-soluble caustic soda content can be minimised by filtering the red mud as a last process step.

In some refineries, high-pressure filtration of red mud is used to produce a relatively low moisture bauxite residue. This by-product can be easily transported over long distances and can be used in applications such as cement and ceramic industries, road construction, etc. It is also possible to use the alkalinity of red mud to absorb $CO_2$ and this is possible where the bauxite production takes place on the same site or close to a primary aluminium smelter or close to another significant source of $CO_2$. Further details are reported in the Reference Document on the Management of Tailings and Waste Rock in Mining Activities [ 332, Tailings Management 2008 ].

**Achieved environmental benefits**
Reduction in energy use in digestion and a reduction of main emissions to all media.

**Cross-media effects**
Use of energy for pumping and compaction.

**Operational data**
Given in the descriptions of the process above.

**Applicability**
These techniques are applicable to most processes depending on the installation. Plants using steam injection for digestion cannot be rebuilt to tube digestion without a total redesign and rebuilding of the plant.

**Economics**
A reduction of energy costs by up to 65 % by using more efficient tube digesters and fluidised bed calciners are reported. Using natural gas as the primary energy source and applying the best design regarding energy consumption, the emissions of $CO_2$ can be reduced from 1.1 t $CO_2$/t $Al_2O_3$,(11 GJ/t $Al_2O_3$) when using coal and they can be reduced to 0.392 t $CO_2$/t $Al_2O_3$, (7 GJ/t $Al_2O_3$) when using natural gas.

120000 t/yr of red mud can be processed in a filter press. The investment cost of the filter-press is EUR 5 million.

**Driving force for implementation**
Reduction of environmental impact and energy costs are the driving forces.

**Example plants**
IR, DE, FR.

**Reference literature**
[ 247, New possible uses of Red Mud, French Report 2008 ], [ 332, Tailings Management 2008 ].

### 4.3.3 Primary aluminium smelting processes (PRIM. AL)

**Description**
The electrolysis cells detailed in Section 4.1 on applied techniques are the techniques to be considered in conjunction with the following features to minimise environmental impact[rr38]:

- Automatic multiple point feeding of alumina in PFPB cells. (this is currently not consistent with the BAT conclusion)
- Computer control of the electrolysis process based on active cell databases and monitoring of cell operating parameters.
- Complete hood coverage of the cell in prebake plants, which is connected to a separate gas exhaust and filter system. The use of robust cell covers and adequate extraction rates taking account of fluoride evaporation and carbon burn-off.
- 98 to >99 % fume collection from the cells on a long-term basis. If a lower collection efficiency is achieved the collection and treatment of ventilation gases should be considered. *(what exactly is meant by ventilation gases and why should treatment take place only in case of low efficient collection?)*

- Minimisation of the time for changing anodes and other actions that need cell covers to be removed. Butt cooling in an enclosure; use of a programmed system for cell operations and maintenance.
- Dry scrubbing of fluoride and HF from the cell fumes using alumina followed by dust removal in a fabric filter system or a combination of this (does this extention makes sense?) and (should this be "or"?) a wet scrubber to achieve a minimum of 99.8 % removal of total fluoride. The alumina should be re-used in the process.
- If sulphur removal (examples?) is practised using a wet scrubber system, the system should be used with a system to remove fluoride, HF and tars.
- If there is a combined anode plant, the use of an alumina scrubber and fabric filter system or carbon-coated filters to remove tar fume from the milling, blending and baking stages; use of the alumina in the electrolysis process.
- The use of established efficient cleaning methods in the rodding plant to recover fluorides and carbon; the collection of fumes that contain fluoride from the cleaning process and from the melting of steel components.
- The use of low sulphur carbon (<2 % S) for the anodes or anode paste where possible from a production point of view taking air quality into account. (In the BAT conclusion is mentioned 2.5 % S)
- The use of rotary gas or flux injection for holding furnaces. *(what is rotary gas?)*

For Søderberg cells, the development of new Søderberg installations is not expected and those plants that will not close should incorporate the following systems:

- complete hood coverage of the anode top, which is connected to a separate gas exhaust and dry alumina scrubber
- dry anode top in combination with stud hole paste and an increase in the anode height (depending on the effectiveness that is demonstrated)
- adoption of a point feeding system for alumina
- well-designed and maintained burners for incineration of CO and low molecular weight PAH and other hydrocarbons in pot exhaust gas, where necessary. *(find a proper wording for pot exhaust gas. Other terms are used like cell fumes, cell process gases,gas from electrolysis etc.)*

**Achieved environmental benefits**

Reduction in total emissions and energy use.

In 1998 OSPARCOM suggested target emission values for a variety of primary aluminium processes. Based on these recommendations, Table 4.38 reports suggested target emission values for different plant configurations [ 272, Al input 2008 ]. It also recommended that a review of the target emission values be undertaken in the year 2001 based on the results of the measurement programme. This has not been reported.

| **Plant/technology** | **Target emission limit values (annual average in kg per tonne of aluminium produced)** | | | |
|---|---|---|---|---|
| | **F total** | **HF (as F)** | **Dust** | **PAH (BaP)** |
| Existing prebake | 0.6 | 0.4 | 2 | |
| Søderberg without ventilation air scrubbers | 0.6 | 0.4 | 2 | 0.01 |
| Søderberg with ventilation air scrubbers | 0.5 | 0.2 | 2 | 0.008 |
| New prebake | 0.3 | 0.2 | 1 | |

**Table 4.38: Suggested target values for emissions to air from primary aluminium electrolysis** [ 286, OSPAR Rec 98/2 1998 ]

The values given in Table 4.38 are based on OSPARCOM target values which are not BAT-AELs. *What is needed are real measured data!*

**Cross-media effects**
No cross-media effects were reported.

**Operational data**
Given in the descriptions of the process above.

**Applicability**
These techniques are applicable to most processes depending on the installation.

**Economics**
No data has been reported.

**Driving force for implementation**
Reduced environmental impact and energy costs are the driving forces.

**Example plants**
NO, DE, ES[rr39].

**Reference literature**
[ 233, Farrell Nordic Mission 2008 ], [ 286, OSPAR Rec 98/2 1998 ], [ 312, VDI 2286 Aluminium Part 1 and 2 2008 ].

### 4.3.3.1 Removal of dust and condensable hydrocarbons using an ESP, an RTO or a catalytic thermal oxidiser (CTO) for tar storage and mixing (PRIM. AL)

**Description**
The volatile hydrocarbons emitted during storage and mixing can be incinerated or condensed. The condensed hydrocarbon particles can be removed from the flue-gas by regular dust abatement techniques like electrostatic precipitators. Condensation can be achieved by external and/or internal cooling with air and/or water systems. Condensation is often achieved within conditioning towers.

Alternatively incineration in a RTO or a CTO can be used and the heat generated can be used in the process for maintaining the temperature of the storage and mixing stages.

**Achieved environmental benefits**
The removal of the condensable hydrocarbon.

| Source | Abatement type | Pollutant | Concentration range (mg/Nm$^3$) |
|---|---|---|---|
| Material handling and storage. Coke | Cyclone | Dust | 20 - 150 |
| | Fabric filter | Dust | 1 - 90 |
| Material handling and storage. Pitch | Re-venting, condensation | Hydrocarbon | 1 - 75 |
| Grinding, mixing and forming | Fabric filter | Dust | <5 |

**Table 4.39: Removal of dust and condensable hydrocarbon**

*(These data are from the existing BREF Table 12.3 and do not fit with the data in section 4.2.2.2.1 Table 4.6. for material handling and storage. We should try to get new data!)*

**Cross-media effects**
Some energy costs for cooling.

**Operational data**

Performance data for CTO

- PAH emissions (EPA16): <0.03 ~~Kg~~kg/h
- production: approx 12 t paste/h
- dust: the plant reported that there are no dust emissions during normal operating conditions

Performance data for RTO

- PAH emissions (EPA16): 2.4 mg/Nm$^3$
- dust: 1.6 mg/Nm$^3$
- outflow: approximately 10000 m$^3$/h
- electricity consumption: 4.4 kWh/t paste
- gas consumption: 2.6 kg gas/t paste

**Applicability**

This technique is applicable to the storage and mixing stages for several process abatement stages.

**Economics**

Investment costs for CTO in 2002 was approximately USD 300000.
Yearly operating cost were approximately USD 6000 (mainly cleaning and catalytic media)
Electrical energy is used for a start-up period of approximately 8 hours (50 kWh). After that period, burn-off-gases from the CTO are used to keep the system in operation.
In addition, electrical energy is used for a fan, to evacuate 1000 m$^3$/hour of gases.

Investment costs for RTO are EUR 1.9 million.
Yearly maintenance costs are EUR 20000.

**Driving force for implementation**

Emissions reduction and recovery of tar are the driving forces.

**Example plants**

NO.

**Reference literature**

[ 272, Al input 2008 ], [ 348, French input for Aluminium 2010 ].

### 4.3.3.2 Use of regenerative thermal oxidiser (RTO) (PRIM. AL)

**Description**

A regenerative afterburner (or regenerative thermal oxidiser - RTO) has been used in a stand alone plant that produces anodes. The process depends on an alternating cycling of gases through a series of support zones where heating, cooling and cleaning cycles take place. The combustible fraction is heated in the heating zone and passes to a common residence chamber where combustion is completed, the hot gases then pass into a cooling section which is heated to become the next heating zone. The zones are changed using a manifold system to allow cleaning and these valves are prone to fouling with carbon which reduces their effectiveness. Pretreatment reduces this fouling and careful design of the valves is also needed [ 318, Fume treatment from Baking Furnaces 2007 ].

The techniques installed comprise four steps and are used in the process that recovers anode butts: *(What does this mean? Is the RTO used in a standalone plant that produces anodes or in a plant that recovers anode butts or in a plant that produces anodes and recovers anode butts? )*

1. Removal of coarse tar components and dust: the off-gas from the baking furnace is led through a packed bed of saddle shaped ceramic elements. The heavy tar components

condense on the bed which is cleaned periodically using the hot gases from the RTO. The off-gases from the cleaning phase pass to the RTO and not the pretreatment stage.

2. Regenerative thermal oxidation (RTO): ceramic beds are used to preheat the off-gas. By switching the direction of the airflow regularly, these ceramic beds are preheated with the off-gas from the combustion room.
3. Combustion chamber: the off-gases are lead to the combustion chamber, where fine tar components and PAHs are destroyed at a temperature of approximately 800 °C.
4. Dry absorption: the off-gases are lead through moving bed reactor with lime to capture fluorides (and a limited amount of $SO_2$).

~~The gases are pretreated to remove tar and PAH before the RTO so that low PAH values can be achieved and additional energy is therefore needed to maintain temperatures in the combustion zone unless the collected tar is used as a fuel. The operational data is given for a plant that uses pretreatment and post-treatment to achieve very low emissions. The RTO alone has not been shown to achieve these very low emission levels. The performance data is shown in Table 4.38. and represents a specific plant that operates with excess capacity.~~

| ~~**Parameter**~~ | ~~**Raw gas**~~ | ~~**Clean gas**~~ |
|---|---|---|
| ~~Flow~~ | ~~80000 $Nm^3$/h~~ | ~~80000 $Nm^3$/h~~ |
| ~~Temperature~~ | ~~150 – 200 °C~~<br>~~Max. 280 °C~~ | ~~>120 °C~~ |
| ~~Under pressure - Outlet furnace~~ | ~~-15 kPa~~ | |
| ~~Condensable hydrocarbons~~ | ~~Avg. 250 mg/$Nm^3$~~<br>~~Max. 500 mg/$Nm^3$~~ | ~~Max. 5 mg/$Nm^3$~~ |
| ~~Volatile hydrocarbons~~ | ~~Avg. 65 mg/$Nm^3$~~<br>~~Max. 200 mg/$Nm^3$~~ | ~~Max. 25 mg/$Nm^3$~~ |
| ~~HF~~ | ~~Avg. 16 mg/$Nm^3$~~<br>~~Max. 60 mg/$Nm^3$~~ | ~~Max. 3 mg/$Nm^3$~~ |
| ~~Dust~~ | | ~~Max. 10 mg/$Nm^3$~~ |

~~**Table 4.38: Design requirements of an RTO**~~
~~[ 242, Nl Anode Input 2008 ], [ 318, Fume treatment from Baking Furnaces 2007 ]~~

**Achieved environmental benefits**
The energy content of the contaminants (hydrocarbon and PAH) is used to heat the support materials. Depending on the pollutant contents of the fumes, autothermal operation may be possible. Odour and emissions of PAH are reduced. *Can authothermal operation really be achieved?*

The performance of an RTO in the production of anodes for the primary aluminium industry in combination with pre and post-treatment of gases is given in .

| **Substance emitted** | **Achieved emission levels:** |
|---|---|
| $SO_2$:. | 174 mg/$Nm^3$ half hour average 2005 |
| $NO_X$: | 61mg/$Nm^3$ half hour average 2005 |
| Dust | 3.5 mg/$Nm^3$ half hour average 2005 |
| Total $C_xH_y$ | 1.9 mg/$Nm^3$ half hour average 2005 |
| PAH (included in total $C_xH_y$) | PAH (PRTR): 2.6 µg/$Nm^3$<br>PAH (EPA): 176 µg/$Nm^3$ |
| Fluorides (as HF) | 1.6 mg/$Nm^3$ half hour average in 2005 |

**Table 4.40: Performance of an RTO in a stand alone plant in combination with pre and post treatment of gases**
[ 242, Nl Anode Input 2008 ], [ 318, Fume treatment from Baking Furnaces 2007 ].

The operational data is given for a plant that uses pretreatment and post-treatment to achieve very low emissions. The RTO alone has not been shown to achieve these very low emission levels. The performance data is shown in Table 4.41. and represents a specific plant that operates with excess capacity. *(What is the implication of this sentence?Are these the raw gas concentrations after pretreatment or prior to pretreatment?)*

| **Parameter** | **Raw gas** | **Clean gas** |
|---|---|---|
| Flow | 80000 $Nm^3/h$ | 80000 $Nm^3/h$ |
| Temperature | 150 - 200 °C<br>Max. 280 °C | >120 °C |
| Under pressure - Outlet furnace | 15 kPa | |
| Condensable hydrocarbons | Avg. 250 $mg/Nm^3$<br>Max. 500 $mg/Nm^3$ | Max. 5 $mg/Nm^3$ |
| Volatile hydrocarbons | Avg. 65 $mg/Nm^3$<br>Max. 200 $mg/Nm^3$ | Max. 25 $mg/Nm^3$ |
| HF | Avg. 16 $mg/Nm^3$<br>Max. 60 $mg/Nm^3$ | Max. 3 $mg/Nm^3$ |
| Dust | | Max. 10 $mg/Nm^3$ |

**Table 4.41: Design requirements of an RTO**
[ 242, Nl Anode Input 2008 ], [ 318, Fume treatment from Baking Furnaces 2007 ]

### Cross-media effects

The gases are pretreated to remove soot, partikels and a condensed~~tar and~~ PAH fraction before the RTO so that lower PAH values can be achieved. ~~and a~~Additional energy is therefore needed to maintain temperatures in the combustion zone unless the collected tar is used as a fuel. Energy consumption can increase from 8 % to 10 % and $CO_2$ and $NO_x$ emissions are increased. [reference?]

### Operational data

~~The techniques installed comprise four steps and are used in the process that recovers anode butts:~~

1. ~~Removal of coarse tar components and dust: the off-gas from the baking furnace is led through a packed bed of saddle shaped ceramic elements. The heavy tar components condense on the bed which is cleaned periodically using the hot gases from the RTO. The off-gases from the cleaning phase pass to the RTO and not the pretreatment stage.~~
2. ~~Regenerative thermal oxidation (RTO): ceramic beds are used to preheat the off-gas. By switching the direction of the airflow regularly, these ceramic beds are preheated with the off-gas from the combustion room.~~
3. ~~Combustion chamber: the off-gases are lead to the combustion chamber, where fine tar components and PAHs are destroyed at a temperature of approximately 800 °C.~~
4. ~~Dry absorption: the off-gases are lead through moving bed reactor with lime to capture fluorides (and a limited amount of~~ ~~$SO_2$).~~

~~The performance of an RTO in the production of anodes for the primary aluminium industry in combination with pre and post-treatment of gases is given in Table 4.39.~~

| ~~**Substance emitted**~~ | ~~**Achieved emission levels:**~~ |
|---|---|
| ~~$SO_2$:.~~ | ~~174 $mg/Nm^3$ half hour average 2005~~ |
| ~~$NO_X$:~~ | ~~61$mg/Nm^3$ half hour average 2005~~ |
| ~~Dust~~ | ~~3.5 $mg/Nm^3$ half hour average 2005~~ |
| ~~Total $C_xH_y$~~ | ~~1.9 $mg/Nm^3$ half hour average 2005~~ |
| ~~PAH (included in total $C_xH_y$)~~ | ~~PAH (PRTR): 2.6 µg/$Nm^3$~~<br>~~PAH (EPA): 176 µg/$Nm^3$~~ |
| ~~Fluorides (as HF)~~ | ~~1.6 $mg/Nm^3$ half hour average in 2005~~ |

~~**Table 4.39: Performance of an RTO in a stand alone plant in combination with pre and post treatment of gases**~~
~~[ 242, Nl Anode Input 2008 ], [ 318, Fume treatment from Baking Furnaces 2007 ].~~

The energy consumption depends on the differential temperature. Heat recovery rates of approximately 95 % can be achieved. ~~PCDD/F were not detected.~~

**Applicability**

This technique is applicable to a variety of processes but is more suitable for gases from closed furnaces. The basic principle is good but the fouling of the change-over valves or change-over to the cleaning phase may cause the emissions of uncombusted material if the design is inadequate or the sealing valves become fouled[rr40]. The pretreatment of the gases before an RTO will remove some combustible organic carbon. However, if an ESP is used for pretreatment, condensed hydrocarbons can partly be utilised in the combustion chamber of the RTO.

**Economics**

Several installations are operating viably. Maintenance cost EUR 74000 per year, gas EUR 3.9 million per year, electricity EUR 530000 per year. Waste disposal (lime residue) EUR 22000 per year

**Driving force for implementation**

Reduction of odour together with reduction of PAH and benzene emissions are the driving forces.

**Example plants**

NL *(only in the NL??)Under economics is said that several installation are in operation.*
*Try to get the info for all plants which apply RTO for anode production. Is it applied for stand alone plants only or can is be found in Al production plants as well?*

**Reference literature**

[ 242, Nl Anode Input 2008 ], [ 318, Fume treatment from Baking Furnaces 2007 ], [ 348, French input for Aluminium 2010 ].

### 4.3.3.3 Use of a regenerative burner

- *(I think this has to be relocated to secondary aluminium smelting! [256] is for AMAG, Austria, which is a secondary aluminium plant.*
- *(I think this is the wrong name in the figure below. RTO ist described in the previous section) RTO is **primarily** used as a cleaning device whereas regenerative burners are used to reduce the energy consumption. )*

**Description**

In a regenerator, exhaust gas and combustion air alternately flow through a chamber filled with a heat storage medium, charging with waste gas flow and discharging with air flow. Regenerators, if constructed from materials which will accept the full exhaust gas temperature from the fired chamber and resist any corrosive elements contained therein, display none of the difficulties usually seen for recuperators.

A twin bed regenerative burner consists of an all ceramic high temperature burner close coupled to a compact, fast cycle, ceramic regenerator. The burner serves double duty, acting as the inlet or the exhaust from the fired chamber, depending on the cycle. One complete twin bed regenerative burner set comprises two burners, two regenerators, reversing valves, and the control system.

While one of the burners fires using cool air fed to the base of its regenerator, exhaust gas is drawn through the other burner and down into its associated regenerator to preheat the packing, then discharged to the gas-cleaning plant. When the regenerator being heated is sufficiently charged, the airflow is reversed so that cool air flows to the newly heated regenerator and is preheated, the previously cooled regenerator being reheated by the exhaust gas generated by the other burner firing. The first and second half of the cycle are shown in Figure 4.12 and Figure 4.13.

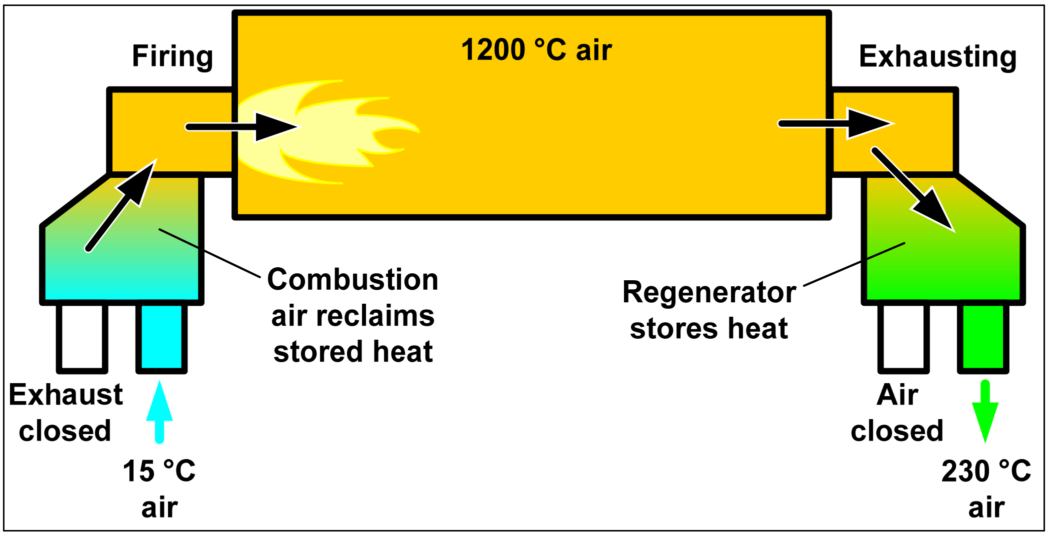


**Figure 4.12: First half of the cycle**

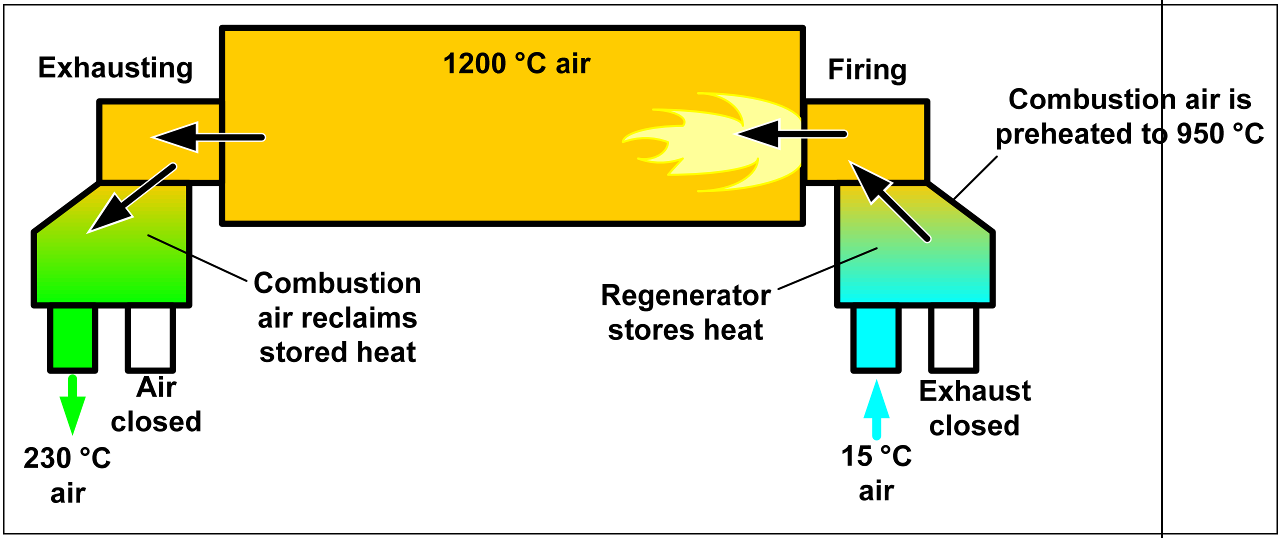


**Figure 4.13: Second half of the RTO cycle** *(I think this is the wrong name. RTO ist described in the previous section) RTO is primarily used as a cleaning device whereas regenerative burners are used to reduce the energy consumption. )*

**Achieved environmental benefits**

The energy content of the hot gases is used to heat the support materials and can reduce the energy consumption by 70 % compared to that of a normal burner. Regenerative burners are reported to use 30 % less energy than recuperative burners.

**Cross-media effects**

None reported.

**Operational data**

Regenerative burners are used in a number of applications. The process depends on an alternating cycling of gases through a series of support zones using ceramic balls where heating and cooling cycles take place. Combustion air can be preheated to approximately 900 °C.

**Applicability**
This technique is applicable to a variety of new and existing processes. Additional post-treatment of the gases might be required depending on input material. *Is this associated to regenerative burners? What means variety in this context. Be more accurate.*

**Economics**
Pay-back time for regenerative burners in the secondary aluminium sector is reported to be less than one year.

**Driving force for implementation**
Improved energy efficiency.

**Example plants**
AT
*(More examples?)*
**Reference literature**
[ 103, Farrell, F. 1998 ], [ 256, Plant visit report AMAG 20071114.doc 2007 ], .

### 4.3.3.4 Modernised Søderberg technology (PRIM. AL)

**Description**
Although Søderberg technology will not be applied to new plants in the EU, there are several existing plants where the cost of replacement by prebake processes would be inordinately expensive. Modernised Søderberg technology can be fitted at a more moderate cost and can achieve particularly good environmental performance when compared to a prebake plant including electrode production. The improved technology consists of equipping the cells with point feeders and improved burners for incineration of PAH so there is no need for regular crust-breaking. Further the use of dry anode paste and either higher anode casing or anode covers to reduce the temperature on the anode top, result in the reduction of PAH emissions from the anode top.
*In figure 4.14. also the treatment of potroom air by seawater scrubbers, the treatment of pot gas by ESP, dry and wet scrubbing and the separate treatment of anode gas by dry scrubbing is applied. A propper description of these treatment steps is missing. What are the raw gas concentrations and what are the concentrations in the cleaned gases for all relevant parameters (i.e. dust, HF, SO2, PFC, PAH). All this is considered to be necessary to decide whether seawater srubbing is needed and if Cell configurations other than CWPB are BAT.*

**Achieved environmental benefits**
These improvements result in a significant increase in the capture of gases [ 226, Nordic Report 2008 ]. Improved Søderberg plants achieve up to 95 % capture efficiency based on HF depending on the degree of modification and the extent of evaporation of HF from the bath which cannot be captured [ 75, Nordheim, E. (EEA) 1998 ], [ 233, Farrell Nordic Mission 2008 ]. HF concentration in the cell room atmosphere can be monitored continuously using an open path continuous monitoring system. Uncaptured HF in the ventilation air is removed by seawater scrubbers [ 233, Farrell Nordic Mission 2008 ]. The results of environmental monitoring in the sea and in air should be taken into account to determine the overall reduction in emissions.

*(This targets the acidification of the sea, look at former authors information on this issue)[502]*
The gas collection and cleaning system is shown in Figure 4.14.

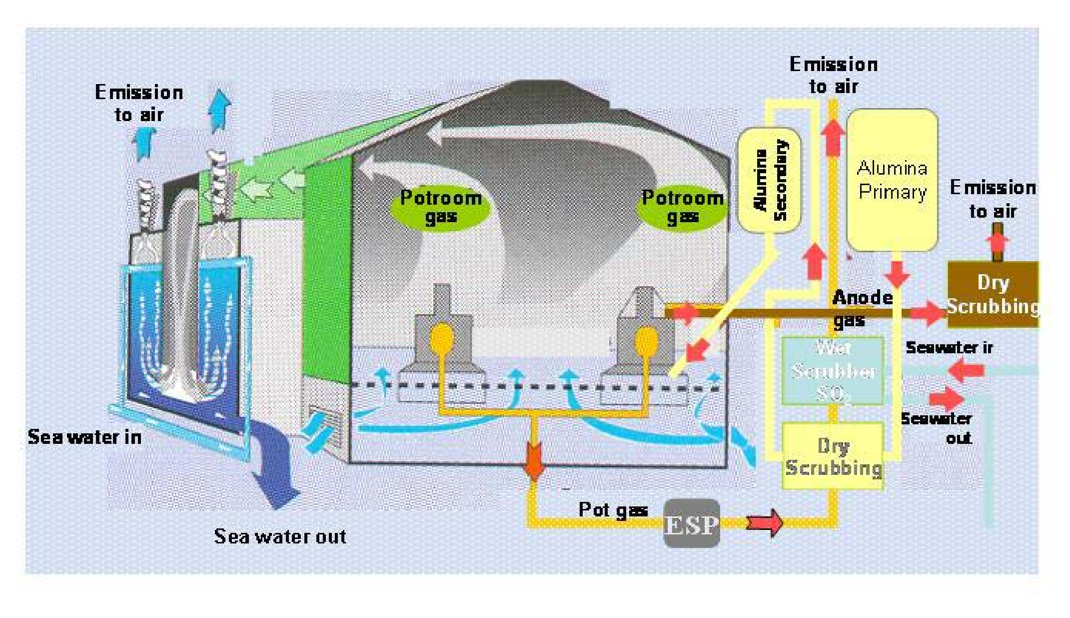


**Figure 4.14:** **Gas collection and cleaning system**

Automatic alumina and $AlF_3$ feeding based on an algorithm determined for the cells have resulted in anode effects being reduced from 2 to 0.1 per cell per day and the duration from 2.5 to 4.5 minutes. *(I guess it should be from 4.5 to 2.5) But in [501a] the average anode effect duraction for Soederberg cells is given to be 1.5 to 2 minutes for almost all Soederberg plants worldwide. So the aforementioned figures seems not to be extraordinary good.*

### Cross-media effects

The use of seawater scrubbers means that PAH and $SO_2$ are released to water and this needs to be assessed. *(This targets the acidification of the sea, look at Franks information on this issue)*

### Operational data

Several improvements have been made to the conventional Søderberg electrode system. The objectives were to reduce anode effects and emissions from the pots to a level comparable with the total emission from prebake pots, including anode baking and the cell layout which is shown in Figure 4.15. The main features are:

- automatic alumina point feeding and control of electrolysis
- complete skirt coverage of bath crust
- the use of dry paste with a lower pitch content *(give more information on this. What means dry? Usually the Søderberg anodes contain more tar pitch binder (25 to 28%)*
- improved burner for incineration of PAH and other hydrocarbons in pot exhaust gas
- improved burner cleaning practice
- complete hood coverage of the anode top, which is connected to a separate gas exhaust and dry alumina scrubber or dry anode top or combination of dry stud hole paste and increased anode height depending on effectiveness.

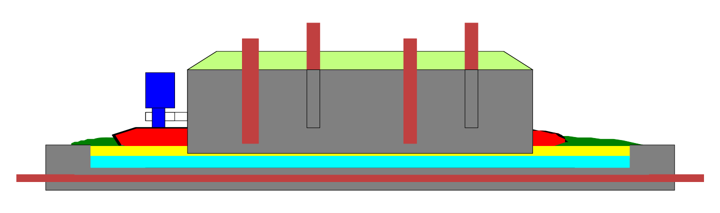


**Figure 4.15: Modified cell layout**

*This picture is not very helpful. Delete!*

**Applicability**

This technique is applicable to all existing Søderberg plants.

*(Which technique? In the aforemention paragraphs many techniques are described?) As it looks different techniques are merged but actually this section focus on dry paste, point feeding and top hood extraction and dry scrubbing.*

**Economics**

Current efficiency is improved by 15 %. *(Which efficiency???)*

Conversion costs for a Søderberg smelter based on the implementation in Norway and other Søderberg plants from 2006 to 2008 are:

- incorporating dry paste, including increased height of anode casing - USD 200/tonne installed capacity
- installation of a point feeding system, including gas manifolds, burners, *(this is unclear, which gas manifolds, which burner?)* other equipment and vehicles - USD 300/tonne installed capacity
- installation of anode top hoods, including dry cleaning of gases with alumina - USD 300/tonne installed capacity.

**Driving force for implementation**

Reduction in environmental impact and compliance with EU Regulations and OSPAR limit values and increased efficiency are the driving forces.

**Example plants**

NO and ES.

**Reference literature**

[ 232, Spanish Mission 2008 ], [ 233, Farrell Nordic Mission 2008 ].

### 4.3.3.5 Control of cell operating conditions (PRIM. AL)

**Description**

The voltage and electrical current are the only parameters for the electrolysis process that can directly be measured on-line. Bath temperature, composition and superheat requirements can be determined periodically.

Process control within the electrolysis process is therefore based on the data from this limited number of parameters. The development of microprocessors has made it possible for modern computers to simulate the electrolysis process by calculating complex models for dynamic kinetics and magnetic fields, based on the limited information available. This results in an improved process control and a more smooth operation of the electrolysis. Smooth process operation will, in general, result in lower emissions of fluorides and dust.

Computerised fluid dynamics (CFD) studies and radioactive tracers have been used to model the movement of fused electrolytes [ 233, Farrell Nordic Mission 2008 ] so that diffuse emissions can be prevented or minimised by optimising gas collection systems. Modification to alumina and $AlF_3$ charging systems to give small, even additions of raw materials have also been developed in parallel and also contribute to the prevention of diffuse emissions.

**Achieved environmental benefits**

The emissions of PFC can be reduced by improved process control. For example, CWPB cells with central point feeding can in general be operated with an anode effect frequency of 0.2 to

0.5 anode effects per pot per day and an anode effect duration of 0.5 to 2 minutes, resulting in a PFC emission of 0.05 to 0.1 kg per tonne aluminium. When modern computers are applied for process control and modern point feeding systems are used for alumina addition, the number of anode effects can further be reduced to a frequency of fewer than 0.1 anode effects per pot per day and the duration of any anode effects can also be reduced. This reduces the emissions of PFC to less than 0.03 kg per tonne aluminium [501].

*Provide real measurement data!*

**Cross-media effects**

Improved process control within the electrolysis process results in a reduction of the electricity consumption. The conversion to point feeding is associated with higher fluoride emissions in the cell gases and will affect the size of the cell gas dry scrubbing system.

**Operational data**

An improved process control reduces the emissions of PFC. The anode effects that cause the PFC emissions are directly related to low alumina concentrations in the cell. The alumina concentration in the electrolyte cannot directly be measured due to the very aggressive nature of this medium and so anode effects are therefore used as an additional method to control the alumina concentration. The anode effects occur when the alumina concentration has decreased below 1 % and are therefore capable of identifying a specific alumina concentration.

By simulating the electrolysis conditions, modern computers are capable of calculating and correcting the alumina concentration. Aluminium fluoride and alumina and additions can then be controlled based on an algorithm of the cell flow pattern and can be added separately to minimise anode effects and reduce their duration. The correction of the alumina concentration in the electrolyte reduces the number of anode effects. This improved process control is often provided with an automated anode effect killing system. This system automatically disturbs the gaseous layer beneath the anode occurring during the anode effects. This can be achieved using compressed air or by changing the anode to cathode distance through raising and lowering of the anode beam.

**Applicability**

This technique is applicable to all Søderberg and CWPB plants that have computer control. There are differences in the control technology and operating philosophy and these need to taken into account but there are opportunities for optimisation in all cases.

*Can control of cell operating conditions in Søderberg plants lead to the aforementioned low emissions?In [500] a range of 0.1 to 0.5 anode effects per day per pot in included.*

**Economics**

Conversion of conventional Søderberg or CWPB plants to point feeder with process controls ~ EUR 100 to 250 per tonne annual capacity.

**Driving force for implementation**

Reduction of greenhouse gas emissions is the driving force.

**Example plants**

NO, FR, NL, ES.

**Reference literature**

[ 97, Lijftogt, J.A. et al 1998 ], [ 233, Farrell Nordic Mission 2008 ], [ 234, UBA Copper, lead, zinc and aluminium 2007 ].

#### 4.3.3.6 Use of dry scrubbing in primary aluminium (PRIM. AL)

**Description**

Dry scrubbing is based on the recovery of fluorides by adsorption on alumina used as the scrubbing agent. The fresh alumina is introduced to a reactor stage together with the process air from the electrolysis. Most of the adsorption of the gaseous fluorides (HF) on the alumina take place in this reactor stage. The mixture of the process air with the alumina then enters a dust removal system where the alumina enriched with fluoride is separated from the process air. In general, fabric filters are used for dust removal. An additional adsorption is achieved in these fabric filters due to the filter cake that is built up on the filters. The alumina removed from the process air is used as alumina feeding for the electrolysis (so called secondary alumina feeding). Control of alumina feeding based on HF concentration in the off-gas allows optimised alumina consumption while stabilising alumina cell feed composition and avoiding emission peaks.

The main purpose of the dry scrubbing system is to remove the fluorides and dust from the process air. An additional adsorption of $SO_2$ on the alumina will also occur. This $SO_2$ is returned to the electrolysis by the secondary alumina feeding. This $SO_2$ captured by the alumina will therefore be completely released by the electrolysis process when the alumina is heated. Hence, the emission of $SO_2$ is not reduced by the dry scrubbing system.

**Achieved environmental benefits**
~~The dry scrubbing system with dust removal ensures very high removal efficiencies, greater than 99.8 % for total fluorides.~~ The exact cleaning efficiency depends on equipment design, alumina properties, plant flexibility and maintenance. The most efficient dry scrubbing installations, operated with alumina with a high specific surface area, i.e. >50 $m^2/g$ [VDI 2286, Part 1], as well as recycling the alumina several times to the reactor, reach average efficiency rates of >99.8 % for total fluorides.
*What is the efficiency for dust?*

**Cross-media effects**
Dry scrubbing requires a significant energy consumption of about 350 kWh per tonne aluminium. No other cross-media effects have been identified.

**Operational data**
A dry scrubbing system is capable of achieving emission levels of:

- gaseous fluorides (HF): 0.03 to 0.2 kg per tonne aluminium
- total fluorides: 0.06 to 0.3 kg per tonne aluminium
- dust: 0.3 to 0.5 kg per tonne aluminium.

(Provide data, use VDI 2286, Part 1) Off gas stream is about 100000 m3/t Al for stack emissions and 1000000 m3/t Al for roof emissions (pot house ventilation).

**Applicability**
This technique is applicable to most installations.

**Economics**
Investment costs of EUR 5 million have been identified to improve the cleaning efficiency of an existing dry scrubbing system with dust removal. Based on anonymous data from plants, the investment costs for new dry scrubbing systems with dust removal range from EUR 10 million to 50 million. Operational costs of EUR 5 to 15 per tonne aluminium were identified.

**Driving force for implementation**
Reduction of HF emissions and dust.

**Example plants**
DE, FR, IT.

**Reference literature**
[ 97, Lijftogt, J.A. et al 1998 ], [ 312, VDI 2286 Aluminium Part 1 and 2 2008 ], [ 316, Dry and Wet Scrubbing 2004 ].
(Only VDI 2286 Part 1 should be mentioned which is from 1998)

*[514} Check and insert data!*

### 4.3.3.7 Use of wet scrubbing in primary aluminium (PRIM. AL)

**Description**
The emissions caused by electrolysis can be abated by wet scrubbing. Wet scrubbing will, in general, be applied as supplementary abatement to the dry scrubbing. The supplementary wet scrubbing is mainly applied for $SO_2$ removal but will also reduce the emissions of fluorides and, to a lesser extent, dust. Wet scrubbing can be applied to gases from the electrolysis cells and to the pot room ventilation gases.

The wet scrubbing process is based on the principle that the pollutants are absorbed and converted by the scrubbing medium. Various cleaning agents can be applied as a scrubbing medium. Within the aluminium industry, seawater is often applied as well as individual applications of sodium hydroxide (NaOH) or sodium carbonate ($Na_2CO_3$). The $SO_2$ is converted into aqueous sulphates by these media. Another possibility is to convert the $SO_2$ to gypsum, using scrubbing agents such as lime hydrate, limestone or mixtures of calcium and magnesium hydroxides.

The scrubbing medium should be refreshed and the medium used should be discharged to allow continuous absorption and conversion.

**Achieved environmental benefits**
The removal of $SO_2$ and other acid gases to reduce the local, regional and long-range impact of these gases.

**Cross-media effects**
All wet scrubbing systems require the absorbed and converted pollutants to be discharged from the system. Discharges can occur as waste water, fluid waste (NaOH and $Na_2CO_3$) or as gypsum. The results of environmental monitoring in the sea and in air should be taken into account to determine the overall reduction in emissions [ 355, Ocean Acidification 2010 ]. The wet scrubbing media used are:

**a) Seawater:** the effluent from the seawater scrubbers (20 to 300 $m^3$ per tonne aluminium) at an aluminium plant is slightly acidic and contains fluorides, sulphite/sulphate, suspended matter and trace contamination (e.g. nickel) and is deficient in oxygen. The plants using seawater will therefore normally have installations for the removal of dust to comply with national legislation for the discharge of this waste water to the sea. Waste water treatment normally includes flocculation and sedimentation. The waste water treatment results in a sludge that should be disposed of. The seawater used in the wet scrubbers can also be treated with biocides, which will also be discharged into the sea. Seawater scrubbing requires an additional energy consumption of about 150 kWh per tonne aluminium.

**b) NaOH:** the scrubbers operated with NaOH require that a concentrated effluent (about 1 $m^3$ per tonne aluminium) be discharged. The pollutants in this effluent can be compared to the pollutants in the discharged seawater but occur in higher concentrations. Nevertheless, the effect on the aquatic environment will remain.

**Operational data**
Removal efficiencies for $SO_2$ of 80 to over 90 % have been identified for wet scrubbers. $SO_2$ emissions can be reduced to concentrations of <10 to 50 mg/$Nm^3$ and loads of 0.9 to 2.9 kg $SO_2$ per tonne aluminium. In addition, the supplementary wet scrubbing results in a reduced emission of fluorides and dust. Emission levels for total fluorides (gaseous and particulate) of 0.02 to 0.2 kg per tonne aluminium have been identified when wet scrubbing is applied as

supplementary abatement. In these situations, dust emissions have been reduced to 0.1 to 0.3 kg per tonne aluminium.

**Applicability**

This technique is applicable when sulphur dioxide concentrations in the air exceed the long-range, local or regional air quality standards. Similar scrubbing techniques may also be applied to remove fluorides, sulphur dioxide and PAH from pot room ventilation air from some SWPB and Søderberg plants. The investment and operating costs are different in these cases.

**Economics**

Cost estimates have been identified for supplementary wet scrubbing of the process air. The cost estimates are presented for scrubbing systems operated with seawater as well as NaOH.

**a) Seawater:** the identified investment costs range from EUR 9 to 36 million. Based on the annual production capacity, investment costs range from EUR 75 to 250 per tonne capacity.

The identified total annual costs range from EUR 2.6 to 7.5 million. Based on the annual production capacity, total annual costs range from EUR 40 to 70 per tonne aluminium.

**b) NaOH:** the identified investment costs range from EUR 12 to 40 million. Based on the annual production capacity, investment costs range from EUR 100 to 250 per tonne capacity. The identified total annual costs range from EUR 4 to 7 million. Based on the annual production capacity, total annual costs range from EUR 100 to 200 per tonne aluminium.

Cost data has been compiled for a variety of process variations and abatement systems. Some costs are included where available with the examples given earlier in this chapter. The cost data is very site-specific and depends on a number of factors but the ranges given may enable some comparisons to be made. Other cost data is provided in an appendix to this note so that costs for processes and abatement systems over the whole of the non-ferrous metals industry can be compared.

The Netherlands have made a comparison between the cost effectiveness of deSO$_X$ abatement techniques of two smelters. The cost effectiveness method that is used is the method described in Section 4.13 of the Netherlands Emission Guideline for Air (NER) and in the BREF cross-media effects and economics as shown in Table 4.42 [ 336, EC 2006 ], [ 241, Netherlands SOX paper 2008 ].

| Cost, effects and cost effectiveness | Plant A | Plant B |
|---|---|---|
| Costs: | | |
| • total investments, EUR million | • 32.4 | • 23.5 |
| • capital costs, EUR K | • 4975 | • 3839 |
| • fixed operation costs, EUR K | • 1002 | • 680 |
| • variable operating costs, EUR K | • 7571 | • 1624 |
| • total net yearly costs, EUR K | • 13548 (A) | • 6143 |
| Effects: | | |
| • yearly unabated load, Ktonne | • 2.67 | • 2.0 |
| • yearly remaining emission, Ktonne | • 0.45 | • 0.3 |
| • avoided $SO_2$ in Ktonne | • 2.2 (B) | • 1.7 |
| Cost effectiveness, EUR per kg: | | |
| • with gas reheating (A/(B*1000)) to prevent occurring of blue mist) | • 6.2 | |
| • without gas reheating | • 3.7 | • 3.6 |

**Table 4.42: Cost effectiveness according to NER methodology**

Data from studies undertaken by Environment Canada and Infomil reports the following economic data for costs per tonne of sulphur dioxide removed [ 303, Canadian Al Rapport final in French.pdf 2008 ] .

- seawater scrubber: EUR 248 - 905.5/t $SO_2$ (annual base): 6 reference plants at coastal sites in Norway
- NaOH-scrubber: EUR 1367 - 1627/t $SO_2$ (annual base): 1 reference plant at an inland site in Norway.

The following processes have not been used in the aluminium sector.

- double alkali scrubber: EUR 1183 - 1270/t $SO_2$ (annual base)
- calcium (carbonate): EUR 1810/t $SO_2$ (annual base)
- calcium (lime): 1954 EUR/t $SO_2$ (annual base).

**Driving force for implementation**
Reduction of all air emissions.

**Example plants**
The only place in Europe where wet scrubbing of the process air from the electrolysis is applied is in Scandinavia. All plants in Norway and Sweden have wet scrubbing. Some of the Søderberg plants also have installed pot room ventilation air scrubbing. These wet scrubbers are mainly in operation at seaside aluminium plants, using seawater as the scrubbing medium. In addition, one plant in Norway has been identified using NaOH as the scrubbing medium, while in the US one plant has been identified operating with $Na_2CO_3$.

**Reference literature**
[ 97, Lijftogt, J.A. et al 1998 ], [ 303, Canadian Al Rapport final in French.pdf 2008 ], [ 316, Dry and Wet Scrubbing 2004 ], [ 347, SO2 EMISSIONS ALCOA EUROPE 2010 ], [ 348, French input for Aluminium 2010 ].

### 4.3.4 Secondary smelting furnaces and gas treatment systems

*(What should be included here are examples for technqiues to consider in the determination for BAT for:*

- *Storage and handling of feedstock materials, e.g. slag,*
    - *Diffuse emissions,prevention, extraction and abatement?*
- *material pretreatment of metal containing feedstock including size reduction, separation methods, dross processing and treatment, swarf processing and treatment such as de-oiling by washing and drying and subsequent compacting*
- *smelting*
    - *dust, NOx, SOx, $Cl_2$, HCl, HF, Total C, PCDD/F, CO, odours, diffuse emissions (charging, melt treatment, slag tapping, skimming, casting) if not sufficiently extracted via rooflights and doors.*
- *mealt treatment such as degassing, purging with inert gas (refining?)*
    - *$Cl_2$, fluorine, HCl, aluminium hydroxide, $AlF_3$*

*including emission data for each process!*

*The cross-references can be considered as not very helpful. In 2.4.3 only very general information is given and furthermore another cross-reference is included to section 2.6 Diffsue emissions from material storage and handling. 2.9. comprises the whole bunch of abatment techniques.*

**Description**
Several of the techniques described in Sections 2.4.3 and 2.9 are applicable to fume extraction and abatement and the process control systems used in this sector but these techniques are not routinely used by all installations. The furnaces that are described in Section 4.1.2 are the

techniques to consider in the determination of BAT when used in conjunction with the following techniques:

- the use of a sealed charging carriage or similar sealing system if possible
- the use of oxy-fuel burners where energy and environmental benefits are established
- the use of low $NO_X$ burners and natural gas as a fuel where available
- the use of regenerative burners to minimise energy ~~use~~consumption.
- the use of enclosures, hoods and targeted fume extraction systems to collect diffuse emissions wherever practicable
- the removal of oil and organic components using swarf drying, centrifuging or other de-coating methods before the smelting or melting stage, unless the furnace and abatement system is specifically designed to accommodate the organic content
- the use of coreless induction furnaces for relatively small quantities of clean metal
- the use of afterburners or RTO where necessary to remove organic carbon including PCDD/F
- injection of carbon together with lime or sodium bicarbonate to reduce acid gases and organic carbon including PCDD/F
- the use of scrap preheating~~, regenerative burners~~ or heat recovery if practicable
- the use of suitable -filtration technology, e.g. fabric or ceramic filters.

Table 4.43 gives an overview of the advantages and disadvantages of secondary smelting and melting furnaces and the raw materials that can be recovered in them.

| Furnace type | Variations | Principal application | Advantages | Disadvantages | Gas collection | Comments |
|---|---|---|---|---|---|---|
| Reverberatory or closed-well | Standard | Melting larger volumes of clean scraps and feedstock contaminated with organic materials | • large metal capacity (100t)<br>• few restrictions on feedstock sizes<br>• no salt use. | • lower thermal efficiency<br>• restricted feedstock types. | Semi-sealed | • high yields due to quality of feedstock<br>• molten metal pumps sometimes used. |
| | Side-well | As above, but enables efficient recovery of some finer feedstocks. | • large metal capacity<br>• wider range of feedstock possible<br>• normally no salt use.. | • lower thermal efficiency | Semi-sealed | • high yields possible depending upon quality of feedstock<br>• molten metal pumps sometimes used. |
| | Sloping hearth | Separation of aluminium from higher melting point metal contamination (i.e. iron/steel) | • very efficient at removing high melting point contaminants. | • lower thermal efficiency | Semi-sealed | • Sometimes incorporated into other furnace types<br>• yield dependant upon level of contamination. |
| Rotary | Fixed axis | Recycling a wide range of feedstocks | • no feedstock restrictions<br>• good thermal efficiency<br>• efficient demagging<br>• no skimmings or dross produced<br>• large charge volumes possible(>65t). | • relatively high usage of salt cover<br>• feedstock size may be restricted. | Semi-sealed | Resultant salt slags must be reprocessed. |
| | Tilting | As fixed axis | • as fixed axis, but lower usage of salt cover and lower capacity. | • feedstock size may be restricted. | Semi-sealed | • tends to be used for lower scrap grades and dross. |
| Induction | Coreless | Melting of cleaner scraps or primary feedstock | • high yields obtained<br>• no combustion gases<br>• no salt cover required<br>• flexible usage (batch and continuous processing possible). | Relatively small load (<10t)<br>Restricted feedstock type<br>Feedstock size may be restricted | Open, hooded | |
| | Channel | As coreless | • high yields obtained<br>• no combustion gases<br>• no salt cover required. | As coreless, but able to have larger capacities(~20 - 25t) | Semi-sealed | |
| Shaft furnace | | Melting clean ingot and process scraps in foundries. | • better thermal efficiency. | • restricted feedstock types<br>• feedstock size may be restricted. | Semi-sealed | • used in Meltower process. |

**Table 4.43: Overview of the advantages and disadvantages of secondary smelting and melting furnaces and the raw materials that can be recovered in them**
[ 272, Al input 2008 ]

**Achieved environmental benefits**
The prevention of dust and metal emissions.

**Cross-media effects**
None reported.

**Operational data**
The re-use of filter dust from secondary aluminium production is demonstrated in Spain and Austria. Dust and fume from a rotary furnace is treated with sodium bicarbonate and activated carbon as the scrubbing medium to remove chlorides produced by the salt cover and sodium chloride is formed. The dust is then collected in a fabric filter and can be included with the salt charged to the furnace.

The use of metal pumping or electromagnetic stirring to increase efficiency, sealed charging systems and intelligent fume collection control to prevent dust emissions and preheat the charge should be used depending on the furnace type. It is necessary to select the feed material to suit the furnace type and abatement systems that are used and to transfer unsuitable raw materials to other operators using equipment designed for them. See also Table 4.43.

**Applicability**
These techniques are applicable to all secondary aluminium plants.

**Economics**
Economics information is not available but most installations are operating viably.

**Driving force for implementation**
Increase in efficiency and recovery and environmental regulation.

**Example plants**
DE, BE, UK, AT, ES.

**Reference literature**
[ 256, Plant visit report AMAG 20071114.doc 2007 ] [ 312, VDI 2286 Aluminium Part 1 and 2 2008 ], [ 272, Al input 2008 ].

### 4.3.5 Salt slag

Salt slag is produced in many installations but the use of salt for the recovery of secondary aluminium is not needed in all cases. Some furnaces use less salt per tonne of aluminium produced than others and some raw materials can also depend less on the use of salt cover. Salt slag is a hazardous waste and should not be landfilled. The following hierarchy should be used when choosing the furnace and raw material input:

- prevent the use of salt where practicable, consistent with achieving the maximum practical yield
- minimise the use of salt, e.g. by using a tilting rotary furnace
- to recover as many by-products as possible from salt slag that is produced when salt fluxes are used.

It is necessary to select the feed material to suit the furnace type and abatement systems that are used and to transfer unsuitable raw materials to other operators using equipment designed for them [ 267, BEFESA 2008 ]. The following examples show how the use of salt cover can be eliminated, reduced in quantity or ultimately recovered.

Each option should be considered in line with the process technology used. Each of these items has its own inherent advantages and disadvantages, such as restrictions in feedstock material or metal volumes, which must also be considered.

#### 4.3.5.1 Use of metal pumping or stirring system to improve efficiency and reduce salt usage

**Description**

This technique uses a reverberatory furnace (also a called chamber or well furnace) with a side well, a charge well and a pumped metal system. Mechanical or electromagnetic stirring transfers heat from the main hearth to the charge well and the absence of a flame reduces oxidation of metal and so is not dependant on the use of salt.

The stirring of the contents using electromagnetic systems situated below the furnace is also used to improve efficiency, in these cases the total contents of a furnace are stirred. The use of a side well allows fine aluminium particles to 'dissolve' in the circulating molten metal and reduce losses due to oxidation (see Figure 4.16).

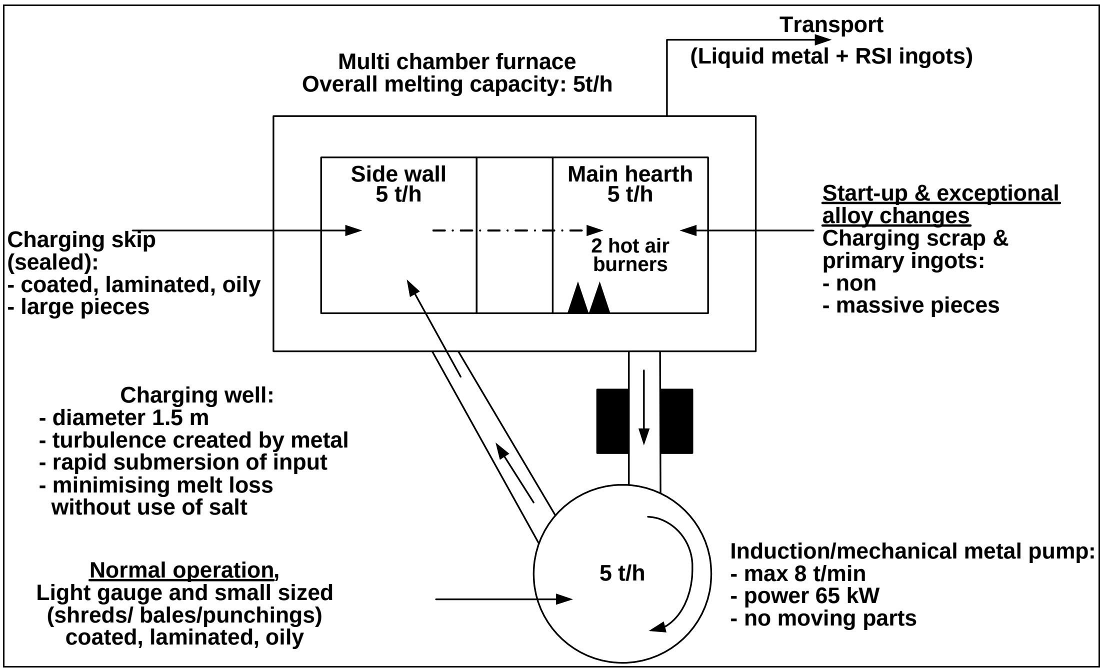


**Figure 4.16: An example of a pumped metal system**

[ 234, UBA Copper, lead, zinc and aluminium 2007 ]

The use of a charge preheating chamber is very effective in combination with stirring systems. Hydrocarbons are emitted during charge preheating as the contents are pyrolised from the scrap. The gases that are produced are directed to the furnace burner system which destroys the hydrocarbons and utilises the energy content for melting.

**Achieved environmental benefits**

The potential elimination of salt cover and a greater range of raw materials than simple reverberatory furnaces as well as an improved capture of furnace gases. A reduction of the amount of waste produced that requires treatment and an associated reduction in energy usage and emissions from the furnace.

**Cross-media effects**

Non have been reported.

**Operational data**
The operational data is included with the description and there is an improvement in metal yield and reduction in energy costs.

**Applicability**
This technique is applicable to new and upgraded reverberatory furnaces that can be adapted to use stirring.

**Economics**
Costs in 1997 of a 30 tonne furnace and electro-magnetic pumping system were EUR 2.73 million. The estimated cost savings (energy, improved yield, flux savings and treatment savings) were EUR 1.26 million per year with a pay back of 2.2 years.

Cost of pumping system and charge well ~ EUR 456000.

**Driving force for implementation**
Reduction of salt slag use, improved yield and improved quality.

**Example plants**
UK, BE, DE, AT, ES.

**Reference literature**
[ 120, McLellan 1998 ], [ 119, McLellan 1998 ], [ 256, Plant visit report AMAG 20071114.doc 2007 ] [ 232, Spanish Mission 2008 ].

### 4.3.5.2 Use of a tilting rotary furnace to improve efficiency and minimise the use of salt cover

**Description**
A tilting rotary furnace can minimisation the amount of salt cover by using improved mixing and agitation to achieve adequate cover of the melt to remove impurities.

**Achieved environmental benefits**
Reduction in the amount of salt slag produced to <0.5 kg salt per kg of non-metallic content of the raw material. Reduction of amount of waste produced that requires treatment and an associated reduction in energy and emissions from treatment process [ 256, Plant visit report AMAG 20071114.doc 2007 ].

**Cross-media effects**
None reported.

**Operational data**
A reduction of the salt usage factor to <0.5 and an improvement in recovery of aluminium and an extension of the range of raw materials that can be used .

**Applicability**
The technique is applicable to new furnaces. There are size restrictions, i.e. very small particles will be oxidised and large items will not fit in the furnace and therefore the technique is not applicable for all feedstock.

**Economics**
Not known – The cost of the furnace less the cost savings from the purchase and treatment of salt are reported to be an economical benefit, several plants are operating viably.

**Driving force for implementation**

Reduction of salt slag production and improved yield of metal.

**Example plants**
Plants in use in AT, DE and UK.

**Reference literature**
[ 142, Boin, U. et al. 1998 ], [ 256, Plant visit report AMAG 20071114.doc 2007 ].

### 4.3.5.3 Full recycling of salt slag

**Description**
Aluminium salt slags are recovered in a full recycling processes. In the full recycling processes, the salt slag is completely recovered to marketable products without producing any residues and it is also possible to avoid the production of waste water. The following components are recovered.

1. Reclamation of 95 % of aluminium metal.
2. Reclamation of 100 % of soluble salt
3. Reclamation of 100 % of insoluble aluminium oxides.

The process is a combination of different physicochemical steps that exploit different material characteristics of the three main salt slag components:

- Metallic aluminium (5 - 20 % in typical salt slag) which is nearly insoluble in water; during crushing it shows distinct ductile material behaviour.
- Oxidic components (35 - 55 % in typical salt slag) which are insoluble in water and are brittle. They form a fine dust when crushed.
- Alkaline chlorides (35 - 55 % in typical salt slag) which are very soluble in water, they are brittle and can be crushed.

The large blocks of salt slag are crushed to a manageable size and sieved to recover metallic aluminium granules (typically up to 10 %). The finely crushed material is then dissolved in water. The soluble chloride goes into solution and forms brine. The coarse aluminium granulates are separated from the insoluble fraction, consisting of metallic oxides (predominately alumina) and fine metallic aluminium powder in a wet sieve.

During the recovery process, hydrogen, ammonia, hydrogen sulphide, phosphine and methane, as well as dust, develop in different plant sections. They are collected and treated either thermally to recover energy or in a wet system to convert ammonia to ammonia sulphate which can be recovered for sale [ 267, BEFESA 2008 ].

The residual metal oxides comprise aluminium, magnesium and calcium oxides (up to 65 % $Al_2O_3$) and also contain sulphates, nitrates and chlorides. By reducing these anions to manageable values in further process steps (washing and drying), a fine aluminium oxide is produced that can be sold to the brick, ceramics, clay, cement and mineral wool industry. The brine solution from the washing can be returned to the dissolution stage. Thus a complete recovery of the materials present in the salt slag is achieved.

There are some variations in the processes that are used (mechanical pretreatment, leaching stage, waste gas treatment, solid/liquid separation). In some plants the grinding system is dry, while in others the last grinding stage is carried out using water. All the grinding installation equipment is sealed to prevent diffuse dust emissions.

**Achieved environmental benefits**
Prevention of land fill, recovery of salt for re-use, aluminium portion for recycling and production of alumina for sale and the production of ammonia sulphate for use as fertiliser. The

full recycling processes are waste water free. The only process waste is activated carbon if used. The emissions to air are shown in .

**Operational data**
Off-gas treatment using activated carbon might have a significant advantage in eliminating phosphine compared to afterburning but the disposal or treatment of spent carbon should be considered. The crushing operations can be very dusty when not being processed under adequate off-gas extraction.

**Cross-media effects**
Energy use is higher compared to partial recycling. There are potential emissions to air of ammonia, phosphine, hydrogen sulphide and dust if off-gas-cleaning is not used.

**Economics**
Not known - cost of process equipment. Several plants are operating viably and treatment costs are similar to disposal costs but avoid "future liability".

**Driving force for implementation**
Recovery of all of the components of the slag and prevention of landfill.

**Applicability**
This technique is applicable to all processes using salt cover.

**Example plants**
DE, ES, FR, UK, IT

**Reference literature**
[ 113, ALFED 1998 ], [ 142, Boin, U. et al. 1998 ], [ 202, Fundación Entorno, Empresa y Medio Ambiente 1999 ], [ 233, Farrell Nordic Mission 2008 ], [ 312, VDI 2286 Aluminium Part 1 and 2 2008 ], [ 234, UBA Copper, lead, zinc and aluminium 2007 ], [ 267, BEFESA 2008 ].

### 4.3.5.4 Partial recycling of salt slag

**Description**
The process follows the same stages as the full recycling processes but not all of the components of the salt slag are recovered. One process recovers the aluminium and potassium chloride and the oxide portion that contains the sodium chloride is used to cover a tailings pile which is ultimately grassed over. Salt is leached from the tailings. Another process recovers all of the solid components and the salt solution is discharged below the biotopical zone of a fjord.

**Cross-media effects**
Potential emissions of phosphine to air if carbon filtration or after-burning is not used. The crushing operations can be very dusty when not being processed under adequate off-gas extraction. Salts leached from the residue or discharged as a solution to the sea can have an impact on the receiving waters or ground water.

**Achieved environmental benefits**
Reduction of land fill, recovery of aluminium portion.

**Operational data**
Two different types of partial recycling processes are used.
In one case, 95 % of aluminium content; 30 % of KCl; 0 % of oxide content are recovered.
In the other case, 95 % of aluminium content; 0 % of KCl; 100 % of the oxide content are recovered.

**Applicability**

Applicable to two existing processes.

**Economics**

Economic data was not available but two plants are operating. They report a reduction in energy use compared to the full recyscling process but in neither case is salt recovered for reuse.

**Driving force for implementation**

Recovery of some components of salt slag.

**Example plants**

DE. NO.

**Reference literature**

[ 233, Farrell Nordic Mission 2008 ], [ 272, Al input 2008 ] [ 312, VDI 2286 Aluminium Part 1 and 2 2008 ], [ 234, UBA Copper, lead, zinc and aluminium 2007 ].

## 4.3.6 Gas collection and abatement

### 4.3.6.1 Use of sealed charging carriage (SEC. AL)

**Description**

A charging car or skip is used to transfer scrap into a reverberatory furnace. The system is sized so that the skip seals against the open furnace door during the discharge of scrap and so maintains furnace sealing during this period. The system can also incorporate a chamber to allow preheating of scrap before charging.

**Achieved environmental benefits**

Prevention of diffuse emissions of smoke and fumes during charging of scrap.

**Cross-media effects**

None reported.

**Operational data**

Included in the description.

**Applicability**

This technique is applicable to some non-rotating furnaces.

**Economics**

No data has been reported but thought to be low-cost for a suitably sized charging skip.

**Driving force for implementation**

Reduction in diffuse emissions and recovery of energy.

**Example plants**

BE, AT, ES.

**Reference literature**

[ 118, Laheye, R. et al. 1998 ], [ 231, FF Mission 2007 ].

*Is there a way to measure the benefit from using this technique?*
*Some parts (high lighted in yellow) should be rephrased.*

### 4.3.6.2 Use of targeted fume collection (SEC. AL)

**Description**

A fume collection system can be designed so that the collection fan capacity can be directed to sources of fumes that change over the charging, melting and tapping cycles. The targeting of fume collection capacity can be achieved by using automatically controlled dampers that are linked to the furnace controls, e.g. door opening, burner state or furnace inclination. Damper operations can therefore be initiated by charging, melting and tapping operations and the fume collection effort can be targeted accordingly.

**Achieved environmental benefits**
The prevention and minimisation of diffuse emissions to air.

**Cross-media effects**
Positive effect from the prevention of diffuse emissions and optimising fan energy consumption.

**Operational data**
No operational data are available but observations indicate that such systems are very effective if designed and controlled well.

**Applicability**
This technique is applicable to most installations.

**Economics**
No data has been reported. Relatively low cost of control and damper system.

**Driving force for implementation**
A reduction in emissions and the ability to access the furnace, reduction of energy use.

**Example plants**
UK, FR, PL.

**Reference literature**
[ 103, Farrell, F. 1998 ], [ 230, FF Mission report 2007 ].

### 4.3.6.3 Collection of fumes (SEC. AL)

*This example is included in the general Chapter 2 and in other sections but in no way specific information hase been given which can be considered as useful.*
*Collection efficiency (diffuse emissions before and after)*
*Costs*
*Cross media / energy versus reduced emissions*
*Real examples*

**Description**
A fume collection enclosure is used to cover both the charging and tapping zones of a rotary furnace to allow the use of a single extraction point, see Figure 4.17.

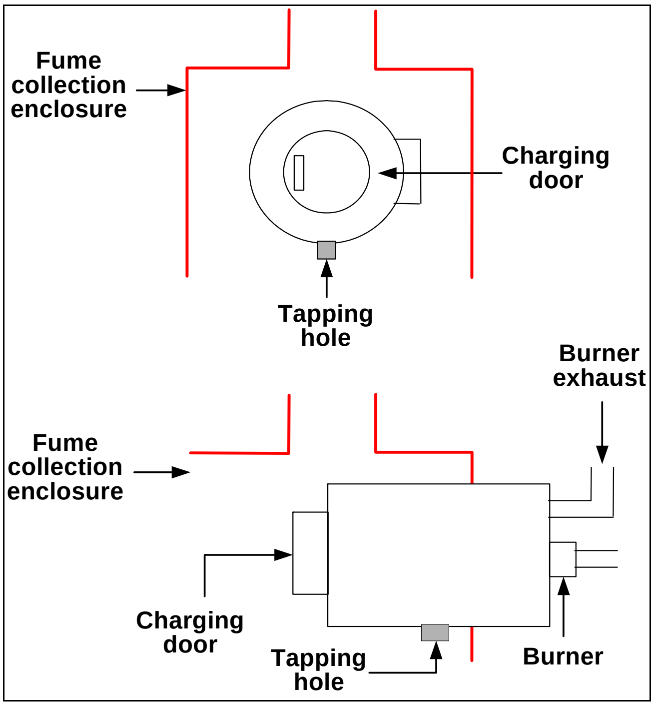


**Figure 4.17: A diagram of an integral fume collection system**
*Can this be considered as a diagram?*

Use in various applications for the production of other non-ferrous metals. The tapping holes on the charging door have been used and allow a more compact enclosure. Furnace lining wear may mean that door end tapping holes may not allow all of the metal to be tapped.

**Achieved environmental benefits**
Easier, effective fume collection from a single point prior to treatment with reduced power consumption.

**Cross-media effects**
No data has been reported.

**Operational data**
No data has been reported but observation shows effective fume capture.

**Applicability**
This technique is applicable to all rotary furnaces.

**Economics**
Low cost of modification, in use viably in several installations.

**Driving force for implementation**
Reduction in emissions, ability to access the furnace, reduction of energy use.

**Example plants**
France, UK.

**Reference literature**
[ 103, Farrell, F. 1998 ].

#### 4.3.6.4 Use of oxygen enrichment in combustion systems (SEC. AL)

*Cross check with sections 2.9.2.4.3 where something is included about oxygen enrichment which should be included here. In and 2.9.2.9. almost the same info as here is presented.*

*Try to get a few good examples about oxygen enrichment and oxy-fuel burners and describe accurately the effect on NOx concentration. So far there are contradictory statements in the document. See sections 4.2.4.1.4, 2.9.2.9, 2.9.2.4.3. Make this section Al specific.*

**Description**
Oxygen enrichment of the combustion air is frequently used in the production processes for non-ferrous metals. The processes use tonnage oxygen directly or in the furnace body. This enrichment is used to allow autothermal oxidation of sulphide-based ores, to increase the capacity or melting rate of particular furnaces and to provide discrete oxygen-rich areas in a furnace to allow complete combustion separately from a reducing zone.

The use of oxygen can give both financial and environmental benefits provided that the plant can accommodate the extra heat released. There is a possibility that higher concentrations of nitrogen oxides can be produced with oxygen enrichment but the associated reduction in gas volume usually means that the mass is reduced.

**Achieved environmental benefits**
The prevention of emissions of metals, dust and other compounds to all media and a potential reduction in energy use are the achieved environmental benefits.
*In [276] are lot of measured values between 2000 and 2007. Include all the information here.*

**Cross-media effects**
No data has been reported.

**Operational data**
Oxygen enrichment can achieve the following improvements:

- The increase in the heat released in the furnace body allows an increase in the capacity or melting rate and a reduction in the quantity of fuel used and an associated reduction in greenhouse gas emissions. It is possible to operate some processes autothermally and vary the extent of oxygen enrichment on-line to control the metallurgical process and prevent emissions.
- A significant reduction in the volume of process gases produced as the nitrogen content is reduced. This allows a significant reduction in the size of downstream ducts and abatement systems and prevents the loss of energy involved in heating the nitrogen.
- An increase in the concentration of sulphur dioxide (or other products) in the process gases allows conversion and recovery processes to be more efficient without using special catalysts.
- The use of pure oxygen in a burner leads to a reduction of nitrogen partial pressure in the flame and therefore **thermal $NO_X$ formation** may be reduced. This may not be the case with oxygen enrichment in or near the burner, or if there is significant leakage of air into the furnace as the higher gas temperature may promote thermal $NO_X$ formation. In the latter case, oxygen can be added downstream from the burner to reduce this effect and maintain the improvement in the melting rate.
- The production of tonnage oxygen on site is associated with the production of nitrogen gas separated from the air [ 115, ETSU (UK) 1996 ]. This is used occasionally for inert gas requirements on site. Inert gases are used for abatement systems when pyrophoric materials are present (e.g. dry Cu concentrates), for degassing molten metal, for slag and dross cooling areas and for fume control of tapping and pouring operations.
- Injection of oxygen at discrete points in a furnace downstream of the main burner allows temperature and oxidising conditions to be controlled in isolation from the main furnace operations. This allows the melting rate to be increased without an unacceptable increase in temperature. An example is the provision of an integral afterburning zone in a blast furnace.

**Applicability**

This is a technique that can be applied to most of the combustion and pyrometallurgical processes in use. The full benefit is achieved with a new plant where the combustion chamber and abatement systems can also be designed for the lower gas volumes. The technique is also applicable to existing plants and can in many cases be retrofitted.

**Economics**

Some data on costs involved in oxy-fuel firing are available for secondary aluminium production (see Table 4.44) which gives a comparison of an oxy-fuel burner with an air-fuel burner. Gas consumption savings of EUR 12/t are reported which, on the basis of an expected production of 13500 t/year (one furnace), represents an annual savings of EUR 152000. Oxygen consumption represents an additional cost of EUR 12/t, which represents an annual cost of EUR 152000. The economical advantages are therefore mainly related to improvements in terms of production rate. In 1999 the fixed costs were around EUR 145/t for two furnaces (22561 tonnes produced/year). The higher productivity allowed by using oxy-fuel burners would result in a cut in these costs to around EUR 122/t (22651 × 145/27000). There is therefore a potential saving of EUR 23/t for a production rate of 27000 t/y.

| Parameter | Benefits/costs | Comment |
|---|---|---|
| Melting time | - 2.45 h/charge | Reduced batch melting time |
| Productivity | + 0.84 t/h | Increased productivity of the furnace |
| Gas consumption | - 80 $m^3$/t<br>(tonne of oxygen) | Reduced consumption of gas |
| $O_2$ consumption | + 126 $m^3$/t | Additional consumption of oxygen |

**Table 4.44: Comparison of an oxy-fuel burner with an air-fuel burner**
[ 276, French PCDD/F Report 2008 ]

**Driving force for implementation**

Reduction of emissions, saving energy.

**Example plants**

Plants in DE, AT, FR, BE, UK.

**Reference literature**

[ 122, ETSU 1994 ], [ 276, French PCDD/F Report 2008 ], [ 103, Farrell, F. 1998 ].

## 4.3.7 Other process stages

**Descriptions**

**a) Refining processes**

- The use of chlorine mixed with argon or nitrogen as the degassing or demagging reagent or the use of aluminium fluoride, KF or $Na_3AlF_6$. The collection and treatment of the resulting gases to remove acid gases.
- The use of in-line flow cells for gas additions to the molten metal.
- The use of in-line ceramic metal filters to remove solid particles from the melt.

**b) Casting processes**

The casting processes that are detailed in the Section 4.1 in conjunction with effective fume extraction of launders and casters where needed.

**c) Skimmings or dross**

The processes for skimmings or dross detailed in the Section 4.1.2.3 in conjunction with the following features to minimise environmental impact are the techniques to consider in the determination of BAT:

- cooling of skimmings or dross in sealed containers under inert gas
- cooling of skimmings or dross in sealed containers
- the prevention of wetting of the skimmings or dross
- the treatment and recovery of skimmings or dross
- minimisation of material for landfill.

**d) Process control**

The principles of process control discussed in Section 2.8 are applicable to the production processes used in this sector. Some of the processes are capable of improvement by the adoption of many of these techniques. The monitoring of cell operating conditions and the use of comparative data-bases to anticipate process disturbances such as anode effects and to control point additions of alumina should be considered for all primary aluminium processes.

**e) Waste water**

This is a site-specific issue; existing treatment systems are reported to be to a high standard. Waste water prevention and reduction systems should be implemented and cooling water should be recirculated. All waste water should be treated to remove solids and oils/tars, absorbed acid gases (e.g. sulphur dioxide, HCl) should be neutralised. The techniques listed in Sections 2.10 and 4.1 are the techniques to consider. In a number of installations; cooling water and treated waste water including rainwater is re-used or recycled within the processes.

**f) Process residues**

The principles of the minimisation and re-use of process residues reported in Section 4.1. Skimmings or dross can be recycled and pot lining can be re-used. Furnace linings and filter dusts can be re-used in certain processes, the use of sodium bicarbonate as a dry scrubbing medium can allow the resulting filter dust to be sent to a salt slag recovery system. Salt slag recovery techniques are available to recover salt, aluminium and aluminium oxide. Skimmings or dross can be re-used in appropriate processes.

**Achieved environmental benefits**

Prevention of emissions of dust, fume and acid gases from the processes and the reduction in waste water volume and loading.

**Cross-media effects**

Use of energy.

**Operational data**

No data has been reported but observations have shown that the processes are effective.

**Applicability**

The processes and techniques are suitable for use with new and existing installations.

**Economics**

There is a low cost of modification and the techniques are in use viably in several installations.

**Driving force for implementation**

Reduction in emissions, the ability to access the furnace and reduction of energy use are the driving forces.

**Example plants**

ES, NO, DE, FR, UK, IT.

**Reference literature**

[ 103, Farrell, F. 1998 ] [ 312, VDI 2286 Aluminium Part 1 and 2 2008 ].

#### 4.3.7.1 Use of spent pot lining

**Description**
The use of SPL carbon content in thermal processes with several successful applications in cement firing, as a carburant in steel and ferro-alloy production and as a coke substitute in rock wool production.

**Achieved environmental benefits**
Use of the energy content of the carbon, use of residual $AlF_3$ as a flux. Destruction of any CN content. Elimination of waste deposited on land. Avoidance of energy input and associated emissions if the SPL is treated thermally.

**Cross-media effects**
None has been reported.

**Operational data**
No data has been reported

**Applicability**
This technique is applicable to all SPL provided that waste transfer regulations allow it.

**Economics**
No net income but avoidance of treatment or disposal charges.

**Driving force for implementation**
Recovery of carbon and prevention of disposal are the driving forces.

**Example plants**
FR, NO, ES.

**Reference literature**
[ 103, Farrell, F. 1998 ], [ 233, Farrell Nordic Mission 2008 ].

### 4.3.8 Gas cleaning techniques

**Descriptions**

**a) Primary aluminium**
The techniques discussed earlier in Section 4.2:

- to seal the cells and maintain collection efficiency for the collection of fume from the cells involved in the production of primary aluminium
- the use of a dry scrubber followed by a fabric filter to remove fluorides
- the collection of the ventilation air from the cell rooms
- the use of secondary hoods for the charging of casting furnaces
- the use of seawater or caustic scrubbers to remove sulphur dioxide may be considered for the reduction of total $SO_2$ emissions.

**b) Integrated anode production**

- the use of the integrated anode production processes outlined in Chapter 12, using the alumina scrubber and fabric filter system from the cell gas treatment from anode production *(this is unclear: from the cellgas treatment from anode production?)*
- the use of a coke filter for the mixing and forming stages.

**c) Stand alone anode production**

- the use of a regenerative afterburner with pre and post treatment of the gases

**d) Secondary aluminium**
The techniques to consider to remove dust, acid gases and PCDD/F for the various process stages involved in the production of secondary aluminium are discussed in Section 2.4.3 and 2.9 of this document. There are several site-specific issues that will apply and some of these are discussed earlier in this Chapter 4. The process technologies discussed in this chapter, combined with suitable abatement will meet the demands of stringent environmental protection.

**Achieved environmental benefits**
Prevention of emissions of dust, fume and acid gases from the processes and of oil, tar, acids and solids to water.

**Cross-media effects**
Use of energy. The cross-media effect on water should be considered on a local basis where seawater is used as a scrubbing medium.

**Operational data**
No data has been reported but observation shows that the processes are effective.

**Applicability**
The processes and techniques are suitable for use with new and existing installations.

**Economics**
Low cost of modification, in use viably in several installations.

**Driving force for implementation**
Reduction in emissions, ability to access the furnace, reduction of energy use.
**Example plants**
ES, NO, DE, FR, UK, IT.

**Reference literature**
[ 103, Farrell, F. 1998 ] [ 312, VDI 2286 Aluminium Part 1 and 2 2008 ].

## 4.4 Best Available Techniques

In understanding this section and its contents, the attention of the reader is drawn back to the Preface of this document and in particular the fifth section of the Preface: 'How to understand and use this document'. The techniques and associated emission and/or consumption levels, or ranges of levels, presented in this chapter have been assessed through an iterative process involving the following steps:

- identification of the key environmental issues for the sector which are:
    - for primary aluminium production: fluorides (including HF), dust, $SO_2$, chlorine, VOCs, fume, greenhouse gases (PFCs and $CO_2$), residues such as bauxite residue, SPL, filter dust
    - for anode production PAH, hydrocarbons, dust, fume, odours, $SO_2$
    - for secondary aluminium: dust, $NO_X$, $SO_2$, VOCs, fume, PCDD/F formation, chlorine, HCl and HF and residues such as filter dust and salt slag.
- examination of the techniques most relevant to address these key issues;
- identification of the best environmental performance levels, on the basis of the available data in the European Union and worldwide;
- examination of the conditions under which these performance levels were achieved; such as costs, cross-media effects, and the main driving forces involved in the implementation of the techniques;
- selection of the best available techniques (BAT) and the associated emission and/or consumption levels for this sector in a general sense, all according to Article 2(12) and Annex IV to the Directive.

Expert judgement by the European IPPC Bureau and the relevant Technical Working Group (TWG) has played a key role in each of these steps and in the way in which the information is presented here.

On the basis of this assessment, best available techniques, and as far as possible emission and consumption levels associated with their use, are presented in this section that are considered to be appropriate to the sector as a whole and in many cases reflect the current performance of some installations within the sector. Where emission and consumption levels "associated with best available techniques" are presented, this is to be understood as meaning that those levels represent the environmental performance that could be anticipated as a result of the application, in this sector, of the techniques described, bearing in mind the balance of costs and advantages inherent within the definition of BAT. However, they are neither emission nor consumption limit values and should not be understood as such. In some cases, it may be technically possible to achieve better emission or consumption levels but due to the costs involved or cross-media considerations, they are not considered to be appropriate as BAT for the sector as a whole. However, such levels may be considered to be justified in more specific cases where there are special driving forces.

The emission and consumption levels associated with the use of BAT have to be seen together with any specified reference conditions (e.g. averaging periods).

The concept of 'levels associated with BAT' described above is to be distinguished from the term 'achievable level' used elsewhere in this document. Where a level is described as 'achievable' using a particular technique or combination of techniques, this should be understood to mean that the level may be expected to be achieved over a substantial period of time in a well maintained and operated installation or process using those techniques.

Where available, data concerning costs have been given together with the description of the techniques presented in the previous sections. These give a rough indication about the magnitude of the costs involved. However, the actual cost of applying a technique will depend strongly on the specific situation regarding, for example, taxes, fees, subsidies, and the technical characteristics of the installation concerned. It is not possible to evaluate such site-specific factors fully in this document. In the absence of data concerning costs, conclusions on economic viability of techniques are drawn from observations on existing installations.

The BAT (including the associated emission and consumption levels) given in this section are 'BAT in a general sense' (i.e. considered to be appropriate to the sector as a whole). It is intended that they are a reference point against which to judge the current performance of an existing installation or to judge a proposal for a new installation. In this way, they will assist in the determination of appropriate 'BAT-based' conditions for the installation or in the establishment of general binding rules under Article 9([8]) of the IPPC Directive. It is foreseen that new installations can be designed to perform at or even better than the BAT levels presented in this section. It is also considered that existing installations could move towards the BAT levels presented in this section or do better, subject to the technical and economic applicability of the techniques in each case.

While the BAT reference documents do not set legally binding standards, they are meant to give information for the guidance of industry, Member States and the public on achievable emission and consumption levels when using specified techniques. The appropriate permit conditions for any specific case will need to be determined taking into account the objectives of the IPPC Directive and the local considerations.

**Recommendation to help users/readers of this document:**

It is strongly recommended that this section on BAT be read in conjunction with the sections of this document that describe the techniques to consider in the determination of BAT. The applicability of the techniques and measures are reported in these sections and have to be taken into account at a local level. To help the reader, references to the appropriate sections are included in the description of BAT.

If not otherwise mentioned, BAT associated emission and consumption levels given in this section are expressed as follows:

- for pollutants emitted to air (except dioxins): expressed on a daily average basis with standard conditions of 273 K, 101.3 kPa, measured oxygen content and dry gas with the plant operating normally under steady-state conditions and no dilution of the gases;
- for dioxins: expressed as the average over the sampling period which should preferably be a minimum of 6 hours;
- for waste water: based on qualified random samples or 24 hour flow proportional composite samples.

As described in the Preface, this document does not propose emission limit values. The BAT and the ranges of emission or consumption levels associated with BAT (BAT-AEL ranges) are related to installations with different sizes, different kinds of operation and different raw materials. In this document, special local considerations cannot be taken fully into account. The determination of appropriate permit conditions will involve taking account of local, site-specific factors such as the technical characteristics of the installation concerned, its geographical location and the local environmental conditions. In the case of existing installations, the economic and technical viability of upgrading them also should be taken into account. Even the single objective of ensuring a high level of protection for the environment as a whole will often involve making trade off judgements between different types of environmental impact, and these judgements will often be influenced by local considerations.

Although an attempt is made to address some of these issues, it is not possible for them to be considered fully in this document. The techniques and emission and consumption levels presented here will therefore not necessarily be appropriate for all installations. On the other hand, the obligation to ensure a high level of environmental protection including the minimisation of long-distance or transboundary pollution implies that permit conditions cannot be set on the basis of purely local considerations. It is therefore of utmost importance that the information contained in this document be fully taken into account.

Section 2.20 to this document reports BAT for the following common processes and the following sections should be referred to for those techniques that are BAT:

- environmental management systems (EMS) (Section 2.20.1)
- material handling and storage (Section 2.20.2)
- process control (Section 2.20.3)
- fume and gas collection (Section 2.20.4)
- the prevention and the destruction of PCDD/F (Section2.20.5)
- sulphur dioxide removal (Section 2.20.6)
- the removal of mercury (Section 2.20.7)
- effluent treatment and water re-use (Section 2.20.8)
- energy efficiency (Section 2.20.9)
- intermediate products, process residues and wastes (Section 2.20.10)
- emission monitoring (Section 2.20.11)
- prevention of the formation of $NO_X$ (Section 2.20.12)
- removal of dust and particles (Section 2.20.13)

BAT for the production of aluminium is the combination of the generally applicable techniques reported in Section 2.20 and the specific techniques indicated in this section.

## 4.4.1 Prevention and control of emissions to air

### 4.4.1.1 Primary aluminium smelting

**a) BAT is to prevent and control diffuse emissions to air from primary aluminium smelting by using centre worked prebake cells with automatic multiple point feeding of alumina for a new plant and for all plant to use all of the techniques given below (see Section 4.3.3).**

- Use of complete hood coverage of the cells and robust cell covers. Use of an adequate extraction system connected to a gas exhaust and filter. Sealed anode butt cooling system *(Anode butt cooling is not described in this BREF).*
- Use of a programmed system for cell operations and maintenance and minimisation of the time taken for opening covers and changing anodes to achieve better than 99 % fume collection from cells on a long-term basis. *Describe how 99 % can be certainly achieved.*
- Use of established efficient cleaning methods in the rodding plant to recover fluorides and carbon. The use of effective extraction and filtration systems in this area.

**b) BAT is to prevent and control emissions of dust, sulphur dioxide, polyfluorinated hydrocarbons and fluorides from the primary smelting process using the techniques given in Table 4.45 (see Sections 2.9.2.2.4, 2.11.3.4, 2.20.13, 4.2.3.2.5, 4.3.3.1, 4.3.3.4, 4.3.3.5, 4.3.3.6 and 4.3.3.7).**

*Maybe it is reasonable and necessary to distinguish between cell extraction and pot room ventilation (stack emissions and roof emissions). In the associated section it says that extraction of pot room emissions is needed when the cells are not properly sealed. This applies i.e. for SWPB and Soederberg cells. In this case extraction and cleaning of these secondary emissions is needed.*

**The emission levels given in Table 4.45 are the BAT-AELs.**

| Pollutant | Techniques | BAT-AELs | Comments |
|---|---|---|---|
| Dust | Fabric filter | <1 to 5 mg/Nm$^3$ | A bag burst detection system should be used. (See Sections 2.9.2.2.4 and 2.20.13) |
| $SO_2$ | Use of low sulphur content anodes (<2.5 % S) (1) | <50 to 200 mg/Nm$^3$ | Lower cross-media effects than wet scrubbing techniques (see Section XX) |
| | Sea water or alkaline scrubbing (2) | <10 to 50 mg/Nm$^3$ | (See Section 4.3.3.7) |
| Polyfluorinated hydrocarbons | Process control based on active cell databases | <0.1 anode effects per cell per day with a maximum duration of 2 minutes | <0.03 – 0.1 kg/t Al (See Section 4.3.3.5) |
| HF<br>Total fluoride | Alumina scrubber and fabric filter | <0.5 mg/Nm$^3$<br><0.8 mg/Nm$^3$ | Used alumina is fed to the electrolytic cells (see Section 4.3.3.6). |
| NB: Collected emissions only. BAT-AELs are given as daily averages based on steady-state operation or, in cases where continuous monitoring is not practicableas the average over the sampling period.<br>(1) This technique is applicable to new and existing plants.<br>(2) This technique is applicable to new plant and existing plant under the conditions set out in Section 4.3.3.7. | | | |

**Table 4.45: BAT and BAT-AELs to prevent and control emissions to air from primary aluminium smelting**

*The values for PFC are not justified by real measured data. <0.1 is quite ambitious. But <0.1 AEF does not correspond to 0.1 kg/t. It should be 0.03 kg/t. (see 4.3.3.5)*
*In the existing BREF from 2001 $SO_2$ abatment was considered to be not applicable.*

### 4.4.1.2 Anode baking and paste plant

**a) BAT is to prevent and control emissions of dust, hydrocarbons, fluorides, sulphur dioxide and PAH to air from anode production and the production of anode paste by using the techniques given in Table 4.46, Table 4.47, Table 4.48 and Table 4.49 or a combination of them (see Section 4.3.3.1, 4.3.3.2 and Section 2.9.2.2.4)**

**The emission levels given in Table 4.46, Table 4.47, Table 4.48 and Table 4.49 are the BAT-AELs.**

| Pollutant | Techniques | BAT-AELs | Comments |
|---|---|---|---|
| Dust | Fabric filter | <1 to 5 mg/Nm$^3$ | A bag burst detection system should be used. (See Sections 2.9.2.2.4 and 2.20.13) |
| Hydrocarbons (Total) as C | Condenser, adsorber. Back venting of gases during delivery. | <25 mg/Nm$^3$ | (See Sections 2.9.2.6 and 4.2.2.2.1 |
| NB: Collected emissions only. BAT-AELs are given as daily averages based on steady- state operation or, in cases where continuous monitoring is not practicable as the average over the sampling period. | | | |

**Table 4.46: BAT and BAT-AELs to prevent and control emissions to air from the storage and handling of coke and pitch**

| Pollutant | Techniques | BAT-AELs | Comments |
|---|---|---|---|
| Dust | Cyclone plus fabric filter | <1 to 5 mg/Nm$^3$ | A bag burst detection system should be used. (See Sections 2.9.2.2.3, 2.9.2.2.4 and 2.20.13) |
| HF | Dry scrubber with alumina or lime | <0.5 mg/Nm$^3$ | If cleaned anode butts are used (See Section 4.3.3.6) |
| NB: Treated emissions only. BAT-AELs are given as daily averages based on steady-state operation or, in cases where continuous monitoring is not practicable as the average over the sampling period. | | | |

**Table 4.47: BAT and BAT-AELs to prevent and control emissions to air from the grinding and mixing stages**

| Pollutant | Techniques | BAT-AELs | Comments |
|---|---|---|---|
| Dust | Alumina scrubber and fabric filter(1) | <1 to 5 mg/Nm$^3$ | Dust should be monitored continuously (See Sections 2.9.2.2.4 and 2.20.13) |
| BaP (1) | Alumina scrubber and fabric filter(1) | <0.5 µg/Nm$^3$ | (See Sections 4.2.2.2.1 and 4.2.3.2.4) |
| PAH (EPA 16) | Alumina scrubber and fabric filter(1) | <1 mg/Nm$^3$ | (See Sections 4.2.2.2.1and 4.2.3.2.4) |
| Hydrocarbons (Total) as C | Alumina scrubber and fabric filter(1) | 1 to 10 mg/Nm$^3$ | (See Sections 2.9.2.6) |
| HF | Alumina scrubber and fabric filter(1) | <0.5 mg/Nm$^3$ | (See Section 4.3.3.6) |
| Total fluoride | Alumina scrubber and fabric filter(1) | <0.8 mg/Nm$^3$ | (See Section 4.3.3.6) |
| NB: Collected emissions only. BAT-AELs are given as daily averages based on steady-state operation or, in cases where continuous monitoring is not practicable as the average over the sampling period. (1)The reacted alumina | | | |

| should be used in the electrolytic cells. |
|---|

**Table 4.48: BAT and BAT-AELs to prevent and control emissions to air from the baking stage of the production of prebaked anodes in a process sharing the abatement system with a primary aluminium smelter**

| Pollutant | Techniques | BAT-AELs | Comments |
|---|---|---|---|
| PAH (EPA 16) | RTO with pretreatment | 170 to 500 µg/Nm$^3$ | The preferred reporting convention is EPA 16 (See Section 4.3.3.2) |
| Hydrocarbons (Total) as C | RTO with pretreatment | 2 to 5 mg/Nm$^3$ | (See Sections 2.9.2.6 and 4.3.3.2) |
| Dust | Dry absorber | <1 to 5 mg/Nm$^3$ | Dust should be monitored continuously (see Section 2.9.2.2.4) |
| Total fluorides (as HF) | Dry absorber | 0.8 mg/Nm$^3$ | (See Section 4.3.3.2) |
| $SO_2$ | Dry absorber | <50 to 200 mg/Nm$^3$ | (See Section 4.3.3.2) |
| NB Collected emissions only. BAT-AELs are given as daily averages based on steady-state operation or, in cases where continuous monitoring is not practicable as the average over the sampling period. | | | |

**Table 4.49: BAT and BAT-AELs to prevent and control emissions to air from the production of prebaked anodes in a stand alone plant**

(This seems to be wrong crossrefered)

| | | | |
|---|---|---|---|
| Total fluorides (as HF) | Dry absorber | 0.8 mg/Nm$^3$ | (See Section 4.3.3.2) |

### 4.4.1.3 Secondary aluminium smelting

**a) BAT is to prevent and control emissions to air from secondary aluminium production including materials pretreatment, swarf drying, melting and the refining and degassing stages by using one of the techniques listed in Table 4.50 and all of the techniques given in Table 4.51 (see Section 4.3.4, Section 4.2.4.1.5 and Section 4.2.4.1.6).**

| Furnace | Raw materials | Comments |
|---|---|---|
| Reverberatory or closed-well (hearth, or chamber) furnace | Most feedstock. No salt cover is used | Use of sealed charging system, charge preheating, metal stirring or pumping |
| Reverberatory or closed-well furnace with side-well or charging well | Large range of feed material. No salt cover is used | Sealed charging system and charge preheating.<br>Metal pumping or stirring |
| Rotary furnace | No feedstock restrictions. Relatively high usage of salt cover | Targeted fume extraction |
| Tilting rotary furnace | Low grade feed including dross. Moderate use of salt cover | Minimum use of salt cover compared to fixed rotary furnace |
| Induction furnace | Small loads of clean metal | Restricted metal capacity and feedstock |
| Shaft furnace (Meltower) | Clean metal | Charge is preheated |

**Table 4.50: BAT for secondary aluminium furnaces**

**The emission levels given in Table 4.51 are the BAT-AELs.**

| Pollutant | Techniques | BAT-AELs | Comments |
|---|---|---|---|

| | | | |
|---|---|---|---|
| Dust | Fabric or ceramic filter | <1 to 5 mg/Nm$^3$ | A bag burst detection system should be used. (See Sections 2.9.2.2.4 and 2.20.13) |
| $NO_X$ | Low-$NO_X$ burner<br>Oxy-fuel burner<br>Regenerative burner | <100 to 300 mg/Nm$^3$ | (See Sections 2.9.2.4.3 and 2.20.12) |
| Total organic carbon as C | Afterburner<br>Optimised combustion | 1 – 10 mg/Nm$^3$ | (See Sections 2.9.2.6 and 4.2.4.1.6) |
| PCDD/F | High efficiency dust removal system.<br>Afterburner followed by quenching.<br>Absorption on activated carbon. | <0.1 ng I-TEQ/Nm$^3$ | (See Sections 2.10.2.1, 2.20.5 and 4.2.4.1.6) |
| Chlorine, $SO_2$ and acid gases | Use of mixtures of chlorine and argon/nitrogen or $AlF_3$, $MgCl_2$ and KCl<br>Dry, semi-dry or wet alkaline scrubber | $SO_2$ <50 to 100 mg/Nm$^3$<br>HCl <5 mg/Nm$^3$<br>Chlorine <3 mg/Nm$^3$<br>HF <1 mg/Nm$^3$ | For the refining and degassing stage for secondary aluminium (See Section 4.2.4.1.6) |
| NB: Collected emissions only. BAT-AELs are given as daily averages based on steady-state operation or, in cases where continuous monitoring is not practicable as the average over the sampling period. For PCDD/F, the BAT-AEL is the average over the sampling period which should preferably be a minimum of six hours. $SO_2$ emissions depend on the fuel used. | | | |

**Table 4.51: BAT and BAT-AELs to prevent and control emissions to air from secondary aluminium production including materials pretreatment, swarf drying, melting and the refining and degassing stages**

*The NOx data for secondary aluminium should be clearly assigned to an type of primary or secondary technique. The information should be relocated to the specific section in chapter 3. There is no need to double mention NOx relvant issues in section 2.20.12. Delete!*

**b) BAT is to prevent and control emissions to air from secondary aluminium production including materials pretreatment, swarf drying, melting and the refining and degassing stages by using all of the following techniques in the process (see Section 4.3.4):**

- selection of the feed material to suit the furnace type and abatement that is used and to transfer unsuitable raw materials to other operators using equipment designed for them;
- removal of oil and organic materials using swarf centrifuge, swarf drying or another thermal de-coating method before the smelting or melting stage unless the furnace is specifically designed to accommodate the organic content and to recirculate gases containing unburnt hydrocarbons back to the burner;
- use of sealed charging or raw material feeding system;
- recovery of any drosses or salt slag that are produced.

### 4.4.1.4 Other process stages

**a) BAT is to prevent and control emissions to air and optimise the use of energy for the production of alumina, for refining, holding and casting stages in primary aluminium production by using the techniques listed in Table 4.52 and Table 4.53 (see Section 4.1.1, Section 4.3.2 and the Reference Document on the Management of Tailings and Waste Rock in Mining Activities [ 332, Tailings Management 2008 ] also see Section 4.2.4.1.5 and Section 4.2.4.1.6).**

| Process Stage | Technique | Comments |
|---|---|---|
| Production of alumina | Bayer process | Optimised to reduce energy, (see Section 4.3.2) remove dust and re-use red mud transport water |

| | | |
|---|---|---|
| Refining or degassing | Use of mixtures of chlorine and argon/nitrogen or $AlF_3$ | Addition via an inline cell for $Cl_2$, Ar, $N_2$ injection Stirring for $AlF_3$ addition. |
| Holding and casting | Fume collection from furnaces and launders, cooling | Casting moulds depend on product. Use of regenerative burners |

**Table 4.52: BAT to prevent and control emissions to air from other process stages in primary aluminium production**

*The comment in the Table 4.50 is unclear because Section 4.3.2 does not contain any data or information about dust removal. In this context it is also unclear which of the requirements in table 4.51 applies for alumina production.*

**The emission levels given in Table 4.53 are the BAT-AELs.**

| Pollutant | Techniques | BAT-AELs | Comments |
|---|---|---|---|
| Dust | Fabric filter | <1 to 5 mg/$Nm^3$ | For the collection of dust from alumina calcination. A bag burst detection system should be used (See Sections 2.9.2.2.4 and 2.20.13) |
| $NO_X$ | Low-$NO_X$ burner<br>Oxy-fuel burner | <100 - 300 mg/$Nm^3$ | Higher values are associated with oxygen enrichment or air preheating to reduce energy use. In these cases, gas volume and mass emission is reduced (See Sections 2.9.2.4.3, 2.20.12 and 4.2.4.1.6) |
| Chlorine and acid gases | Use of mixtures of chlorine and argon/nitrogen or $AlF_3$, $MgCl_2$ and KCl<br>Dry, semi-dry or wet alkaline scrubber | HCl <5 mg/$Nm^3$<br>Chlorine <3 mg/$Nm^3$<br>HF <1 mg/$Nm^3$ | Refining and degassing stage when chlorine and fluorine based fluxes are used.<br>(See Section 4.2.4.1.6) |

NB Collected emissions only. BAT-AELs are given as daily averages based on steady-state operation or, in cases where continuous monitoring is not practicable as the average over the sampling period.

**Table 4.53: BAT and BAT-AELs to prevent and control emissions to air from other process stages in the production of primary aluminium**

*It is always problematic to refer to "other process stages" in such an important document. We should avoid such phrases and try to include defined sections and process stages in order to include appropriate technical examples.*

**b) BAT is to prevent and control emissions to air and optimise the recovery of all components of salt slag by using the full recycling technique (see Section 4.3.5.3) and all of the techniques given in  and Table 4.54.**

**The emission levels given in Table 4.54 are the BAT-AELs.**

| Pollutant | Techniques | BAT-AELs | Comments |
|---|---|---|---|
| Ammonia | Sulphuric acid scrubber<br>Combustor | 1 to 10 mg/$Nm^3$ | (See Section 4.2.4.1.2~~4.2.4.3~~) |
| Dust | Fabric filter | <1 to 5 mg/$Nm^3$ | A bag burst detection system should be used. (See Sections 2.9.2.2.4 and 2.20.13[rr41]) 4.2.4.1.2 |
| Phosphine | Combustor | 0.2 to 0.5 mg/$Nm^3$ | (See Section 4.2.4.1.2~~4.2.4.3~~) |
| Hydrogen sulphide | Combustor<br>Alkaline scrubber | 1 to 3 ppm | (See Section 4.2.4.1.2~~4.2.4.3~~) |

NB: Collected emissions only. BAT-AELs are given as daily averages based on steady-state operation or, in cases where continuous monitoring is not practicable as the average over the sampling period.

**Table 4.54: BAT and BAT-AELs to prevent and control emissions to air from salt slag recovery**

## 4.4.2 Effluent treatment and water re-use

**a) BAT is to prevent and control emissions to water from anode baking, secondary aluminium smelting and salt slag recovery by using a closed water cycle (see Section 4.2.4.2).**

**b) BAT is to prevent and control emissions of solids and oils/tars, absorbed acid gases in waste water from primary aluminium production and to re-use or recycle cooling water and treated waste water including rainwater within the processes (see Section 4.2.4.2).**

## 4.4.3 By-products, process residues and waste

**a) BAT is to prevent and minimise or re-use intermediate products and process residues whenever practical by applying individually or in combination the techniques for waste listed in Table 4.55 and Table 4.56 (see Sections 4.2.3.4 and 4.2.4.3 and also Section 2.20.10 and the Reference Document on the Management of Tailings and Waste-Rock in Mining Activities [ 295, European Commission 2004 ]). If recycling or re-use is not economically possible, secure disposal should be used.**

| Residue | Origin | Techniques | Comments on treatment |
|---|---|---|---|
| Salt slag | Melting in rotary furnace | Recovery via grinding, dissolution and crystallisation techniques. Production of re-usable substances Al granulate, mixed salt, $Al_2O_3$ (and other oxides). | Diffuse emissions of dust and gases such as ammonia, phosphine, hydrogen sulphide and methane should be collected and treated.<br>Ban of landfill. |
| Filter dust | Exhaust gas-cleaning | Partly recovered with salt slag or used in the steel industry | Ban on surface disposal in some countries, thermal treatment possible. |
| Furnace lining | Melting furnace | Recovery with skimmings/dross | Production of injection moulding compounds reported |
| Skimmings /dross | All furnaces not using salt | Smelting in rotary furnace.<br>Recovery in rotary drum furnace.<br>Dross dust recovered with salt slag | Aim is to prevent landfill |

**Table 4.55: BAT for the recycling or re-use of intermediate products or process residues from secondary aluminium production**

*Salt slag is a very difficult issue. Salt recovery plants permitted under which No. in the Annex I of the IPPC directive?*
*If information is included and completed in this BREf in sections 4.3.5.3 and 4.3.5.4 a conclusion should be made to help permit writers. In any case the prevention of the occurrence of salt slag should be included in this conclusion.*

| Source | Techniques |
|---|---|
| Red mud | Use of alkalinity remaining in the mud or liquor<br>Compaction and use as a product |
| Al skimmings or dross | Recovery |
| Filter dust | Re-use in process |
| Spent pot lining | Use of carbon content as carburant<br>Re-use of furnace linings<br>Re-use of cryolite as flux<br>Re-use in the cement, ceramics or brick industries |
| Bricks | Re-use as refractory |

| | |
|---|---|
| Steel | Recovery |
| Carbon dust (anode plant) | Re-use, e.g. as a scrubbing medium |

**Table 4.56: BAT for the recycling or re-use of intermediate products or process residues from primary aluminium production**

### 4.4.4 Energy efficiency

Additional techniques for the aluminium sector are described in this section.

**a) BAT is to minimise energy consumption in the production of alumina by using one or more of the following techniques (see Sections 4.3.2, 4.3.6 and 2.20.9):**

- application of tube digester technology in new plant
- application of plate heat exchangers instead of flash cooling in the liquor cooling area, if the condensate balance allows it
- application of circulating fluidised bed calciners instead of rotary kilns
- recovery of energy wherever possible and avoiding any losses.

**b) BAT is to minimise energy consumption in the production of secondary aluminium by using one or more of the following techniques in secondary aluminium production (see Sections 4.3.3.4, 4.3.4 and Section 2.14.2.1):**

- preheating of the furnace charge by the off-gases
- use of regenerative burners for the furnaces or other forms of heat recovery.
- recirculate gases which contain unburnt hydrocarbons back into the burner systems.

## 4.5 Emerging techniques

- Processes have been developed to use red mud and exploit its properties [ 247, New possible uses of Red Mud, French Report 2008 ]:
    - thickening the mud to obtain a high yield with low production costs or using high pressure filtration for construction applications such as: agronomic support, road embankments, covering of controlled disposal dumps, cavity filling or in the cement industry
    - taking advantage of its colouring properties for potential pigment applications such as: thermoplastic products, cement coatings, paints, special flooring
    - adsorbing and fixing contaminants such as arsenic.

- Inert anodes. Development of new carbon free anodes would make it possible to construct a completely new electrolytic cell without consumable anodes. Oxygen would be produced at the anode instead of carbon dioxide and emissions of PAH eliminated. The technology for this is still at the pilot plant stage and the anodes have not yet been able to withstand the temperatures and corrosive nature of the electrolyte [ 303, Canadian Al Rapport final in French.pdf 2008 ].

- Wettable cathodes. The development of new cathode materials or coatings for existing cathode materials, to achieve better energy efficiency for the electrolysis process. This is at the development stage and has been tested in research cells.

- Alloy separation. Techniques for separation of aluminium scrap into different types of alloy have been tested using laser and eddy current technology. The benefits of this will be easier selection of materials for recycling and the ability to easier produce desired alloys in recycling plants.

- Salt-free dross processing and the recovery of the remaining material in the steel industry. The process involves the dross processing for recovery of aluminium in rotary furnaces without the use of salt fluxes. The process allows for a slightly lower recovery of aluminium from the dross but the remaining skimmings are salt free and can be utilized in steel production using electric arc furnaces. The process allows for both environmental and economic benefits for both industries. The aluminium industry is benefited from the conservation of salt fluxes and the generation of a by-product that can be readily recovered in another industry while the steel industry benefits from better desulphurisation, a decrease in energy consumption, improved metal yield, and replacement of similar, costly raw materials (i.e. $Al/Al_2O_3$ contained fluxes as deoxidisers and slag formers).

- Recovery of spent pot lining in the process currently used for the full recycling of salt slag.

- The use of an electric arc furnace for salt free melting of dross.

- Salt recovery using electro-dialysis rather than concentration.

- Continuous monitoring of HF in stack emissions to allow abatement failure (alumina scrubber/fabric filter) to be detected.

- Continuous HF measurements can also be used to control alumina additions to the dry scrubber, resulting in optimum use of adsorption capacity of the alumina, more homogeneous alumina analysis and better control of emission peaks.

# 5 PROCESSES TO PRODUCE LEAD, ZINC AND CADMIUM (PLUS SB, BI, IN, GE, GA, AS, SE, TE)

## 5.1 Applied processes and techniques

These metals are often associated together in ores and concentrates and a number of techniques are used to win and separate the metals. The chemical state (sulphidic or oxidic) and the relative proportion of the metals usually determine the pyrometallurgical or hydrometallurgical techniques or combinations that are used. Some of the techniques are also used for secondary or mixed primary and secondary raw materials [ 11, Hatch Associates Ltd 1993 ] [ 99, Hähre, S. 1998 ]. In some cases, secondary materials are separated and portions such as battery paste, are sent to other processors who can deal with that material.

### 5.1.1 Primary lead

There are two basic pyrometallurgical processes available for the production of lead from lead sulphide or mixed lead and zinc sulphide concentrates: sintering/smelting in the ISF or by direct smelting. Most ISF processes in EU-27 have now closed. The direct smelting processes may also be used for concentrates mixed with secondary raw materials.

The composition of raw materials varies depending on the ores and their pretreatment. The feasibility of processing certain concentrates, is among others defined by the capability of the process to treat and recover the accompanying metals like Zn, Cd and Hg. Some ranges for the contents of the main constituents are given in Table 5.1.

| Constituent | Content (%) | Constituent | Content (%) |
|---|---|---|---|
| Pb | 35 - 90 | Cu | 0 - 5 |
| Zn | 0 - 15 | Ni | 0 - 1 |
| S | 0 - 35 | Cd | 0 - 0.2 |
| $SiO_2$ | 0 - 10 | Cr | 0 - 10 |
| CaO | 0 - 20 | As | 0 - 5 |
| FeO | 0 - 30 | Hg | 0 - 0.01 |

**Table 5.1: Composition ranges for the main constituents of lead concentrate**
[ 99, Hähre, S. 1998 ], [ 117, Krüger, J. 1999 ]

#### 5.1.1.1 Sintering/smelting using a blast furnace or Imperial Smelting furnace

These processes are no longer used in EU for lead concentrates. The ISF is used in one plant only for the production of zinc and lead from lead/zinc concentrates and the process is reported in Section 5.1.5.

#### 5.1.1.2 Direct smelting

Several processes are used for the direct smelting of lead concentrates and some secondary material to produce crude lead and slag. Bath smelting processes are used, the Ausmelt/ISA Smelt furnaces (sometimes in combination with blast furnaces), Kaldo (TBRC) and QSL integrated processes are used in the EU and worldwide. The Kivcet integrated process is also used and is a flash smelting process. The furnaces are described in Section 2.8 of this document. The Ausmelt/ISA Smelt furnaces and the QSL take moist feed and the Kaldo and Kivcet use dried feed [ 254, VDI (D) 2597 2004 ].The processes are summarised in Table 5.2.

The sintering stage is not carried out separately in this instance. Lead sulphide concentrates and secondary materials are charged directly to a furnace and are then melted and oxidised. Sulphur dioxide is formed and is collected, cleaned and converted to sulphuric acid. Carbon (coke or gas) and fluxing agents are added to the molten charge and lead oxide is reduced to lea and, a slag is formed. Some zinc and cadmium are fumed off in the furnace, their oxides are captured in the abatement plant and recovered [ 117, Krüger, J. 1999 ].

These processes all produce a slag that is rich in lead but the QSL and Kivcet furnaces incorporate an integral reduction zone to reduce the lead content of the slag to an acceptable level, the Kaldo process uses an adjacent slag fuming process. The Ausmelt/ISA Smelt furnace may be operated in two-stage operation with one furnace (batch wise) or with two parallel furnaces (continuous) in order to treat the primary slag for use in similar applications. Otherwise, a single furnace may be operated continuously for the production of raw lead and lead-rich slag for further treatment and recovery of lead.

Heat recovery and the conversion of sulphur dioxide into sulphuric acid is also featured in these processes. Process control is based on the measurement of $SO_2$ in the off-gas and this leads to a delayed reaction of the process, the control of oxygen makes the process control for the sulphuric acid plant far more complex than for sulphur burning.

Dust collected in the abatement plant is returned to the process and can be washed or leached to reduce halides and Zn/Cd in the recycled dust [ 117, Krüger, J. 1999 ]. The silica-based slag from the QSL process is accepted as construction material.

All of these processes have taken some time to commission properly and achieve the anticipated throughput and conversion rates. The Kaldo is a two-stage process [ 11, Hatch Associates Ltd 1993 ], [ 34, UNECE 1995 ], [ 99, Hähre, S. 1998 ] and is well established. The QSL and the Ausmelt/ISA Smelt processes have overcome all of the initial problems and are operating effectively [ 234, UBA Copper, lead, zinc and aluminium 2007 ]. The Ausmelt/ISA Smelt process has now been commissioned for the slag reduction phase and is producing a metallurgical lead concentrate for sale. The Kivcet furnace has been operating successfully since 1990 [ 117, Krüger, J. 1999 ], [ 305, Ausmelt Lead and Copper processes 2009 ].

| Process | Lead content of slag (%) | Comments |
|---|---|---|
| QSL | <3 | Efficient operation. Viable process |
| Kivcet | 3 - 5 | Successful operation |
| Ausmelt/ISA Smelt | No slag produced | Efficient operation. Viable process |
| Kaldo furnace | 2 - 4 | Effective operation - mixed Pb/Cu |

**Table 5.2: Summary of direct smelting processes**
[ 117, Krüger, J. 1999 ]

*This is the table 5.57 from Section 5.4.1.1.*
*Kaldo furnace and Kaldo process is included. What is the difference between these two???*

| ***Technique*** | ***Raw Materials*** | ***Comments*** |
|---|---|---|
| *Kaldo process*<br>*TBRC (totally enclosed)* | *Pb concentrate and secondary material (most grades)* | *Dry feed, variable sulphur dioxide. Operated in a complex installation with a Cu smelter* |
| *QSL* | *Pb concentrate and secondary material* | *Moist feed* |
| *Kivcet furnace* | *Cu/Pb concentrate and secondary material* | *Dry feed* |
| *Kaldo Furnace* | *Pb concentrate and secondary material* | *Moist, pelletised feed* |
| *Ausmelt/ISA Smelt Furnace* | *Pb concentrate and secondary material* | *Moist, pelletised feed* |

## 5.1.2 Secondary lead

### 5.1.2.1 The recovery of lead from scrap batteries

Scrap automotive and industrial batteries (automotive, motive power and standby) are a major source of secondary lead. The Battery Directive 2006/66 contains a target for the recycling efficiency of lead acid batteries of 65 % as of September 2010. A typical composition of lead-acid battery scrap is given in Table 5.3:

| Component | Wt - % |
|---|---|
| Lead (alloy) components (grid, poles,...) | 25 - 30 |
| Electrode paste (fine particles of lead oxide and lead sulphate) | 35 - 45 |
| Sulphuric acid (10 - 20 % $H_2SO_4$) | 10 - 15 |
| Polypropylene | 4 - 8 |
| Other plastics (PVC, PE, etc.) | 2 - 7 |
| Ebonite | 1 - 3 |
| Others materials (glass etc.) | <0.5 |

**Table 5.3: Composition of typical lead-acid automotive battery scrap**
[ 237, Austria M168 2004 ], [ 99, Hähre, S. 1998 ]

There are two main types of processes for the recovery of lead from automotive batteries [ 11, Hatch Associates Ltd 1993 ], [ 34, UNECE 1995 ], [ 99, Hähre, S. 1998 ]:

a) Varta process: Whole batteries are drained of acid and the batteries and fluxes are fed into a blast furnace via a seal and oxygen-enriched air is used in the blast. Antimonial lead bullion is produced, along with a silica-based slag and a lead-iron matte that can be recovered in a primary lead smelter [ 117, Krüger, J. 1999 ] [ 254, VDI (D) 2597 2004 ].

Organic components in the furnace off-gases are oxidised in accordance with the requirements of the Waste Incineration Directive 2000/76 in an afterburner and the gases are then cooled and filtered in a fabric filter. The filter dust is de-chlorinated and returned to the furnace.

b) MA and CX processes: These processes are similar in principle but the technical solutions are quite different for the treatment of battery paste and sulphuric acid. In both cases, batteries are drained of acid, broken and separated into various fractions using automated proprietary equipment. Paste desulphurisation prior to smelting can reduce the quantity of slag produced and, depending on the smelting method used, the amount of sulphur dioxide released to the air [ 254, VDI (D) 2597 2004 ]. The overall process is shown in Figure 5.1.

Both the MA and CX (Engitec) processes use hammer type mills to crush the whole batteries. The crushed material then passes through a series of screens, wet classifiers and filters to obtain separate fractions that contain metallic components, lead oxide-sulphate paste, polypropylene, non-recyclable plastics and rubber and dilute sulphuric acid [ 103, Farrell, F. 1998 ]. Some processes use a second milling stage before the plastic fraction is finally treated. Polypropylene is recycled as far as possible in a wide range of applications.

Battery acid contains 10 to 15 % sulphuric acid and some impurities. Further use depends on the local situation and several alternatives are used to deal with the sulphur contained in the battery materials:

- Prior to smelting, the lead sulphate paste may be desulphurised by reaction with sodium carbonate or sodium hydroxide in the CX and related processes to produce dry, clean sodium sulphate crystals for sale. In the CX process, condensate from the crystalliser is returned to the process and virtually no effluent is produced.
- Lead sulphate paste can be separated and sent to an installation capable of treating the sulphur content in the gases, for example one of the direct smelting primary lead processes.
- The sulphur may be fixed as a Fe-Pb matte for further processing or in smaller amounts in the slag for disposal.
- The production of concentrated sulphuric acid using a cracking process.
- Neutralisation with lime to produce different qualities of gypsum.

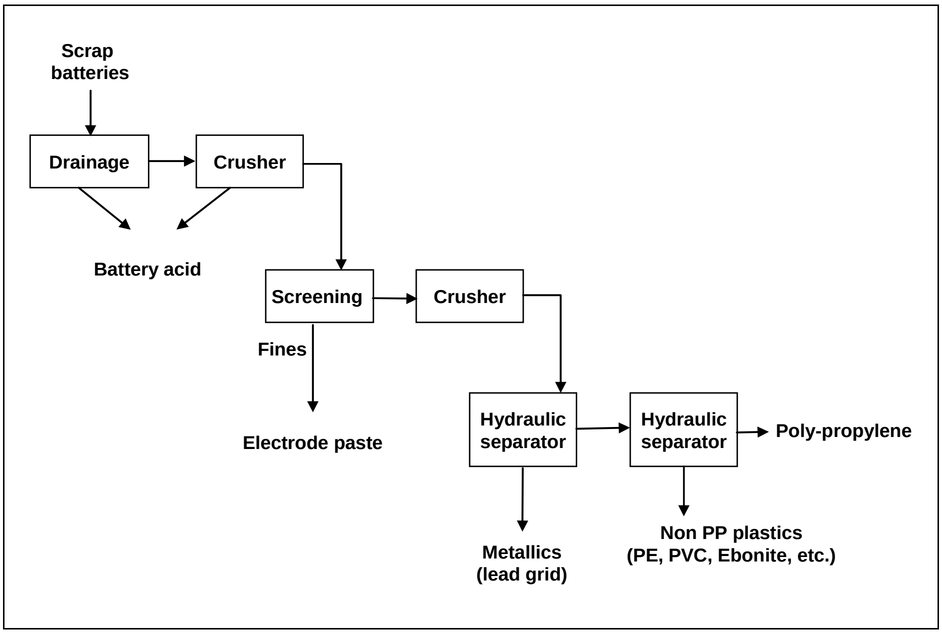


**Figure 5.1: Outline of a typical battery recovery process**
[ 99, Hähre, S. 1998 ]

Smelting can be carried out in the following vessels [ 99, Hähre, S. 1998 ]:

- rotary furnace
- tilting rotary furnace
- reverberatory furnace and blast or electric furnace
- rotary kiln
- Ausmelt/ISA Smelt furnace
- QSL furnace
- electric furnace.

*What about the TBRC (KALDO) furnace which is considered to be BAT???*

Rotary and reverberatory furnaces can be either gas or oil fired and oxygen enrichment is used in several installations. Smelting is usually carried out in batches, slag and metal are tapped out separately and batches of slag are treated to recover more lead and to produce a slag that is stable. The bulk of the sulphur in the charge is fixed in the slag. The slag can be a sodium-iron-sulphur compound with small amounts of lead and other metals or a silica slag which more acceptable for disposal.

In the Ausmelt/ISA Smelt process, sulphur containing paste and reducing agent are continuously fed into the furnace and lead bullion is tapped periodically. When the process vessel contains the maximum volume of slag, reducing agent and fluxes are added to produce a high antimony bullion and a discard slag [ 40, AusmeltAusmelt Ltd. 1996 ] [ 99, Hähre, S. 1998 ]. The slag may also be reduced in a separate furnace.

In the QSL process some battery components such as battery paste are treated together with other secondaries (e.g. dross, sludges, leaching residues, flue dusts) [ 254, VDI (D) 2597 2004 ].

The electric resistance furnace is used for complex secondary materials and uses an open slag bath covered by coke. Raw materials are fed onto the top of the bath where they react to produce metal and slag, which are tapped periodically. The waste gas contains CO and is burnt, flue dust is collected and zinc is recovered from it. It is operated on a campaign basis alternating with secondary copper production in a copper smelter.

Crude bullion produced by either smelting method is refined by the methods described below in Section 5.1.3.

#### 5.1.2.2 Recovery of lead from flue dusts from copper smelting, other residues and scrap

Metallic lead scrap may be in a variety of forms, it may be contaminated by plastic material or bitumen and may be alloyed with other elements, notably tin, antimony and silver. This material is usually recovered in the processes described in the section above as simple melting facilities and cannot cope with the partially burnt material in the off-gases [ 304, KGHM Lead Report 2009 ].

The tilting rotary or the rotary-rocking furnace is used to recover lead from flue dusts from copper smelting and in secondary copper, the TBRC is used to smelt residues and scrap to produce a lead/tin alloy which is further refined using the techniques described below in Section 5.1.3. Tin and lead can be separated from each other by vacuum distillation at high temperature. As a result of this, pure lead can be recovered. This technique is applied by some secondary lead and tin producers.

The electric furnace is also used for the recovery of lead from complex lead-copper and lead-precious metals secondary materials. Afterburning of the gases is used to destroy CO and hydrocarbons including PCDD/F.

Clean scrap is melted in specially designed kettles, which are indirectly heated by oil or gas. Scrap is charged from a hopper situated above the kettle. Dross and tramp materials are skimmed from the surface of the molten metal and then pass through a screen that separates fine and coarse fractions. The dross is the fine fraction and is recycled as a non-metallic residue. The tramp material is mostly metal with a higher melting point than lead, and is treated elsewhere.

Residues, largely non-metallic in character, but often mixed with metallic lead scrap, are smelted with fluxes in rotary furnaces.

The lead or lead alloy recovered from scrap or process residues is refined using the techniques described below in Section 5.1.3.

### 5.1.3 Refining of primary and secondary lead

Lead bullion may contain varying amounts of copper, silver, bismuth, antimony, arsenic and tin. Lead recovered from secondary sources may contain similar impurities, but generally antimony dominates. There are two methods of refining crude lead: electrolytic refining and pyrometallurgical refining. Electrolytic refining uses anodes of decopperised lead bullion and starter cathodes of pure lead. This is a high cost process and is used infrequently and only very small quantities are produced electrolytically.

~~A p~~Pyrometallurgical refinery consists of a series of kettles, which are indirectly heated by oil or gas [ 4, Hatch Associates Ltd 1993 ], [ 99, Hähre, S. 1998 ], [ 304, KGHM Lead Report 2009 ]. Copper is the first element to be removed and separates as sulphide dross. If the crude metal is deficient in sulphur, more must be added in the form of sulphur powder or galena/pyrite. The sulphide dross is removed from the metal surface by mechanical skimmers that discharge into containers.

Arsenic, antimony and tin are removed by oxidation. The usual method, often referred to as 'lead softening', involves a reaction with a mixture of sodium nitrate and caustic soda, followed by mechanical skimming to remove the oxide dross. Air or oxygen can also be used as the oxidising agent. Depending on the crude lead composition, i.e. the amount of impurities, the molten salt mixture may be granulated in water and the impurities separated hydrometallurgically [ 254, VDI (D) 2597 2004 ].

Tin and lead can also be separated from each other by vacuum distillation at high temperature. As a result of this, pure lead can be recovered.

Desilvering is carried out by the Parkes process, which makes use of the preferential solubility of silver in zinc. Zinc is added to the lead at about 470 °C and the mix is then allowed to cool to 325 °C. A silver-lead-zinc alloy separates and forms a crust on the surface. The crust is removed and zinc is separated from the silver by vacuum distillation. The silver bullion is further refined using oxygen to produce crude silver. Excess zinc is removed from the desilvered lead by vacuum distillation and then by treatment with caustic soda.

Bismuth is removed by treatment with a mixture of calcium and magnesium (the Kroll-Betterton process). A calcium-magnesium-bismuth alloy is formed as dross on the surface of the lead and is removed by skimming. The dross is then oxidised using lead chloride, chlorine gas or a mixture of caustic soda and sodium nitrate and the calcium and magnesium oxide is removed by skimming. A bismuth-lead alloy is recovered and undergoes further refining to produce bismuth. A diagram of lead refining processes is given in Figure 5.2.

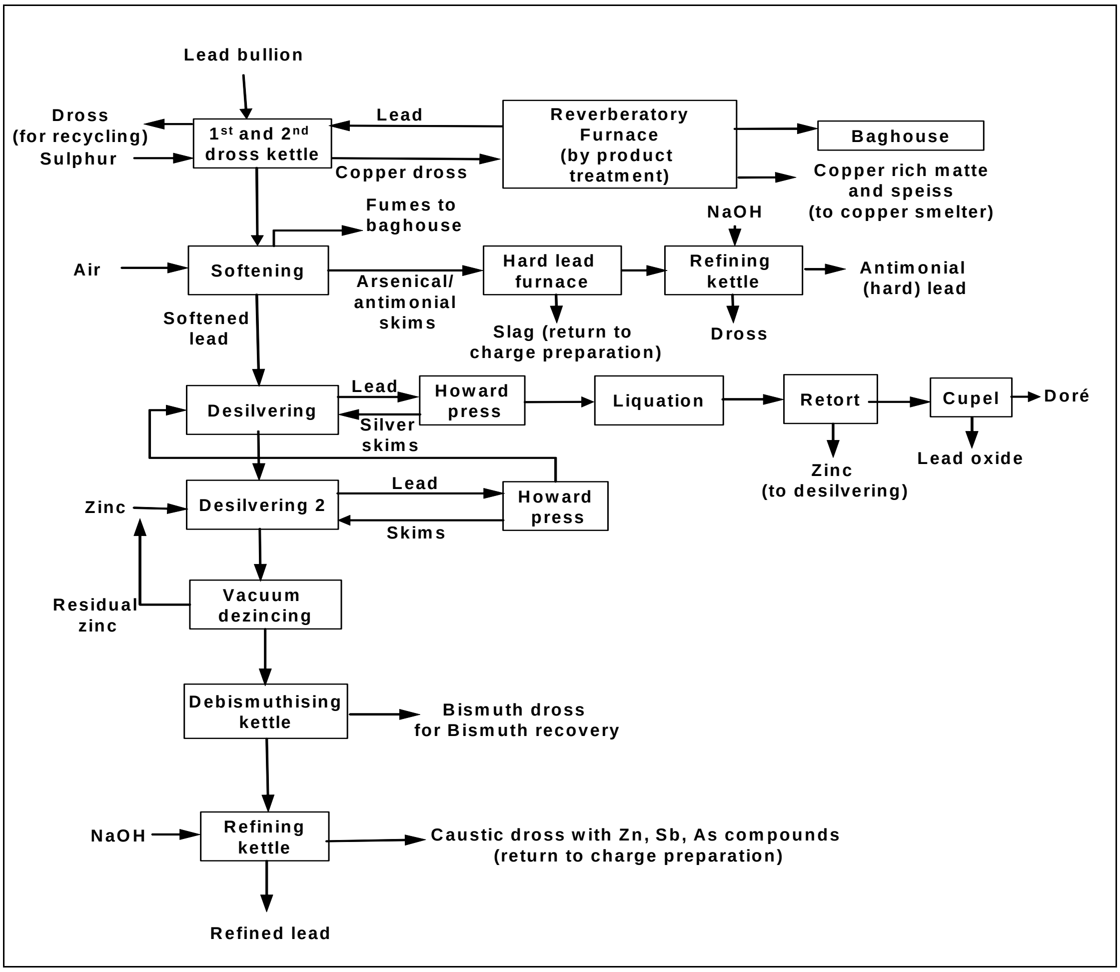


**Figure 5.2:** **Diagram of lead refining processes**
[ 99, Hähre, S. 1998 ]

*See another alternative flow chart from the Technical Guideline for the Environmentally Sound Management of Waste Lead-acid Batteries, Basel Convention series/SBC No 2003/9, page 23.[521]*

If thallium is present it can be removed using zinc chloride and silica to help form a thallium-rich dross which is skimmed off [ 304, KGHM Lead Report 2009 ].

The pure lead is cast into blocks or ingots as pure lead or lead alloy. Fume, dross, litharge and other residues are usually smelted in a small blast furnace or a rotary furnace to produce lead bullion which is recycled to the refining circuit.

## 5.1.4 Melting and alloying processes for lead

Melting and alloying are usually carried out in indirectly heated crucible furnaces or kettles using electricity or, oil or gas. Refined lead is melted in a kettle and alloying elements are added. Temperature control of the melt can be important [ 254, VDI (D) 2597 2004 ]. Lead and lead alloys are usually cast into permanent cast iron moulds [ 4, Hatch Associates Ltd 1993 ].

Static moulds and conveyor casting machines are used to produce blocks, slabs and ingots. Continuous casting machines are used to produce rod for reduction to wire. Fume extraction is used at the launders and tapping points.

## 5.1.5 Primary zinc

Zinc can be produced from primary raw materials by pyrometallurgical or hydrometallurgical methods. Pyrometallurgical methods are used in other parts of the world but have gradually lost their importance and are not used in the EU for simple zinc concentrates. Determining factors are the need for an extra distillation stage to obtain high grade zinc and the relatively low zinc extraction efficiency. The majority of the pyrometallurgical Imperial Smelting Furnace process (ISF) have closed down in EU but one remains open and is operated on a campaign basis to smelt sulphidic and then oxidic materials.

#### 5.1.5.1 The pyrometallurgical route

The pyrometallurgical route is used for mixed zinc-lead concentrates and secondary material and uses the Imperial Smelting Furnace (ISF), which is illustrated in Section 2.8.2.2 and Figure 5.3. The ISF is used on a campaign basis treating sulphidic concentrates and some secondary lead in one campaign and then washed Waelz oxide and other oxidic materials containing zinc and lead in another campaign. The lead containing residues and some lead produced in the sulphidic campaign are used to optimise the zinc to lead ratio for the oxidic campaign.

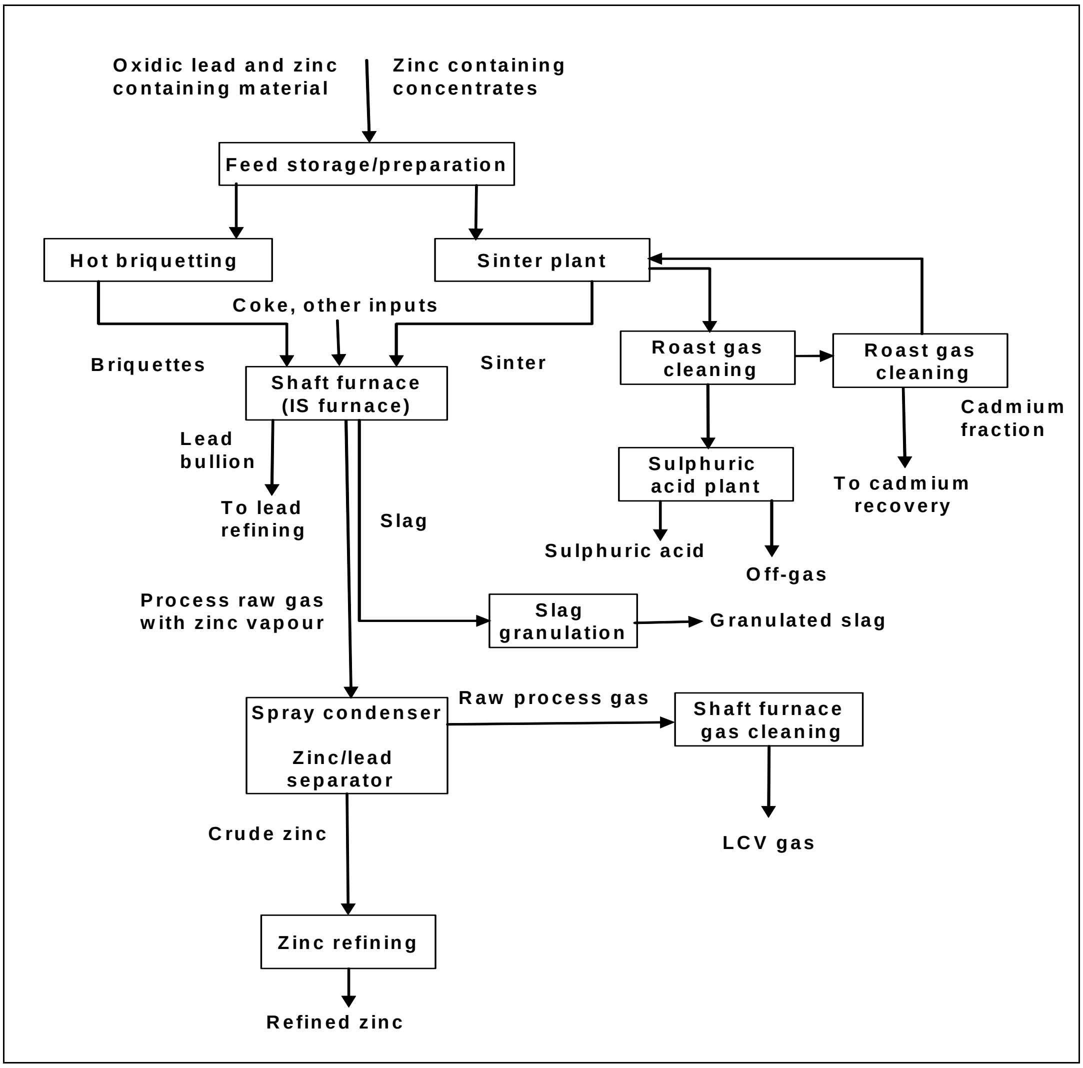


**Figure 5.3: Diagram of a typical Imperial Smelting process**
[ 117, Krüger, J. 1999 ]

Zinc produced in the Imperial Smelting Furnace may contain varying amounts of cadmium, lead, copper, arsenic, antimony and iron and the process uses a refining stage. Zinc from the ISF is refined by reflux distillation in columns that contain a large number of refractory trays (New Jersey distillation). The lower ends of the columns are heated externally by natural gas. The upper ends are not heated and run cool enough to reflux the higher boiling point metals before vapours pass to a condenser [ 11, Hatch Associates Ltd 1993 ], [ 99, Hähre, S. 1998 ]. The New Jersey distillation column is also used for secondary zinc materials [ 117, Krüger, J. 1999 ].

Distillation proceeds in two-stages; first the separation of zinc and cadmium from lead and then separation of cadmium from zinc. In the first stage, molten zinc is fed into a column where all the cadmium and a high proportion of the zinc is distilled. The mixture is condensed and fed directly to a second column. This column is operated at a slightly lower temperature to distil mainly cadmium, which is condensed as a zinc-cadmium alloy as shown in Figure 5.4. The alloy is transferred to a cadmium refinery. The metal run-off from the bottom of the second column is high grade zinc (SHG) of 99.995 % purity [ 117, Krüger, J. 1999 ].

The run-off metal from the first stage is zinc with lead, tin, arsenic, iron, antimony and copper impurities. This alloy is cooled to separate lead, which is recycled to the ISF ~~splash~~ spray condenser, and dross, an intermetallic compound of iron, zinc and arsenic, which is recycled to the ISF itself.

The zinc is then treated with sodium to remove residual arsenic and antimony as sodium arsenides and antimonides, which are also recycled to the ISF. The zinc produced in this way is of a lower grade, but free of cadmium, and is used mainly for galvanising.

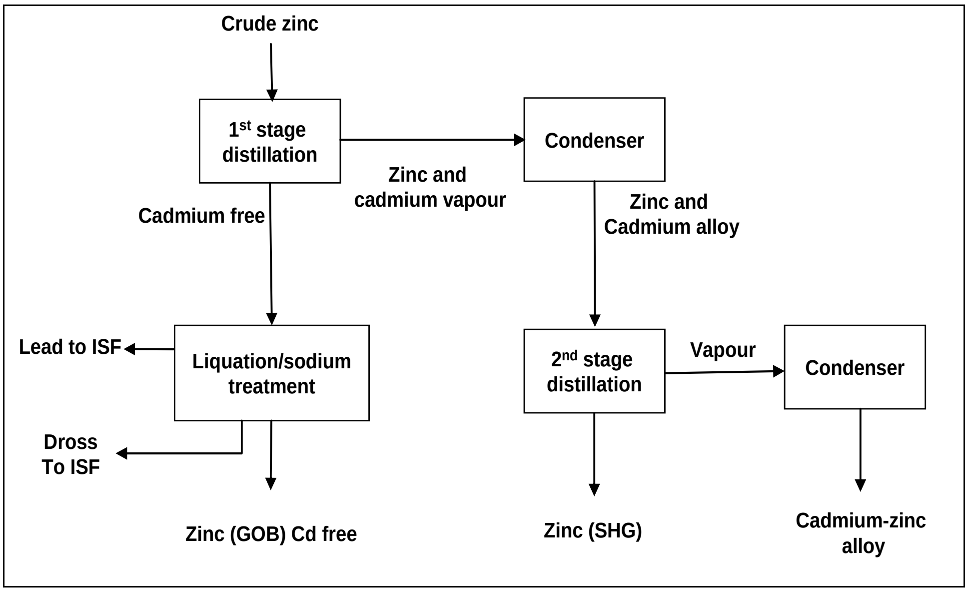


**Figure 5.4:** **Diagram of zinc-cadmium distillation**
[ 99, Hähre, S. 1998 ]
*Changes in the picture:*
*Lead to the spray condenser downstream the ISF*

### 5.1.5.2 The hydrometallurgical route

The hydrometallurgical route is used for zinc sulphide (blendes), oxide, carbonate or silicate concentrates and also for some secondary materials such as Waelz oxide. It is responsible for about 80 % of the total world output [ 98, Lijftogt, J.A. et al 1998 ], [ 99, Hähre, S. 1998 ]. The majority of the EU production facilities use the electrolytic process, with a total production capacity of 2.1~~500000~~ million -tonnes ~~/yr~~ in 2007 [523].

#### 5.1.5.2.1 Roasting

Sulphide concentrates are roasted first in closed, fluidised bed roasters to produce zinc oxide and sulphur dioxide. Up to 25 % of secondary zinc material such as dehalogenated Waelz oxide are added to the roaster feed material. Roasting is an exothermic process and no additional fuel is used, the heat generated is recovered. The zinc oxide (calcine) passes from the furnace and is collected and cooled. Roaster gases are treated in cyclones and hot ESPs to remove dust which is added to the calcine. Other dust and volatile metals such as Hg and Se are removed in a gas-cleaning train that incorporates scrubbing systems and wet ESPs. The sulphur dioxide is then converted to sulphuric acid in a conventional recovery system [ 98, Lijftogt, J.A. et al 1998 ], [ 99, Hähre, S. 1998 ], [ 117, Krüger, J. 1999 ], [ 11, Hatch Associates Ltd 1993 ]. The off-gas of the $H_2SO_4$ conversion is led to candle filters or scrubbers to minimise the remaining acid mist, represented by $SO_3$. The waste water of the gas-cleaning train is treated at the waste water treatment plant.

#### 5.1.5.2.2 Neutral l~~L~~eaching

Leaching of the calcine is carried out in a number of successive stages using a gradually increasing strength of hot sulphuric acid. The initial stages do not dissolve significant amounts of iron but the later ones do. The leaching process is carried out in a variety reactors using open tanks, sealed vessels and pressure vessels or a combination of them [ 98, Lijftogt, J.A. et al 1998

], [ 99, Hähre, S. 1998 ] (See Figure 5.5). The installation of a separate washing step can be required when using a higher share of secondary feed input (>10 % Waelz oxide). In this separate leaching step, the removal of lead as marketable lead sulphate concentrate is practised. The leach liquor is supplemented by the leach liquor from the iron precipitate removal step. If only small amounts of secondary feed are used (<10 % Waelz oxide), the secondary raw material can be added after the roasting step.

Leaching may be stopped after the neutral[rr42] leach. The leach residue can be sent to an ISF or Waelz kiln (with sulphur dioxide recovery) and added to the process feed. Zinc, lead and silver are recovered as metals, sulphur as $H_2SO_4$. A Waelz kiln or zinc fuming furnace may also be used but $SO_2$ absorption is necessary in such a case. Zinc and lead are recovered as oxides and sulphates, the slag in, this case, may be treated further by flotation to recover silver and copper. Due to the closure of nearly all European ISF plants (DE, FR, UK) and the limited availability of European Waelz plants with an $SO_2$ adsorption step there is a limited capacity for pyrometallurgical treatment of the neutral leach residue. The neutral leach residue is treated hydrometallurgically in most plants. A small amount is landfilled.

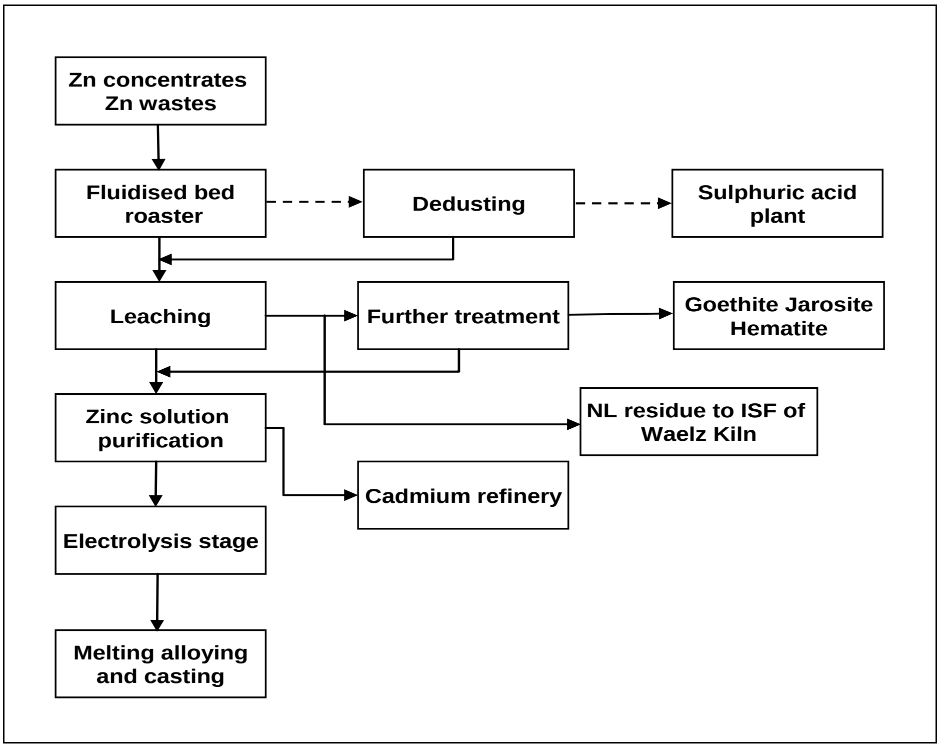


**Figure 5.5: Diagram of the leaching process**
[ 234, UBA Copper, lead, zinc and aluminium 2007 ]

*This figure is not from [234]! I propose to combine the figure at page 164 in [234] with the one from the new reference [ 99] to include direct leaching and storage of materials. For this relocate the figure to section 5.1.5.2 because it shows more than only leaching.*
*Insert the term neutral leach for leaching NL is neutral leaching, write the full word.*
*Exchange the picture by one where direct leaching is included.*

**Iron and other residues**
*This was not an appropriate subheading. Maybe the terms Jarosite, Goethite or other should be inserted here. For this reason it has been modified to normal text.*

One of the main issues in the hydrometallurgical process route is the disposal or use of the precipitated iron. Special containment sites are used for disposal at the moment but pressure on disposal options is increasing, this factor is discussed later and the options are assessed. Several approaches are being developed to help avoid these residues or to help them to be used.

Restricting the process to neutral leaching only is one alternative method that can be used to avoid the production of these intractable wastes. In this case iron remains in the leach residue along with a significant portion of the zinc. This residue is used as the feed for a pyrometallurgical process to recover the zinc, lead, silver and sulphur, and to bring the iron into a slag (*check whether this is an applied technique to consider or just a remark.In the first case try to get additional information)*~~.~~

In addition to zinc, other metals are also dissolved during the process and are removed after leaching. Iron is the major impurity and the iron is precipitated in three basic forms; jarosite, goethite or hematite. The form of these precipitates is used to give the process names [ 98, Lijftogt, J.A. et al 1998 ], [ 99, Hähre, S. 1998 ]. The precipitation stages are:

- As jarosite, using ammonia or other analkaline compound and zinc calcine for neutralisation. Up to three stages are used depending on whether Ag-Pb recovery is undertaken. A single stage process known as the conversion process is also used
- As goethite, using zinc sulphide for pre-reduction, oxygen for re-oxidation and zinc calcine for neutralisation.
- As hematite, using sulphur dioxide or zinc sulphide for pre-reduction and an autoclave with oxygen for precipitation. In this case, a sulphur residue is produced as well as an iron residue.

The main differences in the iron precipitates are their volume and ease of filterability. There are also significant differences in process capital and operating costs [ 117, Krüger, J. 1999 ]. The balance of these with the disposal costs of the residue may be influenced by non-process related costs. The hematite process was thought to be very attractive as the residue volume was lower and hematite was a potential raw material for iron. The process has not proved to be viable and the hematite was not acceptable -to the iron and steel industry.

It has also been reported [ 136, Fugleberg, S. 1999 ] that the jarosite process is capable of high zinc recoveries even with concentrates that contain 10 % Fe. Similar recoveries with the goethite process rely on a low iron content in the calcine (or ZnO) that is used for the precipitation stage.

Concentrate from the Century Mine in Australia, has a high zinc content of 58 %. The concentrate consists mainly of zinc sulphide and also contains small quantities of iron, lead, silica, carbon and silver (Zn 54.18 to 58.69 %; Fe 0.76 to 2.17 %) [ 240, Nl Input on Zn production 2008 ]. There are limited quantities of this concentrate available and the availability might not extend beyond 2015.

In 2000, major changes to the production process enabled Nyrstar, Budel Zink to convert to Century Mine zinc concentrate. In 2007, 80 % of the input of the installation was this concentrate and 20 % was waste material. Calcination is carried out conventionally and zinc from calcine is dissolved in dilute sulphuric acid in two leaching stages.

In addition to zinc, the iron, silica, cadmium, copper and cobalt content are also dissolved from the calcine. In the first leaching stage (neutral leaching), the calcine is mixed with spent acid from the electrolysis department. As the solution is only slightly acidic, most of the zinc oxide is dissolved, however the zinc ferrites and zinc silicates are not affected. Thickeners are used to separate the undissolved solids from the zinc sulphate solution, after which the solution is pumped to the purification stage.

The undissolved solids proceed to a second leaching stage (hot acid leaching). At a high acid concentration and temperature, zinc ferrites and zinc silicates dissolve. Subsequently, the dissolved silica, the bulk of the iron together with undissolved components such as lead sulphate are precipitated from solution. These precipitated solids are separated in thickeners. With a throughput of 240000 tonnes of concentrate t~~T~~he amount of this saleable solid is about 70000 tonnes per year and ~~. T~~total waste produced is quoted as 500 to 2000 tonnes~~ per year from a throughput of 240000 tonnes of concentrate~~ [ 228, IZA plant data 2008 ].

The solution is partially purified in an iron precipitation step and returned to the neutral leaching step. The solids are filtered and washed in two separate filtration steps and are sold as a lead-silver product.

*The text in the box is repeated completely in section 5.3.5.2. It should be deleted either there or here. I propse to move the useful information to section 5.3.5.2, provided that this section will stay in the BREF.*

The conventional iron removal processes are outlined in Figure 5.6 and Figure 5.7.

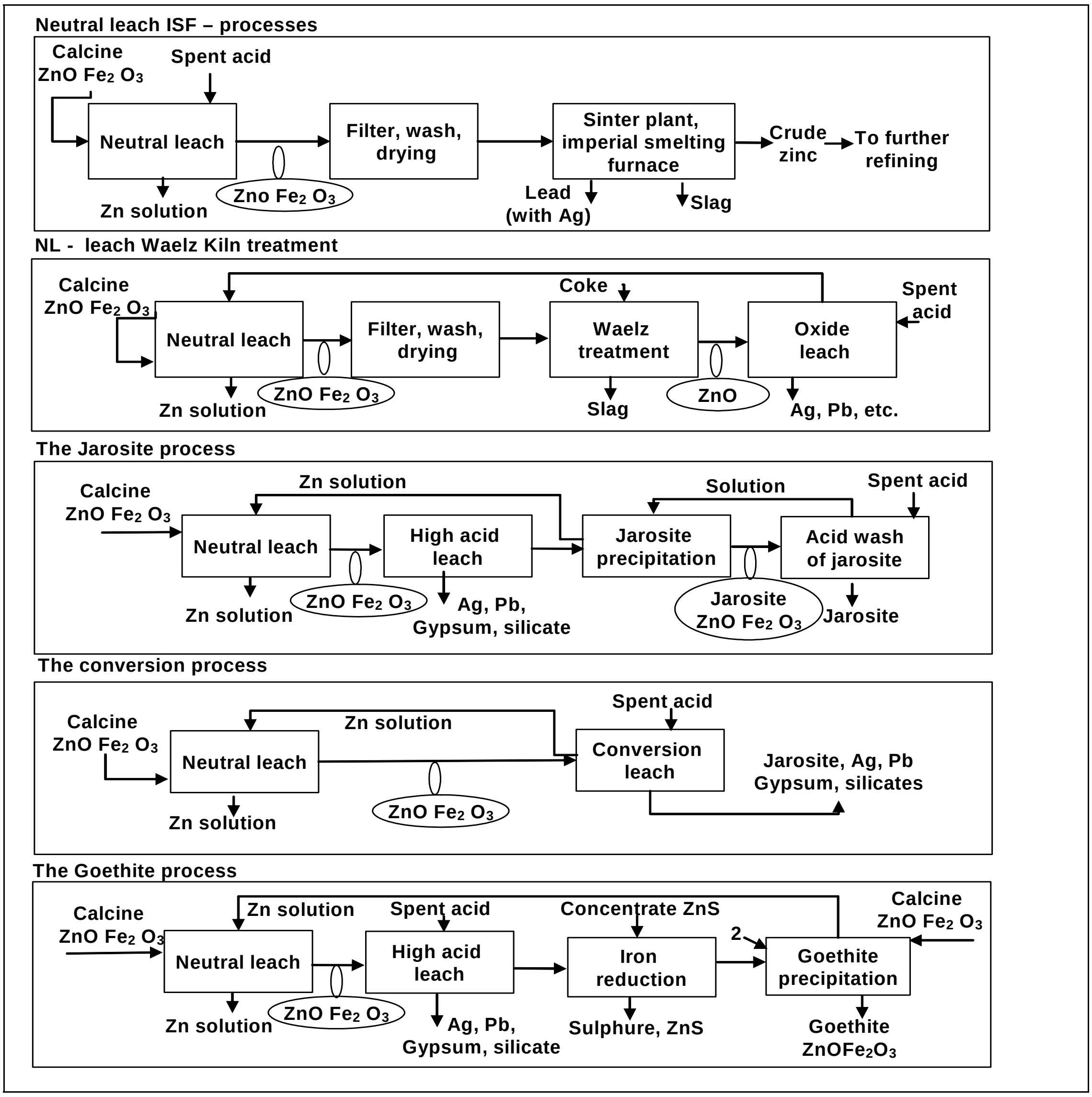


**Figure 5.6: Simplified flow sheets of some iron removal processes**
[ 136, Fugleberg, S. 1999 ]

*In this figure the term NL atsed in the second flow chart of this figure should not be abriviated. It should read 'Neutral leach Waelz kiln process'*

Direct leaching

A few applications are known where concentrate is leached ~~directly~~ directly without[rr43] calcination, i.e. at Korea Zinc and Boliden, Kokkola and one installation that is being commissioned in China. At Korea Zinc the iron is left in solution during the leaching and is then precipitated in a separate step as goethite, whereas at Kokkola, the iron is precipitated as jarosite simultaneously with the leaching of the sulphides.

The concentrate together with the slurry from the conversion process and acid from the electrolyses are fed to the reactors where the leaching takes place by sparging oxygen into the slurry. The rest of the dissolved iron in the solution from the conversion and the iron dissolved from the concentrate is precipitated as jarosite:

$$3ZnS+3Fe_2(SO_4)_3+(NH_4)_2SO_4+9H_2O+1.5O_2=2NH_4(Fe_3(SO_4)_2(OH)_6)+3ZnSO_4+3H_2SO_4+3S$$

A sulphur concentrate is separated from the slurry by flotation and stored separately from the jarosite residue. This sulphur concentrate contains a significant amount of impurities and is disposed of to land and this makes the direct leaching process a very site-specific issue. The equipment used in the process is more complicated than that conventionally used in zinc hydrometallurgy. A flow sheet of the process concentrate leaching process operated by Boliden Kokkola and Odda is shown in Figure 5.7 [ 136, Fugleberg, S. 1999 ].

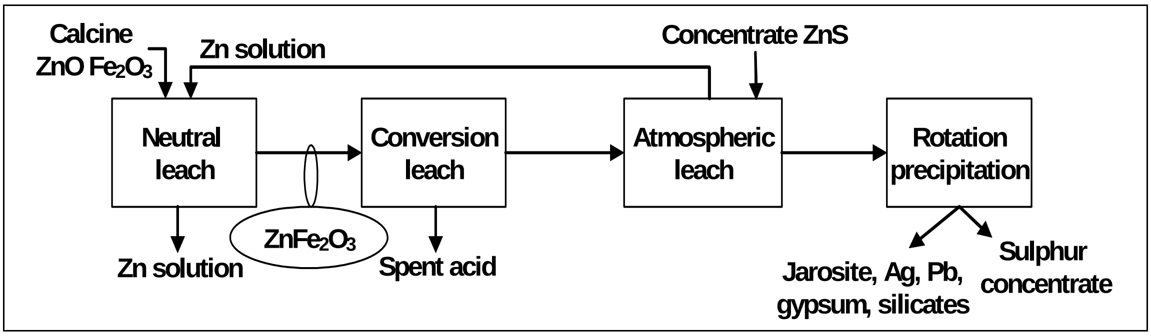


**Figure 5.7: Concentrate leaching process**
[ 136, Fugleberg, S. 1999 ]

A further description of the process is given in [ 283, Zinc Concentrate Leaching 2004 ].

Whatever residue is produced by the various process options, zinc removal is maximised by washing the residue. Other soluble metals may be treated by precipitation as hydroxides or sulphides.

The iron rich residues are stored in totally sealed disposal areas, usually on or near the site to ~~in a manner that~~ isolate~~s~~ them from ground or surface water. Water from the storage area is normally recycled back to the process. Developments have taken place to render them more acceptable-_by fixation in the Jarofix process or by compacting. The neutral leach process does not leach out all of the zinc but this is recovered in a separate pyrometallurgical process.

Slurry from the final leaching stage is settled and the overflow solution is treated to remove impurities. The solid in the underflow is filtered and washed on a filter. The filter cake is disposed of and the filtrate is recycled to the process. Different flow sheets are used depending on factors such as the choice of the iron removal process and the available integrated impurity recovery processes.

For example, more or less extensive treatment of the leach residue is carried out by further leaching or physical separation techniques before it is disposed of [ 117, Krüger, J. 1999 ]. This is reflected in the recovery rates and composition of possible lead or lead-Ag by-products.

#### 5.1.5.2.3 Purification

Purification of the zinc-bearing solution takes place in a number ways using zinc dust and other chemical stages or by solvent extraction. The processes used are dependent on the concentrations of the various metals contained in the concentrate and vary accordingly.

### ~~5.1.5.2.4~~5.1.5.2.3.1 Purification using chemicals

~~Purification of the zinc-bearing solution takes place in a number ways using zinc dust and other chemical stages or by solvent extraction. The processes used are dependent on the concentrations of the various metals contained in the concentrate and vary accordingly.~~

The basic chemical purification processes involve the use of zinc dust or powder to precipitate impurities such as Cu, Cd, Ni, Co and Tl. Precipitation of Co and Ni also involve the use of a second reagent such as As or Sb oxides. Variations in temperature occur from plant to plant. Other reagents such as barium hydroxide and dimethylglyoxime may also be used to remove lead and nickel. The recovery route for the copper by-product can affect the choice of process. Due to the rising amount of secondary feed material, the increasing concentration of Ca in the leaching circuit is solved by using gypsum removal from the leach liquor. The treatment of a partial flow of the liquor can be conducted to remove magnesium chlorides and fluorides. Hydrogen may be evolved and arsine or stibine occurrence is monitored. The continuous removal of Co is more effective in minimising emissions of arsine than batch removal. Collection and treatment of the released gases depends on the presence of these gases, local overall engineering, open air or enclosed building operations can be used but scrubbing the gases from the reactors using an oxidising solution for arsine removal is reported to be most effective [ 136, Fugleberg, S. 1999 ].

### ~~5.1.5.2.5~~5.1.5.2.3.2 Purification using solvent extraction

The electrolyte can also be concentrated and purified using a solvent extraction system such as the modified Zincex process (see Section 2.8.7.4.1). In this case zinc is extracted selectively into a solvent such as di(2-ethylhexyl) phosphoric acid in a specific kerosene to purify and upgrade the pregnant leach solution (PLS). The use of solvent extraction means that other metals are not carried into the electrolyte. Calcium, magnesium and halides are also rejected which would interfere with the electrowinning stage. Zinc is then stripped from the organic phase using spent electrolyte from zinc electrowinning to give a pure electrolyte [ 327, Highlights and hurdles in Zinc production by solvent extraction 2008 ]. This process is also used to concentrate weak solutions of zinc such as those produced by leaching oxidic ores and to purify zinc solutions derived from the recycling of zinc/manganese batteries. The solvent extraction flow sheet is shown in Figure 5.8.

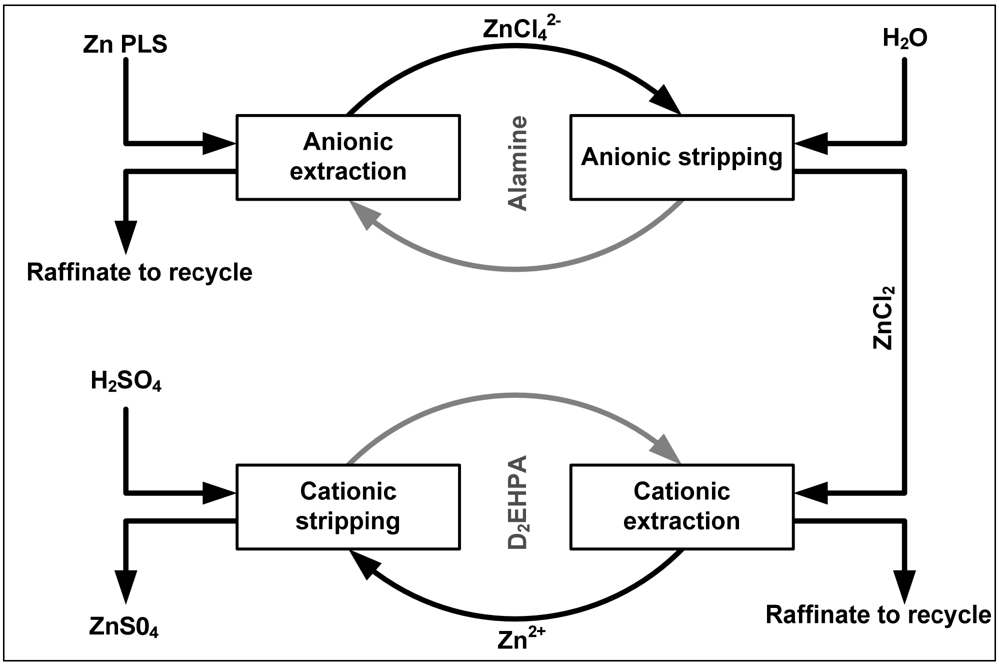


**Figure 5.8: Process diagram of solvent extraction purification**

#### ~~5.1.5.2.6~~5.1.5.2.4 ~~Electrowinning~~Electrolysis

The purified solution from either chemical, cementation or solvent extraction processes passes to a cell house where zinc is electrowon using lead anodes and aluminium cathodes. Zinc is deposited at the cathodes and oxygen is formed at the anodes, where sulphuric acid is also generated and is recycled to the leaching stage. Acid mist is formed during this process and various coverings or maintaining a foam layer can be used on the cells to minimise this. Cell room ventilation air can be demisted and the acid mist recovered. Heat is produced during electrolysis and this is removed in a cooling circuit, this can be designed to optimise the water balance of the process but may be a further source of mists.

The produced zinc is deposited on the aluminium cathodes and is being removed by stripping the cathodes usually every day. For melting , low frequency indusction furnaces are used. [ 117, Krüger, J. 1999 ]. A small part of the zinc produced is made into zinc powder or dust for the purification stages. These can be produced by air, water or centrifugal atomisation of a stream of molten zinc or by condensing zinc vapour in an inert atmosphere.

### 5.1.6 Secondary zinc

Approximately 30 % of the yearly zinc consumption in Europe is secondary or recycled zinc. Approximately 50 % of this secondary zinc is recycled within the industry. This is particularly true in the galvanising and brass sector; scrap arising from the production or processing of products can be recycled almost immediately.

Residues and scrap, which are relevant and significant to the secondary zinc industry, include:

- dust from copper and copper alloy production
- residues from the die casting industry
- ashes, bottom and top dross from the galvanising industry
- old roofing and other sheet materials
- non-ferrous fractions from the shredding of old cars and of other products mainly containing steel
- dust from electric arc steelmaking and cast ironmaking
- residues from the chemical uses of zinc and from burnt tyres.

The process route used to recover zinc depends on the form and concentration of zinc, and the degree of contamination [ 117, Krüger, J. 1999 ].

### 5.1.6.1 General processes

Physical separation, melting and other high temperature treatment techniques are used. Zinc rich residues are used to produce zinc metal, SHG zinc, zinc alloys, zinc oxide or zinc oxide rich products. The impure metals or alloys can be refined, e.g. in a reaffination column to produce SHG zinc or high grade oxide or used directly in a secondary recovery process. If chlorides or other halides are present, they are removed before zinc is won by hydrometallurgical processes due to their aggressive characteristics [ 117, Krüger, J. 1999 ], [ 202, Fundación Entorno, Empresa y Medio Ambiente 1999 ].

Process details are very often confidential but examples of these specific treatments are given below:

- Galvanisers' ashes which arise during galvanisation of work pieces, wire and tubes are essentially a mixture of zinc metal and zinc oxide. The presence of different metal compounds is related to the selected alloying elements of the galvanising bath. They are ball-milled to liberate the phases. Separation is accomplished by sweeping the mill with a stream of air to entrain the non-metallic components, which are then collected by a fabric filter. Alternatively, a screen is incorporated into the mill, which passes the fine non-metallic fraction, but retains the coarse metallic fraction. In either case, the metallic fraction is discharged from the mill, melted and cast into ingots for sale, re-use or further treatment.

- Bottom dross (also called hard zinc or spelter) is a zinc/iron mixture of intermetallic phases with some discrete metal particles which also contain some lead. It is formed in holding furnaces and tanks used for batch galvanising and accumulates. If it is not removed, the quality of the zinc coating is reduced and so automatic removal systems are used. Blockages may also result if it is not removed. Top dross is a zinc-iron-aluminium alloy generated from continuous hot dip galvanising. Dross or skimmings and other residues from the die-cast industry contain a mixture of zinc metal and zinc oxide, with little or no chlorides. The treatment schemes summarised above are all applied to these materials. The same applies to old roofing and other sheet materials as well as to residues from the chemical uses of zinc or zinc products.

- Processing scrap vehicles in a series of mills produces shredder residue. After the removal of the non-metallic fraction, the non-ferrous fraction is separated from other steel-based products by magnetic separation. Heavy media separation and other techniques are then used to treat it followed by selective melting to recover zinc.

The residue is melted in two-stages in a gas-fired reverberatory furnace. In the first stage, lead is melted at 340 °C and is tapped and cast into ingots. In the second stage, the temperature is raised to 440 °C and zinc is melted, tapped and cast into ingots. An alternative process uses an indirectly fired rotary kiln with a perforated inner lining. Zinc melts and flows out through the liner into a holding furnace from where it is cast into ingots. Further refining is always necessary.

### 5.1.6.2 Solvent extraction processes for secondary zinc

*(Consider Sections 2.8.7.4, 5.1.5.2.3.2, 5.3.5.7, 5.3.6.5. Check and merge where necessary.*

Solvent extraction can be used to selectively concentrate a zinc containing solution secondary raw materials. D2EHPA is the complexing agent and kerosene is used as the solvent [ 327, Highlights and hurdles in Zinc production by solvent extraction 2008 ].

When applied to secondary raw materials the process involves the upgrading and purification of the pregnant leach solution by solvent extraction (SX) to separate halides and metals from the zinc solution. The resulting purified electrolyte can fed to a conventional RLE process.

The SX stage is used to recover zinc from dirty secondary raw materials such as batteries. Other sources of zinc secondary materials include dusts and fumes from pyrometallurgical processes (e.g. copper smelters, steel electric arc furnaces, etc.); from combustion processes (e.g. domestic wastes incineration, spent tyres incineration, etc.); secondary zinc oxides from fuming processes like Waelz and Primus furnaces; etc.

*It has to be clarified where this process is applied and to which process step it belongs.*

### 5.1.6.3 Waelz kilns

Waelz oxide is a zinc-rich intermediate product for use in zinc-winning processes. It is produced from residues, in particular the dust from electric arc steelmaking furnaces. Waelz kilns and slag fuming furnaces can be used.

The process is designed to separate zinc and lead from other materials by reducing, volatilising and oxidising zinc and lead again [ 99, Hähre, S. 1998 ], [ 117, Krüger, J. 1999 ]. The dust from electric arc steelmaking (EAF dust), other zinc-rich materials such as neutral leach or other residues from the RLE process, coke breeze and materials that contain CaO are stored separately. For optimum process conditions, the feed materials can be homogenised and pelletised. They are then sent directly to the kiln feeding system or for intermediate storage. Weighing equipment can be used to control the quantity of reduction materials (coke) according to the zinc content of the raw materials and of fluxes for the desired slag quality. There are some variations in the process depending on the slag basicity that is achieved [ 99, Hähre, S. 1998 ], [ 117, Krüger, J. 1999 ].

The normal operating temperature inside a Waelz kiln is about 1200 to 1400 °C. Inside the kiln, solid materials are first dried and then heated up by the countercurrent flow of hot gas and contact with the refractory-lined walls. Depending on the inclination, length and rotation speed, the material has an average residence time of between 4 and 6 hours in the kiln. In the strongly reducing atmosphere of the solid bed, zinc, lead and other metals are reduced. Zinc and lead are evaporated into the gas and chlorides and alkalis are vaporised together with other volatile metals and elements. As there is a surplus of air in the kiln, the metal vapours are oxidised. The mixed oxides are drawn from the kiln with the process gases and separated in the gas treatment system. (See Figure 5.9).

The SDHL process (named by its inventors: Saage, Dittrich, Hasche, Langbein) is a development of the conventional Waelz process using the basic slag system to reduce the energy consumption and to improve the zinc yield and throughput [ 246, French Report on SDHL process 2008 ]. It was patented in 2000. It can be retrofitted to existing Waelz plants. In a conventional Waelz process, the coke is fed at a rate above stoichiometric requirements and results in residual coke in the slag. In the SDHL, process coke is added substoichiometrically (only about 70 % of the coke needed) and the metallic iron portion is reoxidised at the kiln end by the targeted addition of air to provide the extra process heat.

Due to the release of energy by the oxidation of iron, no additional natural gas input is needed at normal operation. Up to 40 % reduction of coke breeze input is possible and higher throughput, higher zinc recovery and a reduction of $CO_2$ emissions are achieved [ 234, UBA Copper, lead, zinc and aluminium 2007 ].

The results indicate that the basic slag system achieves a PCDD/F reduction by a factor of about 10, a fluorine fixation in the slag with a share of 60 % and a longer lifetime of the lining can be achieved.

The gas treatment system typically comprises a settling chamber for the removal of coarse dust that is carried over mechanically which is fed directly back to the furnace. The hot process gases are cooled down using various direct or indirect coolers. An electrostatic precipitator or fabric filter is used to separate the Waelz Oxide from the cooled gases. Techniques to minimise and remove PCDD/F are used where needed and these are covered in Section 2.9. In Waelz plants, an adsorbent comprising Waelz oxide, lignite or activated carbon is used in a two-stage process. A post-combustion chamber can be used to minimise the emission of VOCs.

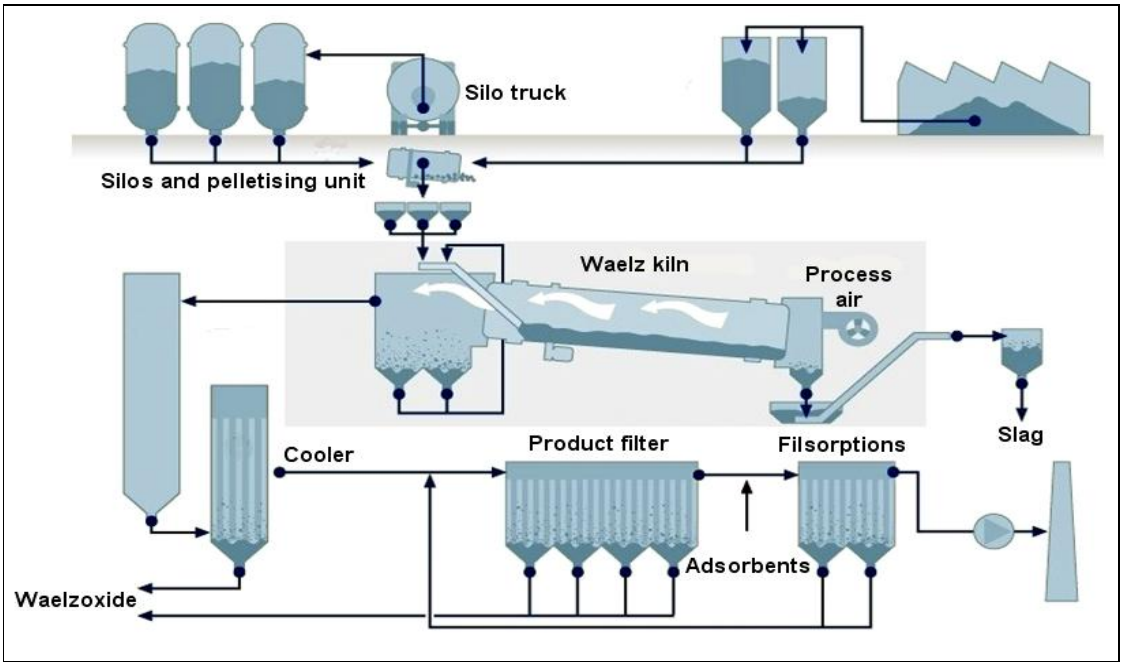


**Figure 5.9: Flow sheet of the Waelz process**
[ 234, UBA Copper, lead, zinc and aluminium 2007 ]

The slag produced is discharged continuously from the end of the furnace into a water quench system. After cooling, screening and crushing, the slag from the SDHL process can be used as a material in civil engineering, e.g. for road construction after suitable leachability tests. Slag from the Waelz processes used to treat residues from zinc production processes can be treated in a flotation process after the slag has been crushed. The flotation process produces a copper rich portion which is returned to a copper or lead smelter for metal recovery. This method is used where the tailings can be adequately treated (see the Reference Document on Tailings and Waste Rock in the Mining Industry).

The Waelz oxide that is produced can be processed in a number of ways. The most basic process is hot briquetting or sintering for sale to pyrometallurgical zinc plants, e.g. Imperial Smelting process. If the lead oxide content is high, a calcination step can also be used to volatilise the lead.

Waelz oxide can also be washed with water and sodium carbonate, sodium bicarbonate or possibly sodium hydroxide in a two or three-stage process using the countercurrent flow principle. By these additions, metal chlorides can be precipitated as metal carbonates or hydroxides. Besides the removal of chloride, this washing process allows the removal of fluoride, sodium and potassium. The alkalis of the rich liquor from the first washing step can be removed by a crystallisation step to produce a salt residue and an alkali-free condensate. The salt residue is disposed of underground. The condensate can be recycled; in this case the total process can work without producing waste water. The washing processes are shown in Figure 5.10 and Figure 5.11.

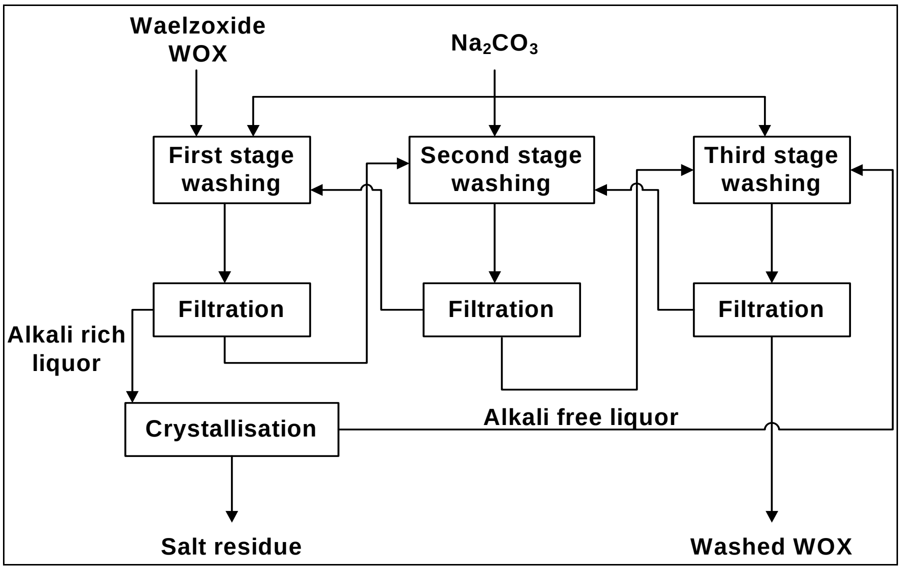


**Figure 5.10:** **Waelz oxide three-stage washing process**
[ 234, UBA Copper, lead, zinc and aluminium 2007 ]

*Both figures 5.10 and 5.11 are included in Section 5.3.6.4 and should be deleted either here or there.*

A two-stage process and effluent treatment can be carried out as the discharge of the bleed that contains chlorine is possible. In comparison to the washing and crystallisation process, the advantages of the two-stage washing are the lower energy consumption, the lower operational costs, the lower investment costs and the avoidance of a solid residue.

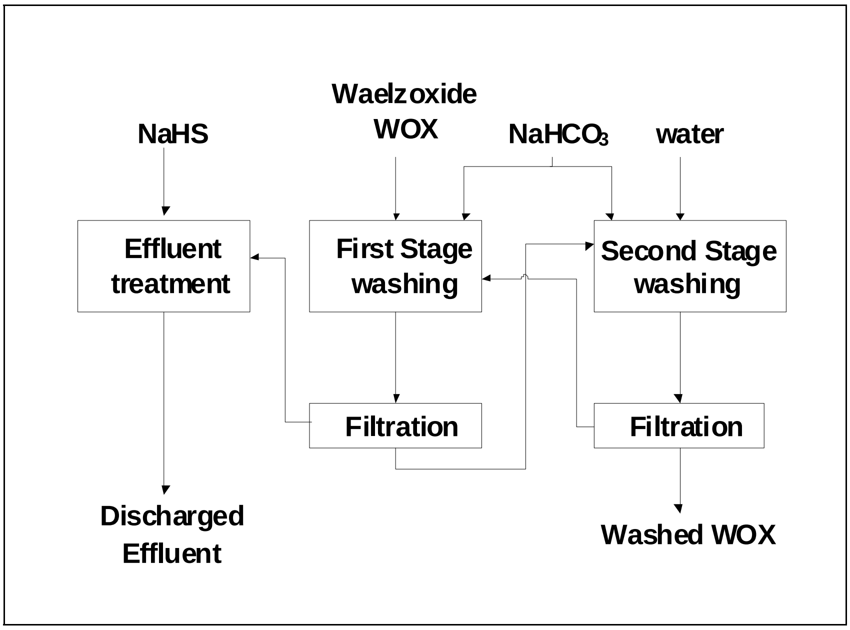


**Figure 5.11:** **Waelz oxide two-stage washing process**
[ 234, UBA Copper, lead, zinc and aluminium 2007 ]

### 5.1.6.4 Slag fuming processes

These processes are also used to recover zinc from residues. Electric arc furnace dust, most of the slags from lead smelting operations and other residues from zinc reduction processes contain lead and zinc that will be lost if they are not treated further. These materials may be fumed with a source of carbon such as coal, to recover lead and zinc and to raise heat from the process [ 117, Krüger, J. 1999 ].

Cyclone or converter type furnaces are used to raise the temperature above 1200 °C to volatilise the metals and then form the oxides that are then recovered from the gases in a filtration stage. The cyclone furnace is operated with oxygen-enriched air but the converter is operated with substoichiometric air. Excess heat is produced and this is recovered in a waste heat boiler and electricity is generated. The slag produced is used for construction purposes.

The Ausmelt/ISA Smelt furnace, the multiple hearth furnace and the submerged plasma furnace is also reported to be used to treat steelmaking dust, leaching residues and coating sludges to recover zinc as an alternative to the Waelz process [ 227, IZA Report 2008 ]. It is reported to be used to produce steel and other metals from the residues in conjunction with a reduction furnace [ 257, Paul Wurth 2008 ].

#### 5.1.6.5 Remelting and refining

Clean and unmixed secondary zinc scrap is remelted or refined to secondary zinc grades. Impurities, like Al or Fe bearing materials, are mainly removed mechanically in the separation step before the melting, if possible. Mixed scrap can be pretreated in a separation melting furnace to remove zinc from metals with a higher melting point.

Melting is mainly conducted in induction furnaces. After the melting the segregation and alloying step follows. In the first step impurity elements can be partly or completely removed depending on the solubility of the element in the melt. Alloying elements can be added, if required.

### 5.1.7 Melting and alloying processes for zinc

Melting and alloying are usually carried out in indirectly-fired crucible furnaces or induction furnaces, temperature control is practised to ensure that zinc is not volatilised forming fumes. The fuel is usually either gas or oil. The gas or oil burner can be located outside the crucible, which is encased in a combustion box, or inside the crucible as an immersion tube heater [ 12, HMIP (UK) 1994 ], [ 98, Lijftogt, J.A. et al 1998 ].

In both cases, temperature control is critical, as the casting temperature must not exceed 450 °C for most alloy compositions to avoid metal loss by fuming. Alloy additions are usually made as solids, but in certain operations, molten aluminium is added from an adjacent melting furnace.

When alloys are made from impure raw materials, fluxes are needed to absorb the impurities. The standard flux contains zinc chloride, magnesium chloride and sodium silicofluoride. The use of this flux results in the emissions of gaseous silicon tetrafluoride, which are removed by wet scrubbing. The tetrafluoride is decomposed to form hydrogen fluoride that is absorbed by the scrubbing medium.

### 5.1.8 Casting processes for zinc

Zinc is melted in electric furnaces and temperature control is practised to prevent fuming. The zinc bath is periodically skimmed to remove solid dross: zinc oxide and zinc chloride. A flux is often added to reduce the loss of zinc in the dross. The dross can be recycled within the ISF or back to the roaster in the electrolytic zinc process.

Metal is usually cast into permanent moulds that are commonly made of cast iron or cast steel. Stationary or continuous conveyor casting machines are used.

Static moulds and conveyor casting machines are used to produce blocks and ingots. Continuous casting machines are used to produce rod for reduction to wire.

### 5.1.9 Production of zinc dust

Zinc dust is produced as a product for other industrial processes and as a reagent for use during the leach liquor purification route. Molten zinc produced by the same techniques outlined above is sprayed under pressure through an atomising nozzle and is then rapidly cooled in an inert atmosphere to produce dust [ 117, Krüger, J. 1999 ]. Air, water or centrifugal atomisation of a stream of molten zinc can also be used to produce dust. The dust is removed in a fabric filter system and conveyed to the process or packaged.

### 5.1.10 Cadmium

#### 5.1.10.1 Production of cadmium from lead and zinc processes

Cadmium is produced as a by-product from many of the metal recovery processes. The production of zinc and lead are the main sources [ 117, Krüger, J. 1999 ].

In the Imperial Smelting furnace (ISF), cadmium is recovered via two separate routes. Some cadmium follows zinc and is eventually recovered as condensate from the second stage distillation. The balance is recovered from the flue dust from the gas-cleaning section that precedes the sulphuric acid plant. It is leached with sulphuric acid and is then stripped from this liquor.

Cadmium cementate, recovered from the purification of zinc solutions is also refined hydrometallurgically. In this process, the cementate is leached in a sulphuric acid medium, the solution purified, and cadmium metal is electrowon. The purified $ZnSO_4$ solution is returned to the main zinc circuit [ 234, UBA Copper, lead, zinc and aluminium 2007 ].

Cadmium is also recovered as cadmium chloride liquor by an ion exchange process. The liquor is directed to an immersed trommel with high grade zinc strip that starts an exchange reaction and results in the production of cadmium sponge and zinc chloride liquor. The sponge, from this process, from the cementate process or from sulphate solutions, is melted with caustic soda (sodium hydroxide) flakes to remove the remaining zinc and the product is cast and sold or if impure, sent to further cadmium refining. Cadmium can also be recovered as the carbonate and electrowinning techniques can be used to recover it.

In the cadmium refinery, cadmium from both routes is combined and distilled at high temperatures. The condensate is cadmium that contains approximately 1 % zinc and the run-off is high grade zinc. The distilled cadmium is melted with caustic soda and sodium nitrate to remove residual zinc. Cadmium recovered from hydrometallurgical routes is treated in a similar way but a vacuum distillation stage is also used.

#### 5.1.10.2 Production of cadmium from batteries

The other main source of cadmium is from the recycling of Ni-Cd batteries. Several recycling initiatives exist and they supply batteries to the industry for automatic sorting and recovery. Ni-Cd batteries are first of all pretreated thermally to remove plastic coatings and open the battery cases. The opened batteries are then heated in a closed retort to volatilise and then condense the cadmium, which is then cast into moulds. Nickel and iron residues are recycled. Each of the process stages uses high quality extraction and abatement systems to remove dust, metals and VOCs such as PCDD/F. The process is dry and is isolated from the drainage system.

### 5.1.11 Production of other metals (In, Ge, Ga, As, Te, Sb, Bi, Se)

Other metals are sometimes present in the concentrates that are used for zinc and lead production. They tend to be concentrated in the slags, dross, flue dusts and residues produced during processing and these residues comprise the feed material for these metals.

Recovery processes can be complex and many are commercially confidential. The processes combine several techniques such as leaching, cementation, solvent extraction, chlorination, electrowinning and vacuum distillation. These techniques can be followed by zone refining and crystal growth techniques to produce ultra pure metals.

## 5.2 Current emission and consumption levels

The main environmental issues of the zinc and lead industry are air and water pollution and the generation of hazardous wastes. The facilities generally have their own waste water treatment facilities and waste water recycling or re-use is usually practised.

By using the crystallisation step after washing, the Waelz oxides, the subsequent hydrometallurgical operation can be carried out without producing waste water. This is established in Germany. Surface water can be captured to supplement the water demand of the process and losses due to evaporation.

Many wastes are re-used but the main item is leach residue that has a high environmental impact [ 98, Lijftogt, J.A. et al 1998 ], [ 99, Hähre, S. 1998 ]. Some local aspects, like noise, are relevant to the industry. Due to the hazardous nature of some solid and liquid waste streams, there is also a significant risk for soil contamination [ 237, Austria M168 2004 ].

Table 5.4, Table 5.5, Table 5.6, Table 5.7, Table 5.8, Table 5.9, Table 5.10, Table 5.13 and Table 5.11 give input and output balances for some lead and zinc plants in Europe.

| Input | (t/yr) | Output | (t/yr) |
|---|---|---|---|
| Battery lead paste | 107000 | Lead bullion | 113000 |
| Lead concentrates | 60000 | Sulphuric acid | 45000 |
| Battery grids | 32000 | Lead concentrate | 35000 |
| Other secondary | 6200 | Silver | 170 |
| Coal or coke | 4900 | Furnace lining | 660 |
| Oxygen | 13300 | $CO_2$ | 18000 |
| Natural gas | 110000 MWh/yr | Waste water (process) | 5 $m^3$/h |
| Electrical energy | 21000 MWh/yr | Off-gas | 32000 to 49000 $m^3$/h |

**Table 5.4: Input and output data for the Ausmelt/ISA Smelt furnace**
[ 234, UBA Copper, lead, zinc and aluminium 2007 ]

| Input | (t/yr) | Output | (t/yr) |
|---|---|---|---|
| Lead concentrates | 145000 | Lead bullion | 135000 |
| Secondaries | 100000 | Sulphuric acid | 100000 |
| Fluxes | 8000 | Slag | 75000 |
| Coal | 15000 | Copper-lead-matte | 4500 |
| Oil | 100 | Silver | 260 - 300 |
| Oxygen | 50000000 $Nm^3$/yr | Zn-/Cd carbonate | 250 |
| Natural gas | 3300000 $Nm^3$/yr | $CO_2$ | 61500 |
| Electrical energy | 9000000 MWh/yr | Off-gas | 20400 $m^3$/h |
|  |  | Waste water (cooling) | 2 $m^3$/h |

**Table 5.5: Input and output data for the QSL plant**
[ 234, UBA Copper, lead, zinc and aluminium 2007 ]

| Input | | | Output | | |
|---|---|---|---|---|---|
| Melting materials | t/t Pb | 2.12 | Products | | |
| Battery scrap | % | 63 | Lead and lead alloys | *t/t Pb* | 1 |
| Other melting materials | % | 21 | Battery paste | *t/t Pb* | 0.5 |
| Bullion, scrap lead | % | 16 | Polypropylene compounds | *t/t Pb* | 0.07 |
| *Reagents* | *t/t Pb* | 0.14 | *Residues* | | |
| Steel borings | % | 46 | Residual plastics | *t/t Pb* | 0.10 |
| Petrol coke | % | 32 | Slag | *t/t Pb* | 0.23 |
| Soda | % | 22 | *Others*<br>Exhaust gases | $Nm^3$/t Pb | 70000 |
| Others: Electric energy | MWh/t Pb | 0.26 | | | |
| Natural gas | MWh/t Pb | 1.19 | | | |
| PP chips (external) | *t/t Pb* | 0.04 | | | |

**Table 5.6:** **Input and output data for a battery recovery plant without desulphurisation (1998)**
[ 99, Hähre, S. 1998 ]

| Inputs | (t/yr) | Outputs | (t/yr) |
|---|---|---|---|
| Melting materials | | | |
| Battery scrap | 42000 | Crude lead | 43000 |
| Lead scrap | 5400 | Polypropylene-chips | 1800 |
| Secondaries | 2600 | Slag | 10000 |
| Internal returns | 10700 | Sodium sulphate | 4700 |
| Fluxes | | Furnace lining | 35 |
| NaOH | 7000 | $CO_2$ | 10800 |
| Steel borings | 2300 | Off-gas | 22000 $m^3$/h |
| Soda | 2200 | Waste water (process) | 105000 $m^3$/yr |
| Leaded glass | 1700 | Slag | 10000 |
| Energy | | | |
| Coke | 2400 | | |
| Oxygen | 3700000 $Nm^3$/yr | | |
| Natural gas | 1400000 $Nm^3$/yr | | |
| Electrical energy | 3800000 kWh/yr | | |

**Table 5.7:** **Input and output data for a battery recovery plant with desulphurisation (preparation and short rotary furnace)**
[ 234, UBA Copper, lead, zinc and aluminium 2007 ]

| Input | (t/yr) | Output | (t/yr) |
|---|---|---|---|
| Battery scrap | 65000 | Refined lead and alloys | 28000 |
| Battery plates | 4000 | Battery paste | 32500 |
| Scrap lead | 6000 | PP fine grains | 2750 |
| | | Ebonite and separators | 3500 |
| | | Slag | 3300 |

**Table 5.8:** **Input and output data for a battery recovery plant with paste removal (1998)**
[ 99, Hähre, S. 1998 ]

| Inputs | (t/yr) | Outputs | (t/yr) |
|---|---|---|---|
| Used batteries, dry | 50000 - 60000 | Lead bullion | 49000 - 50000 |
| Other lead scrap, waste | 13250 - 16500 | Flue dust | 2500 - 2800 |
| Other inputs (iron) | 5500 - 7000 | Excess slag | 650 - 750 |
| Slag (return) | 12500 - 14000 | Return slag | 12500 - 14000 |
| Sludge from water treatment | 3850 - 4450 | Off-gas | 65000 Nm$^3$/h |
| Flue dust | 500 - 650 | Iron/lead matte | 9800 - 10200 |
| Coke | 4950 - 5950 | Spent Acid | 4000 - 4500 |
| Coal | 0 | Lead dross | 3500 - 4000 |
| Oxygen | 1000000 Nm$^3$/yr | $CO_2$ | |
| Natural gas | 477500 Nm$^3$/yr | Off-gas | 65000 m$^3$/h |
| Electrical energy | 10390000 Wh/yr | Waste water (process) | 0 m$^3$/yr |
| | | Furnace lining | 110 |

**Table 5.9: Input and output data for a battery recovery plant with whole battery smelting (Shaft furnace)**

[ 234, UBA Copper, lead, zinc and aluminium 2007 ]

| Material | Description | |
|---|---|---|
| Feed | Concentrates (47 - 56 % Zn)<br>Waelz oxide (55 - 70 % Zn) | 1.3 - 1.8 t/t SHG Zn<br>possibly 0.03 - 0.58 t/t SHG Zn |
| Products | SHG Zinc (99.99 %)<br>Cadmium(1)<br>Sulphuric acid, e.g. 96 % | <br>0.003 - 0.004 t/t SHG Zn<br>1.23 - 1.68 t/t SHG Zn |
| Waste | Goethite(1) or jarosite(1)<br>Dewatered acid sludge<br>Cadmium residue(1)<br>Hg/Se sludge<br>Precipitated sludge | 0.3 - 0.8 t/t SHG Zn<br><0.0005 t/t SHG Zn<br>0.003 - 0.004 t/t SHG Zn<br>0.0003 t/t SHG Zn<br>0.007 - 0.015 t/t SHG Zn |
| Intermediate-/ By-Products | Pb/Ag concentrate(1)<br>Pb Sulphate(1)<br>Cu Concentrate<br>Zn/Fe concentrate (neutral leach residue)(1)<br>Calomel(1)<br>Gypsum | 0.083 t/t SHG Zn<br>0.115 t/t SHG Zn<br>0.007 - 0.015 t/t SHG Zn<br>0.5 t/t SHG Zn<br><1 t/t SHG Zn<br><0.004 t/t SHG Zn |
| Typical production | SHG Zn<br>Sulphuric acid<br>Cadmium(1) | 130000 t/yr<br>225000 t/yr<br>480 t/yr |
| (1) depending on the process window | | |

**Table 5.10: Typical data for a German zinc electrolysis plant with integration of secondary raw material**

[ 234, UBA Copper, lead, zinc and aluminium 2007 ]

| Inputs | t/t of dry product | Outputs | t/t dry product |
|---|---|---|---|
| **Step 1: Waelz kiln operation** | | | |
| Zn residues (EAF dust, etc.) | 2.68 | Waelz oxide (unwashed) | 1 |
| Coke breeze | 0.48 | Slag, dry | 1.63 |
| CaO, lime | 0.21 | Clean off-gas (Nm$^3$/tProduct,dry) | 2.07 |
| Industrial water (m$^3$/tProduct, dry) | 1.22 | | |
| Natural gas(1) (Nm$^3$/tProduct, dry) | 3.66 | | |
| Electrical energy (kWh/t Product, dry) | 240 | | |
| Diesel oil (m$^3$/tProduct,dry) | <0.001 | | |
| (1) natural gas in Waelz kiln only for preheating, not for normal operation mode | | | |

**Table 5.11: Input and output data for a Waelz process SDHL**

[ 234, UBA Copper, lead, zinc and aluminium 2007 ]

| Inputs | t/t dry product, | Outputs | t/t dry product, |
|---|---|---|---|
| **Step 2a: Washing operation with crystallisation** | | | |
| Waelz oxide (unwashed) | 1.13 | Waelz oxide (washed) | 1.0 |
| Sodium carbonate | 0.06 | Alkali residue | 0.13 |
| Industrial water ($m^3$/t dry product) | 1 | | |
| Natural gas ($Nm^3$/t dry product) | 15 | | |
| Electrical energy (kWh/t dry product) | 94 | | |
| **Step 2b: Washing operation without crystallisation** | | | |
| Waelz oxide (unwashed) | 1.13 | Waelz oxide (washed) | 1.0 |
| Sodium hydrogen carbonate | 0.06 | Effluent ($m^3$/t dry product) | 4 |
| Industrial water ($m^3$/t dry product) | 4 | | |
| Natural gas ($Nm^3$/t dry product) | 33 | | |
| Electrical energy (kWh/t dry product) | 36 | | |

**Table 5.12: Input and output data for a Waelz oxide washing process**
[ 267, BEFESA 2008 ]

The typical composition of feed and products for a zinc electrolysis plant with integration of secondary raw material are given in Table 5.13

| Metal (%) | Zn concentrate | Zn/Fe concentrate | Cu-concentrate | Pb sulphate | Pb/Ag concentrate | Jarosite |
|---|---|---|---|---|---|---|
| Zn | 54 | 18 - 21 | 8 | 4 | 2.5 | 5.5 |
| Fe | 6.7 | 17 - 19 | 0.3 | 2 | 5 | 27 |
| Pb | 2.1 | 7 - 8 | 4 | 40 | 25 | 4.9 |
| S | 32 | 6 - 9 | 2 | 11 | | |
| Cu | 0.4 | 0.6 - 1 | 51 | 0.05 | | 0.2 |
| Cd | 0.2 | 0.1 - 0.2 | 1.2 | - | 0.2 | 0.06 |
| Ag | 0.01 | 0.04 - 0.06 | <0.01 | 0.04 | 0.01 | |
| $SiO_2$ | - | 4 - 7 | 0.7 | 2 | 25 | 0.24 |

**Table 5.13: Typical composition of feed and products for a zinc electrolysis plant with integration of secondary raw material**
[ 234, UBA Copper, lead, zinc and aluminium 2007 ]

## 5.2.1 Energy

The energy requirement for the different lead and zinc processes varies to a large extent. It depends on the quality of the feed and the products, the use of latent or waste heat and the production of by-products. Table 5.14 and Table 5.15 show the average energy requirements of the different processes excluding the energy content in the raw material.

| Process | Electric (kWh/t Pb) | Coke (kg/t Pb) | Coal (kg/t Pb) | Gas (Nm$^3$/t Pb) | Fuel Oil (l/t Pb) | $O_2$ (Nm$^3$/t Pb) | Total energy MJ/t Pb including contribution from plastic burnt |
|---|---|---|---|---|---|---|---|
| Pb shaft furnace secondary | 211 | 80 - 90 | 800 - 900 | 10 | - | 20 | 10420 |
| Rotary furnace with CX system and $Na_2SO_4$ production | 250 - 280 | - | 30 | 100 | 15 - 20 | 160 | 6488 |
| QSL | 70* | - | 80 – 120 | 25 | - | 370 | 4002 |
| Ausmelt/ISA Smelt | 190 | 40 | - | 97 | - | 83 | 5490 |

**Table 5.14: Energy requirement of various lead processes**
[ 234, UBA Copper, lead, zinc and aluminium 2007 ]

*Compare with [504] a contribution from Mr. Steil, 16/11/2009 submitted 23November 2009 per email (see lead folder)*
*Figures for Coal in shaft furnaces is totally unclear.*

| Process | Product | Electrical (kW/h per t) | Coke (kg/t) | Natural gas (Nm$^3$/t) | Water for leaching (m$^3$/t) |
|---|---|---|---|---|---|
| Use of concentrate with low iron content(1) | SHG zinc | 3850 – 4905 | 0.48 GJ/t average for other energy | 12 | |
| Zinc roast leach electrowin | SHG zinc | 4000 - 4100 | | | |
| ISF & NJ distillation | Zinc<br>Metal | 1050<br>750 | 1100<br>785 | 220<br>160 | |
| Waelz kiln | | | | | |
| SDHL without washing | WO unwashed | 240 | 480 | 4(2) | |
| SDHL with 3 stage washing and crystallisation | WO washed | 360 | 540 | 19 | 1 |
| SDHL with 2 stage washing | WO washed | 300 | 540 | 38 | 6 |
| Slag fuming | slag | 150 | 250 | | |

(1) Total energy 13.86 – 20.00 GJ/t without energy credits.
(2) For preheating only.

**Table 5.15: Energy requirement of various zinc processes**
[ 234, UBA Copper, lead, zinc and aluminium 2007 ]

### 5.2.2 Emissions to air

*I propose to distinguish more accurately between lead and zinc.*
*Much better values and emission concentration values are available for zinc production (i.e. in reference 99)*

The emissions to air are either captured as stack emissions or can escape the process as diffuse emissions depending on the age of the plant and the technology used. Stack emissions are normally monitored continuously or periodically and reported. Diffuse emissions are a cause of concern and should be captured.

The main emissions to air from zinc and lead production are:

- sulphur dioxide ($SO_2$), other sulphur compounds and acid mists
- oxides of nitrogen ($NO_X$) and other nitrogen compounds
- metals and their compounds
- dust
- VOCs and PCDD/F.

Other pollutants are considered to be of negligible importance for the industry, partly because they are not present in the production process and partly because they are immediately neutralised (e.g. chlorine or HCl) or occur in very low concentrations (e.g. CO). Emissions are to a large extent bound to dust (except cadmium, arsenic and mercury that can be present in the vapour phase) [ 98, Lijftogt, J.A. et al 1998 ].

Figure 5.12 shows the significance of plant improvements on diffuse emissions of dust, lead and cadmium from the Ausmelt/ISA Smelt furnace.

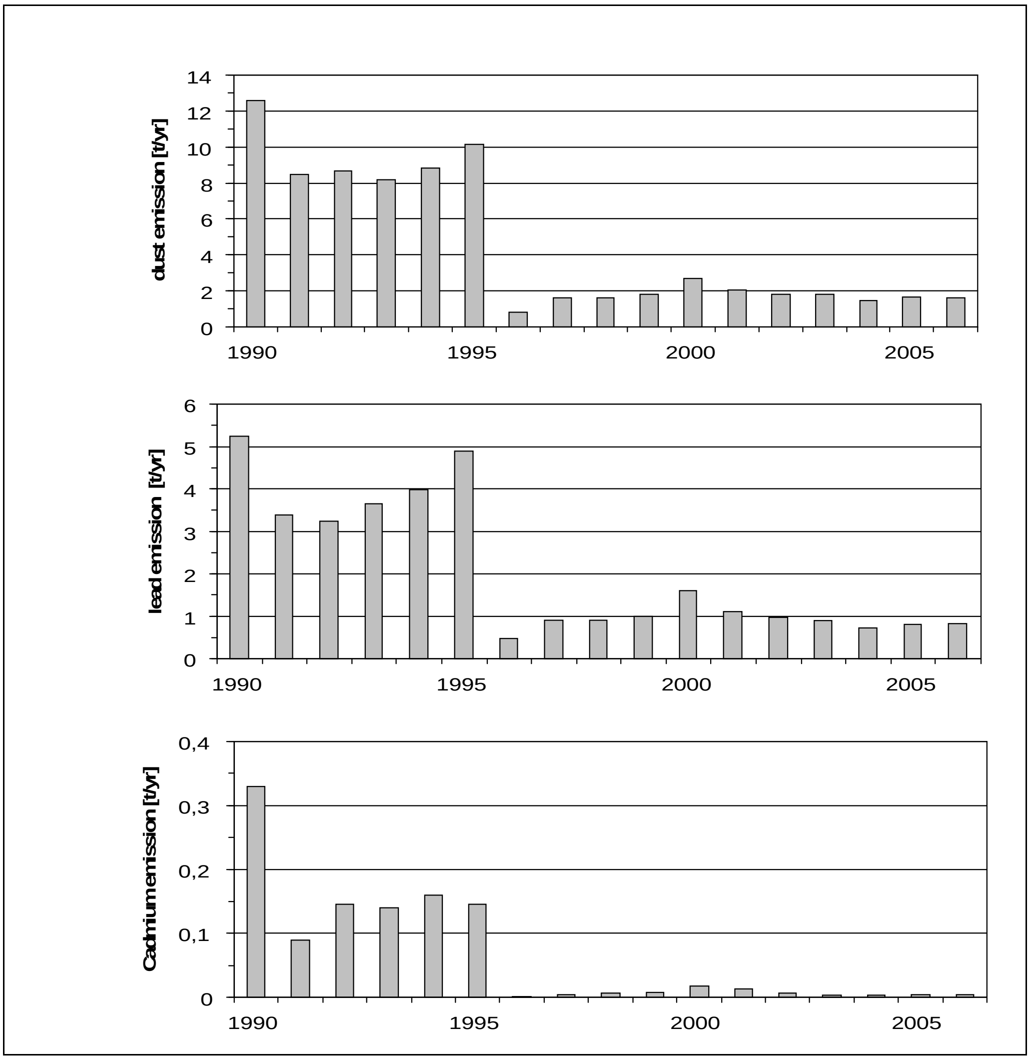


**Figure 5.12**: **Significance of plant improvements on diffuse emissions of dust, lead and cadmium from the Ausmelt/ISA Smelt furnace**

[ 234, UBA Copper, lead, zinc and aluminium 2007 ]

The sources of emissions depend on the process used and are shown in Table 5.16 and can be:

- roasting (most emissions occur during unscheduled shutdown)
- other pretreatment (battery breaking)
- transport and handling of material
- sulphuric acid plant
- smelting and refining
- leaching and purification
- electrolysis
- casting.

*What about slag granulation. Where are the processes and emissions included?*

| Component | Roasting sintering smelting | Leaching and purification | Electrolysis | Battery Breaking | Casting, etc. | Sulphuric acid plant |
|---|---|---|---|---|---|---|
| Sulphur oxides | ••(1) | • | •• (acid mist) | • | • | ••• |
| Nitrogen oxides | •(1) | | | | • | • |
| Dust and metals | •••(1) | • | • | ••• | ••• | |
| VOC and PCDD/F | •(••)(2) | | | | •(1) | |

NB: ••• more significant – • less significant.
(1)The direct emissions from the roasting or smelting stages are treated and/or converted in the gas-cleaning steps and sulphuric acid plant; the remaining emissions of sulphur dioxide and nitrogen oxides of the sulphuric acid plant are still relevant. Diffuse or non-captured emissions are also relevant from these sources. Secondary smelting of battery paste is a source of $SO_2$.
(2) PCDD/F and VOCs may be present if secondary materials are used that contain PCDD/F or are contaminated with organic materials. VOCs may also be present during solvent extraction processes used for the production of Ga, Ge, etc.

**Table 5.16: Significance of potential emissions to air from lead, zinc and cadmium production**

*What about the refining stage??*
*Refining is a severe source for dust emissions, metal fumes and SO2 from the copper removal stage! Ask TWG about SO2 emissions from refining.*
*I don't think it is a good idea to have one table for lead and zinc. VOC emissions are different from both plants. Emissions from roasting and sintering are both treated in sulphuric acid plants and thus the techniques mentioned under 5.4.1.3 are not applied for |VOC treatment.*

Besides process emissions, diffuse emissions occur. The major diffuse emission sources are [ 98, Lijftogt, J.A. et al 1998 ]:

- dust from the storage and handling of concentrates (10 t/yr)
- leakage from roasters and smelters
- aerosols and dust from the exhaust gases of leaching and purification vessels (1 t/yr)
- exhaust gases of cooling towers of the leaching and purification units (0.7 t/yr)
- exhaust gases of cooling towers of the electrolysis process (0.8 t/yr)
- dust from the exhaust gases of casting furnaces (1.8 t/yr)
- miscellaneous (0.7 t/yr).

Although diffuse emissions are difficult to measure and estimate, there are some methods that have been used successfully see Section 2.4.2. Table 5.17 gives some emission data based on the significance of upgrading of a lead process from blast furnace to Ausmelt/ISA Smelt [ 99, Hähre, S. 1998 ] and illustrates the potentially high level of diffuse emissions.

| | Conventional plant (1990) (kg/yr) | | | Ausmelt/ISA Smelt plant (1997) (kg/yr) | | | Reduction rate (%) | | |
|---|---|---|---|---|---|---|---|---|---|
| **Emissions** | **Controlled** | **Diffuse** | **Total** | **Controlled** | **Diffuse** | **Total** | **Controlled** | **Diffuse** | **Total** |
| Lead | 5236 | 19555 | 24791 | 911 | 540 | 1451 | 83 | 97 | 94.1 |
| Cadmium | 330 | 242 | 572 | 3.81 | 0.24 | 4.05 | 99 | >99 | 99.3 |
| Antimony | 151 | 309 | 460 | 25.8 | 1.77 | 27.57 | 83 | >99 | 94 |
| Arsenic | 77.6 | 141.5 | 219.1 | 4.03 | 1.55 | 5.58 | 95 | 99 | 97.5 |
| Thallium | 21.9 | 16.1 | 38 | 1.27 | <0.01 | 1.27 | 94 | >99 | 96.7 |
| Mercury | 16.7 | 0.4 | 17.1 | 0.87 | <0.01 | 0.87 | 95 | >97 | 95 |
| Sulphur dioxide (t/yr) | 7085 | - | 7085 | 140.4 | - | 140.4 | 98 | - | 98 |

NB: Preliminary data for the Ausmelt/ISA Smelt plant. Lead production 1990 - 96724t; and in 1997 - 86941t.

**Table 5.17: Significance of plant improvements on diffuse emissions**

[ 99, Hähre, S. 1998 ]

*See also table 3-45 from the DFIU report! There a comparison has been made between QSL and conventional furnaces.*

### 5.2.2.1 Sulphur dioxide and other sulphur compounds

The major sources of sulphur dioxide emissions are diffuse emissions from the oxidation stages, direct emissions from the sulphuric acid plant and the emissions of residual sulphur in the furnace charge. Good extraction and sealing of the furnaces prevents diffuse emissions and the collected gases from oxidation stages are passed to a gas-cleaning plant and then to the sulphuric acid plant.

After cleaning, the sulphur dioxide in the gas from the sintering, roasting or direct smelting stages is converted to sulphur trioxide ($SO_3$) and this is reported in Section 2.11. During startup and shutdown there may be occasions when weak gases are emitted without conversion. These events need to be identified for individual installations, many companies have made significant improvements to process controls to prevent or reduce these emissions [ 98, Lijftogt, J.A. et al 1998 ], [ 99, Hähre, S. 1998 ].

Lead sinter and some secondary raw materials contain residual sulphur and sulphates. It has been reported [ 126, Madelin, B. et al. 1991 ] that 10 % of the sulphur content of lead concentrate remains in the sintered material that is fed into the furnaces. Similarly, the sulphate content of battery scrap may be significant depending on the way it is pretreated [ 266, Italy Report on Desulphurisation 2008 ] and whether the paste is included. In most cases the sulphur is fixed in the slag or in other by-products. The extent of fixation depends on the fluxes used and the other metals associated with the process, for example copper matte may be produced when Pb/Cu concentrates are treated together. Pb-Fe matte is produced under reducing conditions when iron turnings are added. In other cases, $SO_2$ may be emitted and may need further treatment.

During electrolysis, emissions of aerosols (diluted sulphuric acid and zinc sulphate) take place to the hall. These emissions leave the cell room via the (natural) ventilation or from the cooling towers. The emissions are small compared with the emissions from the sulphuric acid plant but as they are in the form of an aerosol, they can be dealt with in mist eliminators or dust abatement [ 98, Lijftogt, J.A. et al 1998 ]. Some processes use coverings for the cells such as foam or plastic beads to reduce mist formation [ 136, Fugleberg, S. 1999 ].

Emissions from several zinc and lead processes are shown in Table 5.18 below.

| Process | Product | Total metal production (tonnes per year) | Sulphur dioxide produced (g/t of metal) |
|---|---|---|---|
| Concentrate with low iron content | Zinc + cadmium | 238800 | 280 |
| Roasting & Electrolysis | Zinc | 65000 to 482000 | 200 to 4000 |
| ISF and sinter plant. | Zinc + lead | 100000 Zn<br>45000 Pb | 5000 to 9000 |
| QSL | Lead | 135000 | 1300 |
| ISA | Lead | 120000 | 3500 |
| Battery - Whole | Lead | 50000 | 4500 |

| | | | |
|---|---|---|---|
| Battery -<br>desulphurised paste | Lead | 35000 to 50000 | 1070 to 2000 |
| Battery -<br>paste excluded | Lead | 35000 | 3200 |
| Batteries + Extra Paste | Lead | 10000 | 210 (FGD system) |
| Lead shaft furnace and sinter plant | Lead | 110000 Pb | 10000 to 45000 |
| Batteries - MA process | Lead | 33000 | 6600 |

**Table 5.18: Sulphur dioxide production from several zinc and lead processes**
[ 234, UBA Copper, lead, zinc and aluminium 2007 ]
*Question: Do we need these production data? Do they reflect only for Germany?*

One plant has been modified to improve roasting and to collect diffuse emissions from the whole of the process. Sulphur dioxide emissions were reduced from 3000 to 1200 g per tonne of metal produced. Other improvements to process control systems have allowed more constant $SO_2$ concentrations for the acid plants and together with caesium-doped catalysts and the incorporation of a fifth contact pass have resulted in very low emissions [ 228, IZA plant data 2008 ].

Mists from battery breakers can also be responsible for similar emissions. Emissions from the smelters using battery-derived material contain $SO_2$, the concentration depends on whether the paste is smelted or is desulphurised first or is fixed with the slag. Typical figures are 50 to 500mg/Nm$^3$ [ 99, Hähre, S. 1998 ].
*There is only little information for SO2 included here. Maybe more info can be found in chapter 2. Anyhow, we need better information about the options to reduce SO2 and the achieved emission levels for* ***each*** *of the relvant process steps given in table 5.16. This should not be aggregated in one BAT.*

### 5.2.2.2 Nitrogen oxides

The roasting and smelting stages are potential sources of nitrogen oxides ($NO_X$). $NO_X$ may be formed out of nitrogen components that are present in the concentrates or as thermal $NO_X$. The sulphuric acid produced can absorb a large part of the $NO_X$ and this can therefore affect sulphuric acid quality. If high levels of $NO_X$ are present after the roasting stages, treatment of the roasting gases may be necessary for product quality and environmental reasons. Other furnaces that use oxy-fuel burners can also show a reduction in $NO_X$[rr44]. The range for all of the processes is 20 to 400 mg/Nm$^3$.

### 5.2.2.3 Dust and metals

Dust carryover from the roasting and smelting processes are potential sources of direct and diffuse emissions of dust and metals. The gases are collected and treated in the gas-cleaning processes and finally in the sulphuric acid plant. Dust is removed and returned to the process.

The gases leaving splash condensers in the ISF, from distillation columns and from the tapping points are also potential sources. Good extraction and abatement is needed at these points to prevent diffuse emissions. Slag treatment and quenching also gives rise to dust. The range of dust emissions from these captured sources is <1 to 20 mg/Nm$^3$. The slags and dross produced during the recovery of lead from batteries can contain Sb. When these residues become wet, there are potential emissions of stibine which is a poisonous gas.

De-aeration of vessels in the leaching and purification stages can emit dust and metals. Arsine can be emitted from the purification stages of zinc <0.5 mg/Nm$^3$ is achievable using an oxidising scrubber. Cadmium can be emitted from the distillation stages and the cadmium plants.

Emissions of aerosols takes place in the cell room and battery breakers and can contain metals. The range of mist and dust emissions from these sources is 0.1 to 4 $mg/Nm^3$.

The melting, alloying, casting and zinc dust processes are potential emission sources of dust and metals. The range of dust emissions is reported to be 200 to 900$mg/Nm^3$ in the raw gas [ 98, Lijftogt, J.A. et al 1998 ], [ 99, Hähre, S. 1998 ]. Fume collection and abatement systems are used and cleaned gas values are below 10 mg dust/$Nm^3$ [ 99, Hähre, S. 1998 ].

Metals are associated with the dusts emitted, approximately 50 % is zinc. Cadmium and lead are not present when pure zinc is melted, alloyed and cast.

Whereas controlled emissions have known sources and can be captured and treated, diffuse emissions can evolve almost anywhere on a plant site. The main sources of diffuse emissions are material storage and handling, dust sticking to vehicles or streets and open or not abated working areas. Mass release of metals from some European processes are given in Table 5.19.In the recent years some companies reduced their diffuse emissions efficiently by adequate measures such as [ 234, UBA Copper, lead, zinc and aluminium 2007 ]:

- higher burden of the shaft furnace and improving the off-gas collection
- renewal of off-gas collection and filter units
- reduction of furnace downtime by improved refractory lining concept (thereby reduction of startup and shutdown times which cause higher emissions for a limited time)
- closing the roofs of the process buildings and modernisation of filters
- closing, enhousing of delivery, material storage, refining areas and the installation of off-gas collection
- improving material handling (e.g. by wetting of bulk materials before and during loading) and reduction of transport frequencies (e.g. by use of bigger wheel loaders)
- installation of obligatory vehicle washing (for plants and external vehicle)
- reinforcement of plant areas and driveways and optimised cleaning
- closing and decontamination of old slag disposal areas.

| **Process** | **Product** | **Production (tonnes)** | **Dust $(g/t_{product})$** | **Zn $(g/t_{product})$** | **Pb $(g/t_{product})$** | **Cd $(g/t_{metals})$** | **As $(g/t_{metals})$** |
|---|---|---|---|---|---|---|---|
| Roasting, purification & electrolysis (without casting) | Zinc | 130000 - 150000 | NA | 6.6 - 7.6 | NA | <0.05 | NA |
| Roasting, purification & electrolysis (with casting) | Zinc or Zinc alloys | 130000 - 150000 | 3 - 17 | 1 - 15 | <0.3 | <0.05 | <0.03 as oxide |
| Roasting, purification & electrolysis (all process stages from concentrate with low iron content) | Zn + Cd | 238850 | 50.3 captured<br>38.2 diffuse | 31 | 1.5 | 0.20 | 0.003 |
| Waelz process | Waelz oxide | 29000 to 60000 | 14 - 73 | 4 - 21 | 0.3 - 2.0 | 0.13 - 0.42 | <0.1 |
| Remelting, refining | Zinc | 40000 | 60 | 15 | <3 | NA | |
| QSL | Lead | | | | | | |
| -process | Pb bullion | 120000 | 1 | NA | <0.1 | <0.01 | <0.0001 |
| -refinery | pure Pb, Pb alloys | 135000 | 5.4 | NA | <0.1 | <0.01 | <0.01 |

| Process | Product | Production (tonnes) | Dust (g/$t_{product}$) | Zn (g/$t_{product}$) | Pb (g/$t_{product}$) | Cd (g/$t_{metals}$) | As (g/$t_{metals}$) |
|---|---|---|---|---|---|---|---|
| -secondary(1) | | | 12 | NA | 2.3 | 0.03 | 0.09 |
| Ausmelt/ISA Smelt | Lead | | | | | | |
| -process | Pb bullion | 113000 | <1 | 0.09 | 2.5 | <0.1 | 0.01 |
| -refinery | pure Pb and Pb alloys | 120000 | NA | 1 | 4 | 0.01 | 0.02 |
| -secondary(1) | | | NA | 0.04 | 0.3 | <0.01 | <0.01 |
| Battery-Whole (shaft) | Lead | | | | | | |
| -process | | 49000 | 10 - 25 | 0.1 | 2.5 | <0.1 | <0.15 |
| -refinery | | 53000 | 0.49 | NA | 0.024 | NA | NA |
| -secondary(1) | | | <2 mg/Nm$^3$ | NA | <0.01 mg/Nm$^3$ | NA | NA |
| Battery - desulphurised paste | Lead | | | | | | |
| -process | | 43000 | 1 - 3 | NA | 0.1 - 1 | 0.01 | 0.18 |
| -refinery | | 52000 | 4 | NA | 0.5 | 0.02 | 0.24 |
| -secondary(1) | | | 6 | NA | 0.3 | NA | 0.02 |
| Battery - whole (short rotary) | Lead | | | | | | |
| process | | 10000 | 15 - 35 | NA | <0.5 | NA | <0.3 |
| (1)Secondary hood dedusting. | | | | | | | |

**Table 5.19: Mass release of metals from some European processes**
[ 228, IZA plant data 2008 ].
*The caption ..from some European processes is not very helpful.*

### 5.2.2.4 PCDD/F

The formation of PCDD/F in the combustion zone and in the cooling part of the off-gas treatment system (de novo synthesis) may be possible in some processes particularly if plastic components are included in the secondary materials that are fed into a process [ 237, Austria M168 2004 ]. PCDD/F have also shown to be present in some dusts from Waelz kilns treating EAF dust.

Due to the conversion of the former acidic Waelz processes to a basic slag system, a reduction of the PCDD/F concentration in the raw gas of up to the factor 10 can be achieved. Organic compounds can be reduced by postcombustion systems, if required.

In the production of lead, the emissions of PCDD/F are on average below 0.1 ng ITEQ/Nm$^3$, maximum values are usually below 0.4 ng ITEQ/Nm$^3$ and are independent of the feed material due to applied abatement techniques [ 234, UBA Copper, lead, zinc and aluminium 2007 ].

## 5.2.3 Emissions to water in the production of lead, zinc and cadmium

Metals and their compounds and materials in suspension are the main pollutants emitted to water. The metals concerned are Zn, Cd, Pb, Hg, Se, Cu, Ni, As, Co and Cr [ 25, OSPARCOM 1996 ], [ 98, Lijftogt, J.A. et al 1998 ], [ 99, Hähre, S. 1998 ], [ 27, M. Barry et al. 1993 ], [ 234, UBA Copper, lead, zinc and aluminium 2007 ].

Other significant substances that are emitted to water are~~:~~

~~☐metals~~
~~☐materials in suspension~~

~~□~~ chlorides, fluorides, sulphates.

And the possible waste water streams that contain the aforementioned substances ~~m~~ are:

- waste water from wet scrubbers
- waste water from wet electrostatic precipitators
- waste water from the mercury removal step
- waste water from battery breaking and classification stages
- waste water from slag granulation
- waste water from various hydrometallurgical processes
- anode and cathode washing liquid effluent
- sealing water from pumps
- general operations, including cleaning of equipment, floors, etc.
- discharge from cooling water circuits
- rainwater run-off from surfaces (in particular storage areas) and roofs.

Waste water from the gas-cleaning of the smelter and fluidised bed roasting stages are the most important sources. Other sources are the process effluent from electrolysis, battery breaking and cleaning plus miscellaneous sources.

### 5.2.3.1 Waste waters from abatement plants

Generally, wet gas-cleaning systems operate with liquid recycling. A monitored bleed keeps suspended solids and dissolved salts within certain defined limits. The bleed is either treated separately or in an integrated water treatment plant to remove solids and dissolved species before discharge. The destination of the separated material depends on the origin of the waste water.

Wet scrubbers after the roasting process are operated with a $SO_2$ saturated acidic solution. The scrubber removes fluorides, chlorides, most mercury and selenium and some particles that pass the mechanical gas treatment. To avoid the buildup of contaminants, some liquid should be bled continuously from the scrubber. Dissolved $SO_2$ is removed during treatment prior to the discharge.

Wet electrostatic filters will also produce an acidic scrubber liquid. This is recycled after filtering. Some liquid should be bled from this circuit to remove buildup of contaminants. This bleed liquor is treated and analysed before discharge [ 98, Lijftogt, J.A. et al 1998 ].

The mercury removal step takes place prior to the sulphuric acid plant and involves a gas-liquid contact tank or spray tower in which the liquid contains a reagent that combines with mercury and removes it. Mercury chloride ($HgCl_2$) is frequently used as the reagent and reacts with metallic mercury from the gas to form a solid precipitate of $Hg_2Cl_2$ (so-called "calomel"). The relatively clean liquid is discharged as waste water for further treatment. The solid $Hg_2Cl_2$ is sold for mercury recovery or treated to produce mercury chloride again or stabilised for final disposal. Table 5.20 provides an indication of the composition of the gas-cleaning liquids before treatment.

| Component | Concentration (dissolved) | Composition of Suspended solids |
|---|---|---|
| Solids | | 250 - 1500 mg/l |
| Sulphate | 13 - 25 g/l | |
| Chloride | 1.3 - 1.8 g/l | |
| Fluoride | 0.3 - 0.5 g/l | |
| Mercury | 0.1 - 9 mg/l | 5 - 30 % of suspended solids |
| Selenium | 0.1 - 50 mg/l | 10 - 60 % of suspended solids |
| Arsenic | 5 - 95 mg/l | <0.05 % of suspended solids |

| | | |
|---|---|---|
| Zinc | 0.1 - 2.5g/l | 2 - 6 % of suspended solids |
| Cadmium | 1 - 95 mg/l | |
| Lead | 1 - 13 mg/l | 5 - 50 % of suspended solids |

**Table 5.20: Typical gas-cleaning effluents before treatment**
[ 99, Hähre, S. 1998 ]

### 5.2.3.2 Waste waters from b~~B~~attery recovery

The battery breaking and washing stages produce an effluent which is acidic and contains lead and other metals in suspension and solution. This effluent is neutralised and the water is recycled in the process. If possible, the acid is used elsewhere. A portion is usually bled from the system to control dissolved salts. Cooling water can also arise from cooling the crushing process [ 237, Austria M168 2004 ].

These processes also produce contaminated surface water and consequently this water is also treated and re-used. It is common practice to discharge a bleed of this sealed water circuit after further treatment and analysis. Road and surface contamination is minimised by the frequent wet cleaning of roads, hard standing areas and lorries and by techniques for cleaning up spillages[rr45].

The quality and quantity of waste water depends on the process used, the composition of the raw materials that are used in the process and the practices used by the operators. The re-use of process water and rainwater is common.

### 5.2.3.3 Electrolyte bleed effluent

Electrolyte may be bled from the cells to control the build-up of impurities, e.g. magnesium, which may have a detrimental impact on the operation of the electrolytic cells. For zinc production, the flows in the electrolytic cells belong to the same (closed) water circuit as the leaching and purification stages. The sulphuric acid formed during electrolysis is fed to the leaching process and the remaining liquid is purified and fed to the electrolysis [ 98, Lijftogt, J.A. et al 1998 ], [ 99, Hähre, S. 1998 ].

The effluent bleed of the electrolytic, leaching, purification circuit is strongly acidic and contains high concentrations of zinc and suspended solids. The volume of the bleed depends strongly on the composition of the zinc concentrates that are used in the roasting. Components that tend to buildup in the circuit, especially magnesium, will determine the bleed flow and the treatment required. The increasing amount of Ca in the leaching circuit, due to the use of secondary feed material, is controlled by gypsum removal from the leach liquor. A bleed from the system can be treated to remove MgO, chlorides and fluorides [ 320, Biologically produced Sulphide 2004 ].

### 5.2.3.4 Waste waters from ~~Miscellaneous~~ miscellaneous sources

The electrodes used during the electrolysis need to be rinsed periodically to remove deposited material upon the surface. Manganese dioxide is formed on the surface of the anodes by the reaction of oxygen with dissolved manganese. The $MnO_2$ remains on the surface of the anodes, forms a sludge on the bottom of the electrolytic cells or forms a solid layer in the pipes. All these remainders are removed mechanically or by high pressure water periodically. The manganese is separated from the rinse water for external re-use or disposal. Cathodes are cleaned after removal of the zinc or lead sheets. The anode and cathode washing liquid effluents are acidic and likely to contain copper, zinc, lead and suspended solids [ 98, Lijftogt, J.A. et al 1998 ], [ 99, Hähre, S. 1998 ].

Typical waste water analyses of some processes are given in Table 5.21.

|  | **Effluent** | **Flow** | **Main components (mg/l)** |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|
| **Process** | **(m$^3$/yr)** | **(m$^3$/h)** | **Pb** | **Cd** | **As** | **Zn** | **Ni** | **COD** |
| Electrolysis |  | 40 - 200 | 0.01 - 0.8 | 0.001 - 0.15 | 0.01 | 0.01 - 1.9 |  |  |
| ISP |  | 380 - 420 | 0.05 - 0.5 | 0.005 - 0.035 | 0.005 - 0.1 | 0.05 - 1.0 |  |  |
| Waelz kiln SDHL process with washing, without crystallisation | 190000 to 228000 | 35 | <0.2 | <0.1 | <1.0 | <1.0 | <0.5 | <200 |
| CX + Rotary Furnace | 190000 | <0.2(1) |  |  |  |  |  |  |
| MA + rotary furnace | 124000 |  | 0.02 | 0.07 | <0.0005 | 0.27 | 0.09 |  |
| Whole battery | 150000 | 40 | 0.4 | 0.01 | <0.001 | 0.01 | <0.05 | 96 |
| Shaft furnace | 17000 |  | <0.2 | <0.1 |  | <0.3 |  |  |
| QSL | 158000 | 18 | 0.06 | 0.02 | 0.04 | 0.15 | 0.01 | 20 |
| CX + rotary furnace + Pb refinery | 105000 | 2.1 | 0.13 | 0.01 | 0.01 |  | 0.03 |  |
| Ausmelt/ISA Smelt | 110000 | 13 | 0.01 - 0.09 | 0.001 - 0.01 | 0.001 - 0.1 | 0.01 - 0.2 |  | 50 - 200 |

(1) The CX process produces condensate from the crystalliser which has very low metal content and a conductivity of <10 micro siemens

**Table 5.21: Typical waste water analyses**
[ 234, UBA Copper, lead, zinc and aluminium 2007 ]

~~In the Waelz process no effluent is generated.~~ If the Waelz oxide is washed, the use of crystallisation can result in an effluent free process. Alternatively an effluent treatment can be carried out prior to discharge.

A summary of potential waste water sources and treatment techniques is given in Table 5.22.

| Process unit | Operation/source | Use/treatment options |
|---|---|---|
| General | Rainwater from roads, yards, roofs,<br>wet cleaning of roads,<br>cleaning of lorries, etc. | Waste water treatment plant then re-use or recirculation, |
| Battery separation | Spills | Used for the desulphurisation/waste water treatment plant |
| Paste desulphurisation | Spills | Used in the desulphurisation process/waste water treatment plant |
| Smelting and melting operation | Cooling water from furnace, machinery and equipment | Recirculation |
| Slag granulation | Wet ESP effluent<br>Granulation water | Recirculation, waste water treatment plant<br>Recirculation |
| Gas cleaning system | Condensate from gas cooling and wet ESP<br>Condensate from mercury removal<br>Leakage | Removal of suspended dusts and re-use as feed, waste water treatment plant<br>After mercury removal to waste water treatment plant<br>Recirculation |
| Sulphuric acid plant | Cooling water equipment<br>Leakage | Recirculation<br>Waste water treatment plant |
| Cadmium plant | Solution after cadmium removal<br>Leakage | Return to Zn leaching circuit or waste water treatment plant |
| Feed storage | Surface water (rain/wetting) | Waste water treatment plant |
| Sinter plant | Scrubber (sinter fine cooling) | Waste water treatment plant |
| Roast gas-cleaning | Wet gas-cleaning | Waste water treatment plant |
| Cadmium leaching | Cadmium leaching | Return to Zn leaching circuit or waste water treatment plant |
| IS furnace | Gas cleaning<br>Gas cleaning coke heating chamber | Waste water treatment plant; recirculation |
| Slag granulation | Granulation waste water | Recirculation and cooling, waste water treatment plant~~,~~ |
| Roasting/roast gas-cleaning | Wet cleaning of roast gases | Waste water treatment plant |
| Leaching | General operations including wet gas-cleaning | Return to leaching |
| Purification | General operations | Return to leaching |
| Electrolysis | Cleaning of cells, anodes and cathodes | Return to leaching |
| All process units | Maintenance | Waste water treatment plant |
| Waste water treatment plant | Effluent treatment | Re-use for certain applications/discharge |

**Table 5.22: Potential waste water sources and treatment techniques**

Cooling water from the granulation of slag or cooling pond is usually recirculated in a closed circuit system.
*Slag granulation is double mentioned. Roast gas cleaning double mentioned. Necessary?*

### 5.2.4 Production residues such as waste and b~~B~~y-products~~, process residues and waste~~

The production of metals is related to the generation of several by-products, residues and wastes, which are also listed in the European Waste Catalogue (Council Decision 94/3/EEC) *I am afraid, but there is no waste Catalogue any more.* The most important process specific residues are listed below.

*Commission Decision of 3 May 2000*

*replacing Decision 94/3/EC establishing a list of wastes pursuant to Article 1(a) of Council Directive 75/442/EEC on waste and Council Decision 94/904/EC establishing a list of hazardous waste pursuant to Article 1(4) of Council Directive 91/689/EEC on hazardous waste*

*THE COMMISSION OF THE EUROPEAN COMMUNITIES,*

*Having regard to the Treaty establishing the European Community,*

*Having regard to Council Directive 75/442/EEC of 15 July 1975 on waste(1), as amended by Directive 91/156/EEC(2), and in particular Article 1(a) thereof,*

*Having regard to Council Directive 91/689/EEC of 12 December 1991 on hazardous waste(3), and in particular Article 1(4), second indent thereof,*

*Whereas:*

*(1) Several Member States have notified a number of waste categories which they consider to display one or more of the properties listed in Annex III to Directive 91/689/EEC.*

*(2) Article 1(4) of Directive 91/689/EEC requires the Commission to examine notifications from Member States with a view to amending the list of hazardous wastes laid down in Council Decision 94/904/EC(4).*

*(3) Any waste inserted in the list of hazardous wastes must also be included in the European Waste Catalogue laid down in Commission Decision 94/3/EC(5). It is appropriate, in order to increase the transparency of the listing system and to simplify existing provisions, to establish one Community list which integrates the list of wastes laid down in Decision 94/3/EC and that of hazardous wastes laid down in Decision 94/904/EC.*

*(4) The Commission is assisted in this task by the Committee established by Article 18 of Directive 75/442/EEC.*

*(5) The measures laid down in this Decision are in accordance with the opinion expressed by the aforementioned Committee,*

*HAS ADOPTED THIS DECISION:*

*Article 1*

*The list in the Annex to this Decision is adopted.*

*There should be a bullet list with the relevant residues, waste to prepare the reader for the following subsections. The explaination in the section 5.2.4 could be shortened.*

Solid residues derived from various processes and abatement stages may have one of three possible destinations:

- recycling in or upstream of the process
- downstream treatment to recover other metals
- final disposal after treatment to ensure safe disposal.

The following solid waste arisings are significant:

The electrolytic production of zinc is one of the main sources of solid waste in the non-ferrous industry. Relatively large quantities of iron-based solids are generated by the leaching process. Jarosite and goethite are classified as hazardous waste because of the content of leachable elements such as Cd, Pb and As. Techniques are available to reduce the leachability and sometimes the permeability of the residues such as:

- compaction
- the Jarofix process
- treatment in a pyrometallurgical process.

The leaching and purification processes and electrolysis of zinc and the refining stages of lead also generate other metal-rich solids. These are usually rich in a specific metal and are recycled to the appropriate production process.

The ISF or direct smelting furnaces are also significant sources of solid slags. These slags have been subjected to high temperatures and generally contain low levels of leachable metals, consequently they may then be used as construction materials after suitable_-tests [ 289, USEPA Method 1311 and 1312 2008 ]. The Landfill Directive specifies CEN Standard leaching tests for granular waste EN 14405 and EN12457/1-4.

Solid residues also arise as the result of the treatment of liquid effluents. The main waste stream is gypsum waste ($CaSO_4$) and metal hydroxides that are produced at the waste water neutralisation plant. These wastes are considered to be a cross-media effect of these treatment techniques but many are recycled to the pyrometallurgical process to recover the metals.

Dust or sludge from the treatment of gases are used as raw materials for the production of other metals such as Ge, Ga, In and As, etc. or can be returned to the smelter or into the leach circuit for the recovery of lead and zinc.

Mercury and selenium residues arise at the pretreatment of mercury or selenium streams from the gas-cleaning stage. This solid waste stream amounts to approximately 40 to 120 t/y in a typical plant Because of the restrictions in mercury use, mercury recovery from Hg-Se residues or from calomel from the mercury removal stage, is no longer an option. Both by-products need to be stabilised for final disposal. In exceptional cases when the Se to Hg ratio is high, recovery of selenium can be an option.

### 5.2.4.1 Leaching residues

The production of iron based solids (goethite, jarosite or hematite) accounts for the greatest volume of waste depending on the process used. The composition is shown in Table 5.23.

| Process | Fe (%) | Zn (%) | Pb (%) | Cu (%) | Cd (%) |
|---|---|---|---|---|---|
| Hematite (with integrated direct leaching) | 65 - 67 | <0.2 | <0.01 | <0.02 | <0.01 |
| Hematite (without direct leaching) | 59 | 1 | 0.01 | 0.02 | 0.02 |
| Goethite | 40 - 42 | 5 - 9 | <2 | <0.3 | <0.1 |
| Para-goethite | 40 | NA | NA | NA | NA |
| Conventional jarosite | 20 - 30 | 2 - 6 | 0.2 - 6 | <0.2 | 0.05 - 0.2 |
| Low contaminant jarosite | 32 | 0.3 | 0.1 | 0.2 | 0.001 |
| Dor jarosite | 26 | 1 | 4 | 0.08 | 0.05 |
| Jarosite/sulphur residue (40-50 % S) | 9 – 11 | 2 – 5 | 8 – 10 | <0.4 | <0.1 |
| NA: not available | | | | | |

**Table 5.23: Example compositions of different types of residues**
[ 98, Lijftogt, J.A. et al 1998 ], [ 117, Krüger, J. 1999 ]

Typically, these residues account for:

- jarosite - 0.35 to 0.80 tonnes per tonne of zinc produced
- goethite - 0.3 to 0.35 tonnes per tonne of zinc produced
- hematite - 0.2 tonnes per tonne of zinc produced.

Hematite processes have been unable to compete in economic terms as the process is significantly more complex and expensive to operate. In addition, hematite has not proved to be acceptable as a raw material in other industries.

The use of concentrates that have very low iron concentrations allows the production of these residues to be avoided [ 227, IZA Report 2008 ], [ 240, Nl Input on Zn production 2008 ]. In some cases, the process can be stopped at the neutral leach stage and the remainder of the zinc can be recovered in a Waelz kiln or a slag fuming process.

There are still some leachable metals in the slurry after filtering and washing. The residue can be treated to a less leachable form with neutralisation and sulphide treatment. The disposal of these residues can be costly as specially constructed, lined ponds or isolated areas are used to contain the material. Particular care is taken about leakage and these ponds have a major need to monitor groundwater [ 98, Lijftogt, J.A. et al 1998 ], [ 99, Hähre, S. 1998 ]. There is a significant cross-media effect compared to processes that are capable of producing an inert residue. The Council Decision on the treatment of wastes should be taken into account when assessing the treatment or disposal requirements.

As reported earlier in Section 5.1.5.2, leaching residues with higher amounts of Zn or Pb can be treated in ISF or Waelz kilns (Zn-Fe concentrates) and in a lead smelter ($PbSO_4$ concentrates). The Jarofix process is available to stabilise the residues with lime and cement [ 228, IZA plant data 2008 ] and compaction can be used to decrease the moisture content and volume of the iron residue. Pyrometallurgical treatment of these residues is also practised in Korea to produce a non-leachable slag and recoverable metal oxides [ 40, AusmeltAusmelt Ltd. 1996 ], [ 41, Ausmelt Ltd. 1996 ]. Problems with contaminant buildup have been reported. Other developments are reported in Emerging Techniques Section 5.5.

### 5.2.4.2 Pyrometallurgical slags and residues

Slags from the blast furnace, ISF, direct smelting and Waelz kiln processes (if EAF dust or similar feed is treated) usually contain very low concentrations of leachable metals. They are therefore generally suitable for use in construction [ 99, Hähre, S. 1998 ]. The slag output is between 10 and 70 % of the weight of the metal produced depending on the raw materials used.

Slags from the battery processing plants account for 13 to 25 % of the weight of lead produced. They may be suitable for construction uses depending on the leachability of the metals they contain. The leachability is influenced by the fluxes used and the operating conditions [ 99, Hähre, S. 1998 ]. The use of sodium-based fluxes ($Na_2CO_3$) to fix sulphur in the slag causes an increase in the quantity of leachable metals. These slags and dross from battery recovery processes can contain Sb. This is normally recovered, but storage in damp conditions can cause the emission of stibine.

A number of standard leachability tests are used by Member States and these are specific to the country in question. Processes are under investigation to lower the contents of entrained metals in order to ensure the future suitability for construction and other applications. Table 5.25 and Table 5.26 give some eluate values based on the German leaching test method DEVS4.

| Component | Eluate (according to DEVS4) (mg/l) |
|---|---|
| Zn | 0.02 - 0.1 |
| Pb | 0.005 - 0.1 |
| As | 0.001 - 0.02 |
| Fe | 0.05 - 0.2 |
| Cu | <0.001 - 0.05 |
| pH | 7 - 11 |

**Table 5.24:** **Eluate values of granulated ISF slag**
[ 99, Hähre, S. 1998 ]

| Component | Waelz slag Eluate (according to DEVS4) (mg/l) |
|---|---|
| Zn | 0.05 |
| Pb | 0.02 |
| As | 0.008 |
| $Cr_{tot}$ | 0.002 |
| Ni | 0.005 |
| Fe | 0.5 |
| Cu | 0.05 |
| F | 1 |
| Cl | 5 |
| pH | 9.9 |

**Table 5.25: Eluate values for acidic Waelz slag**
[ 99, Hähre, S. 1998 ]

| Component | Eluate (according to DEVS4) (mg/l) |
|---|---|
| As | 0.05 |
| Cd | 0.001 |
| Cu | 0.005 |
| Pb | 0.02 - 0.2 |
| FeO | <0.05 |

**Table 5.26: Eluate values for slag from QSL process**
[ 99, Hähre, S. 1998 ]

The dross and solids, removed during the zinc and lead melting and refining stages, contain metals that are suitable for recovery and Table 5.27 gives some of the solid material from the refining of lead bullion.

| Refining step | Solid output | Use/treatment options |
|---|---|---|
| Drossing/de-copperising | Copper dross | Further processing to recover copper and lead |
| Softening (Harris process/ oxygen softening) | Harris slags<br>Antimony slag | Hydrometallurgical treatment for metal recovery.<br>Pyrometallurgical treatment for metal recovery |
| De-silvering | Zinc-silver crust | Recovery of noble metals |
| De-zincing | Zinc metal | Re-use for de-silvering |
| De-bismuthising | Bismuth crust | Recovery of bismuth |
| Removal of alkali metals and alkaline-earth metals | Mg-Ca oxide dross | Internal recycling as flux |
| Finishing | Caustic dross | Internal recycling |

**Table 5.27: Solid material from the refining of lead bullion**
[ 13, HMIP (UK) 1994 ]

### 5.2.4.3 Plastics from battery processing~~Other materials~~

*This heading is not correct because this subsection contains only text for plastic from battery processing and tables with lots of information about the aforementioned residues.*

The battery processing plants also produce polypropylene from the crushed battery cases. The total plastic content accounts for 11 to 20 % of the weight of lead produced [ 99, Hähre, S. 1998 ]. There are a number of plastics fabricating plants designed specifically for this material and they produce granular polypropylene for the automobile industry. Effective washing of the polypropylene fraction and separation of other plastic components such as ebonite or PVC is essential to produce products within specification.

-Table 5.28, Table 5.29 and Table 5.30 show the use or treatment options for the residues produced by several processes.

| Production step | Product or process residue | Quantity (kg/t Zn) | Use or treatment option |
|---|---|---|---|
| **Leach/electrolysis.** | | | |
| Roaster/sulphuric acid plant | Sulphuric acid | <1200 - 1700 | Sale |
| | Steam | <1700 - 2000 | Energy conversion |
| | Hg product (calomel) | <0.1 | Controlled disposal[rr46] |
| | Hg/Se residue | 0.4 | Controlled disposal |
| | Dewatered acid sludge | <0.5 | Controlled disposal |
| Leaching plant | Neutral leach residue (Zn-Fe concentrate) | 500 | To ISF, Waelz kiln or hot acidic leach, controlled disposal |
| | Jarosite | 400 | Controlled disposal |
| | PbAg concentrate | 80 | Ag recovery |
| | Final residue if Pb/Ag concentrate removed | 150 | Controlled disposal or Pb/Zn smelter |
| | Jarosite/sulphur residue | 600 | Controlled disposal |
| Purification | Cadmium sponge | 3 - 4 | Sale or controlled disposal |
| | Cu cementate | 7 - 15 | Sale |
| Cell house | Gypsum | 3 - 4 | Cement plant or controlled disposal |
| Waste water treatment | Precipitated~~.~~ sludge | 7 - 100 (1) | Disposal or to Pb/Zn smelter |
| **ISF** | | | |
| Sinter plant/ sulphuric acid plant | Acid sludge | 0.25 | Controlled disposal |
| | Hg product | 0.15 | Controlled disposal |
| | Flue dust | 200 | To Cd-plant |
| | Sulphuric acid | 1300 | Sale |
| Cadmium plant | Cadmium carbonate | 18 | Sale |
| | Thallium sulphide | 0.25 | Controlled disposal |
| | Leach residue | 180 | To sinter plant |
| Imperial Smelting Furnace | ISF slag | 600 - 900 | Sale or controlled disposal(2) |
| Waste water treatment | Precipitated sludge | 30 | Recycled to sinter plant |
| **New Jersey Distillation** | | | |
| Liquation | Lead | 15(3) | To Pb refining or ISF |
| | Hard zinc | 25 - 50(3) | Return to ISF |
| As removal | Dross | <1 – 5(1) | Return to ISF |
| Waste gas treatment | Flue dust | 10 | Return to sinter plant |
| **Waelz process with washing and crystallisation** | | | |
| Slag granulation | Waelz Slag, dry kg/t product | 1600 | Construction material on disposal site |
| WOX washing | Salt residue(2) kg/t product | 130 | Disposal in mines |
| Off-gas treatment | Adsorbent(2) | NA | Controlled disposal |
| **Remelting, refining** | | | |
| Remelting, Refining | Hard zinc/zinc bottom dross | 25 | External recycling to ZnO |
| Off-gas treatment | Zinc-Ash concentrate | 130 | External recycling in Waelz-Process or ISF (if available) |
| Scrap sorting, melting furnace | Al-Fe-scrap | 50 | External recycling as Al- or Fe-rich scrap |

| Production step | Product or process residue | Quantity (kg/t Zn) | Use or treatment option |
|---|---|---|---|
| (1)estimated value<br>(2) depending on the process, quality and regulations.<br>(3) amount may vary with the feed. | | | |

**Table 5.28: Residues from zinc processes**
[ 117, Krüger, J. 1999 ], [ 234, UBA Copper, lead, zinc and aluminium 2007 ]

| Production step | Product or process residue | Quantity (kg/t Pb) | Use or treatment option |
|---|---|---|---|
| **Slag fuming plant** | | | |
| Slag fuming | Slag | 700 | Water resistant construction material |
| | Matte | 2.5 - 25 | To Cu smelter |
| | Steam | 2500 | Energy conversion |
| **Battery process - short rotary** | | | |
| Physical treatment of batteries | $Na_2SO_4$ (CX) | 220 | Sale |
| | Battery paste (MA) | 700 | To primary smelter |
| | Polypropylene | 100 - 130 | Sale |
| | Residual plastics | 70 - 80 | Disposal or incineration |
| Smelting | Lead bullion | 830 | To refinery |
| | Slag | 80 - 120 | Disposal |
| | Flue dust | 30 - 50 | After treatment back to Pb smelter |
| Refining | Dross | 60 - 90 | To primary smelter |
| Waste water | Precipitated sludge | | Return to smelter |
| All stages | Slag, flue dust, etc. | 500 - 550 | Internal recirculation |
| **Battery process - blast furnace** | | | |
| Feed preparation | Spent acid | 80 | External use or neutralisation |
| Shaft furnace | FePb Matte | 190 | Sale to primary PbCu smelter |
| | Slag | 50 | Road construction |
| | | 500 | Return slag |
| | Flue dust | <50 | External/internal recycling |
| Refining | Dross | 80 | Sale to metal recovery |
| All stages | Slag, flue dust, etc. | 500 - 550 | Internal recirculation |

**Table 5.29: Residues from lead processes**
[ 117, Krüger, J. 1999 ]

| Production step | Product or process residue | Quantity (kg/t Pb) | Use or treatment option |
|---|---|---|---|
| **Kivcet process** | | | |
| Smelter | Slag<br>Flue dust I<br>Flue dust II<br>Steam | 700<br>110<br>100<br>1300 | Controlled disposal<br>Return to smelter<br>To zinc leach<br>Energy conversion |
| $H_2SO_4$ plant | $H_2SO_4$<br>Calomel<br>Acid sludge | 1100<br><0.10<br>0.5 | Sale<br>Sale<br>Controlled disposal |
| Water treatment | Sludge | | |
| **Kaldo process** | | | |
| TBRC (Kaldo) | Slag<br>Flue dust<br>Steam | 350<br>160<br>700 | To fuming<br>Return to smelter<br>Energy conversion |
| $H_2SO_4$ plant | $H_2SO_4$<br>Calomel<br>Acid sludge | 500 | Sale |
| Water treatment | Sludge | | |
| **QSL process** | | | |
| Smelter | Slag<br>Flue dust<br>Copper dross<br>Steam | 550<br>60<br>100<br>1300 | Road construction<br>Return to smelter *After Cd-leach*<br>Sale<br>Energy conversion |
| Refining | Silver | 2 | Sale |
| $H_2SO_4$ plant | $H_2SO_4$<br>Calomel<br>Acid sludge | 700<br>0.02 - 0.05<br>0.5 | Sale<br>Sale<br>Return to smelter |
| Dust leaching | CdZn precipitate | 1.9 | Controlled disposal |
| Water treatment | Sludge | | Return to smelter |
| All stages | Slag, flue dust, sludges, etc. | 130 - 150 | Internal recirculation |
| **Ausmelt/ISA Smelt furnace** | | | |
| Smelter | Dross<br>ZnO-dust<br>Steam | 125<br>50<br>NA | Return to smelter(1)<br>To zinc-smelter<br>Energy conversion |
| $H_2SO_4$ plant | $H_2SO_4$<br>Acid sludge<br>Hg precipitate | 400<br><1<br>0.2 | Sale<br>Return to smelter<br>Calomel production |
| Dust leaching | CdZn precipitate<br>Lead residue | 1.1<br>40 | To zinc smelter<br>Return to smelter |
| Water treatment | Sludge | <5 | Return to smelter |
| All stages | Slag, flue dust sludges, etc. | ~420 | Internal recirculation |
| (1) Special campaigns for slag reduction. | | | |

**Table 5.30: Residues from direct smelting lead processes**

[ 117, Krüger, J. 1999 ], [ 234, UBA Copper, lead, zinc and aluminium 2007 ], [ 305, Ausmelt Lead and Copper processes 2009 ]

## 5.3 Techniques to consider in the determination of BAT

*If this section needs further structureing it should be related to the metals: Lead, Zinc, Cadmium.*

***The following is the structure from the BREF Draft 2.***
*5.3.1 Material handling and storage*
*5.3.2 Pretreatment processes*
*5.3.3 Smelting processes*
*5.3.4 Other lead process stages*
*5.3.5 Primary zinc*
*5.3.6 Secondary zinc*
*5.3.7 Cadmium*

***Most probably the section will be:***
*5.3.1 Techniques to consider in the determination of BAT for the production of lead*
*5.3.1.1 Material handling and storage*
*5.3.1.2 Pretreatment processes*
*5.3.1.3 Smelting processes*
*5.3.1.4 Other lead process stages*

*5.3.2 Techniques to consider in the determination of BAT for the production of zinc*
*5.3.2.1*
*5.3.2.2*

*5.3.3 Techniques to consider in the determination of BAT for the production of Cadmium*
*5.3.3.1*
*5.3.3.2*

The sections of this document entitled 'Techniques to consider in the determination of BAT' set out techniques considered generally to have potential for achieving a high level of environmental protection in the industries within the scope of the document. The background to the way the techniques are described is given in Section 2.1.2 and Table 2.2.

This section presents a number of techniques for the prevention or reduction of emissions and residues as well as techniques for reducing the overall energy consumption. They are all commercially available. Examples are given in order to demonstrate techniques which illustrate a high environmental performance. The techniques that are given as examples depend on information provided by the industry, European Member States and the valuation of the European IPPC Bureau. The general techniques described in Chapter 2 as common processes apply to a large extent, to the processes in this sector and influence the manner in which the main and associated processes are controlled and operated.

The control of furnace operating parameters and the prevention of diffuse emissions from furnaces and the tapping and pouring processes is also important. Techniques used by other sectors are also applicable particularly those relating to the use of sulphur recovery systems.

The techniques to consider on a site-by-site basis are strongly influenced by the raw materials that are available to a site, in particular the type and variability of the concentrate or secondary raw materials, the metals they contain can be crucial to the choice of process. Some processes have a dedicated single source of raw material but the majority of installations in Europe buy concentrate on the open market and need to maintain flexibility in processing a range of raw materials. In a similar manner, the standard of collection and abatement systems used worldwide in the industry reflects local, regional and long-range environmental quality standards and direct comparison of the environmental performance of process combinations is therefore difficult. For $SO_2$ or total carbon removal, the variation in raw gas concentration during batch processes may affect the performance of the abatement system. It is possible however, to judge how a particular process can perform with the appropriate modern abatement equipment.

The processes described above are applied to a wide range of raw materials of varying quantity and composition and are also representative of those used worldwide. The techniques have been developed by the Companies in this sector to take account of this variation. The choice of pyrometallurgical or hydrometallurgical technique is driven by the raw materials used, their quantity, the impurities present, the product made and the cost of the recycling and purification operation [ 117, Krüger, J. 1999 ]. These factors are therefore site-specific. The basic recovery processes outlined above therefore constitute techniques to consider for the recovery processes when used with appropriate abatement stages. The techniques to consider for collection and abatement stages and other aspects of process operation and control are covered in Sections 2.5, 2.8, 2.4.3 and 2.9.

### 5.3.1 Material handling and storage

**Description**

The raw materials are concentrates, secondary raw materials, fluxes and fuel. Other important materials are products, sulphuric acid, slags, sludges and process residues. Important aspects are the prevention of leakage of dust and wet material, the collection and treatment of dust and liquids and the control of the input and operating parameters of the handling and feeding processes.

The potentially dusty nature of concentrates and fluxes means that closed conveyors, storage, handling and treatment systems may be needed in these instances. Areas under conveyors should be paved so that spillages are collected before they are dispersed. Any waste water systems should discharge to treatment facilities. The dust generated by some crushing operations means that collection and abatement may be applicable for this process. Similarly, granulation water may require settlement or other treatment prior to discharge.

Acid produced during the process can be stored in double walled tanks or tanks placed in chemically-resistant bunds. The treatment of acid slimes from the sulphuric acid plant and weak acid from scrubbing systems depends on local processing or disposal requirements unless there is a local use for the material.

Sludges and other metallic residues that are destined for recovery off site can be stored in drums or other suitable ways depending on the material. Sludges produced during the process that are destined for on-site disposal should be pretreated to reach the standards in Council Decision 2003/33/EU, e.g. washed free of zinc or other metals and dewatered as far as possible. Disposal facilities should be totally contained and leak proof, they are subject to local control and regulation. Water from the sludge containment areas can be returned to the process.

There are a variety of secondary raw materials used and they range from fine dusts to large single items. The metal content varies for each type of material and so does the content of other metals and contaminants. Batteries are a common source of lead and can contain acid. The storage and handling, therefore, should take account of the acid content and any acid mists that can be formed. Nickel cadmium batteries are usually dry but other batteries may be present and leakage of electrolyte is possible, this should be taken into account in the storage and separation method used. The techniques used for storage, handling and pretreatment will therefore vary according to the material size and the extent of any contamination. These factors vary from site to site and the techniques discussed in Section 2.5 will be applied on a site and material-specific basis.

The following issues apply to this group of metals:

- The storage of raw materials depends on the nature of the material described above. The storage of fine dusts in enclosed buildings, silos or in sealed packaging is used. Secondary raw materials that contain water soluble components are stored under cover.

The storage of non-dusty, non soluble material (except batteries) in open stockpiles and large items individually in the open can be used.

- Fine dusts can be stored and handled in a manner that prevents the emission of dust. They are often blended and agglomerated to provide a consistent feed to the furnace.

Storage, handling and pretreatment methods for lead, zinc and cadmium are shown in Table 5.31.

| Material | Storage | Handling | Pretreatment | Comment |
|---|---|---|---|---|
| **Primary Raw Materials.** | | | | |
| Coal or Coke | Covered Bays, Silos. | Covered conveyors if non-dusty. Pneumatic. | | |
| Fuel and other oils | Tanks or drums in bunded areas. | Secure pipeline or manual system. | | |
| Fluxes | Enclosed (Silo) | Enclosed conveyors with dust collection. Pneumatic. | Blending with concentrates or other material. | |
| Concentrates. | Enclosed | Enclosed with dust collection. Closed conveyor or pneumatic. | Blending using conveyors. Drying or sintering | |
| **Secondary Materials.** | | | | |
| Fine Dust | Enclosed, drummed or silos. | Closed conveyor or pneumatic. | | EAF dust |
| Coarse dust (raw material or granulated slag) | Covered Bays | Mechanical loader. | | Oil collection |
| Lump (raw material or slag). | Open | Mechanical loader. | | Oil collection |
| Whole Items | Open or Covered Bays | Mechanical loader. | | Oil collection |
| Batteries<br>Lead Acid<br>Ni/Cd | <br>Covered storage<br>Sealed drums or containers | <br>Mechanical loader and conveyor.<br>Mechanical loader and conveyor. | <br>Crushing or whole feed.<br>Plastic removal and pyrolysis | <br>Acid collection. Re-use if possible.<br>Separation of Fe and Ni |
| **Products and Residues.** | | | | |
| Acids: | | | | |

| | | | | |
|---|---|---|---|---|
| Waste acid<br>Product Acid | Acid resistant tanks.<br>Acid resistant tanks. | | Use in process or neutralisation.<br>Sale | |
| Products<br>Cathodes, ingots and sows.<br>Dust | Covered concrete area.<br>Drums, bags or silos. | Mechanical loader | | |
| Process residues for recovery. | Covered or enclosed depending on dust formation. | Depends on conditions. | | Appropriate drainage system.<br>Potential of Sb and As to hydrolyse. |
| Wastes for disposal. | Covered or enclosed bays or sealed (drums) depending on the material. | Depends on conditions. | | Appropriate drainage system. |

**Table 5.31: Storage, handling and pretreatment methods for lead, zinc and cadmium**
[ 117, Krüger, J. 1999 ]

**Achieved environmental benefits**
Prevention and capture of dust and reduction of emissions are the achieved environmental benefits.

**Cross-media effects**
Non are reported.

**Operational data**
Given in the description of the processes above.

**Applicability**
This technique is applicable to most installations.

**Economics**
None reported.

**Driving force for implementation**
Environmental impact and energy costs due to lost material.

**Example plants**
UK, ES, DE, PL.

**Reference literature**
[ 117, Krüger, J. 1999 ], [ 227, IZA Report 2008 ].

### 5.3.2 Pretreatment processes

*Specific information about pretreatment processes and associted emissions are needed.*

**Description**
Concentrates are mixed with fluxes to produce a fairly constant feed. Therefore the general practice is sampling and analysis to characterise the concentrates and to store individual concentrates separately so that an optimum blend can be prepared for smelting.

Feed blends can be prepared from dosing bin systems using belt weighers or loss in weight systems. Final mixing and homogenisation can take place in mixers, pelletisers or in the conveying and metering systems. Enclosed conveyors or pneumatic transfer systems are used for dusty material. Hot gas rotary dryers or steam coil dryers can be used if the process requires a dry feed. Steam coil dryers use waste heat from other parts of the process provided that the heat balance allows it. The drier and associated dust abatement stage therefore depends on site-specific conditions such as the reliability of the steam supply. Fabric or ceramic filters achieve better dust removal efficiencies than ESPs when used at this stage of the process. The pretreatment processes feature:

- Pretreatment stages are often used, to dismantle materials or to remove casings or coatings and to separate other metals, to achieve smaller grain sizes with a higher specific surface or to agglomerate material as sinter, briquettes or pellets. Milling and grinding techniques are used with good dust extraction and abatement. The fine dust that is produced may be treated to recover other metals, pneumatic or other density separation techniques are used.
- Sintering is used to prepare concentrates for some of the smelting processes up-draught and down-draught sintering machines can be used and recent developments of a steel belt sintering process may be appropriate. Collection of fume and gases is important and the up-draught sintering process is inherently easier for fume capture. Gases contain sulphur dioxide and will have abatement and sulphur dioxide recovery processes downstream. The sulphur dioxide content is usually low and variable and this influences the design of the sulphuric acid plant.
- Zinc concentrates are roasted prior to hydro metallurgical processing. Fluidised bed roasters are almost universally used and need good extraction and calcine removal systems. Gases are treated in integrated abatement and sulphur dioxide recovery processes.

**Achieved environmental benefits**
Prevention of dust and improvement of the process dynamics.

**Cross-media effects**
Use of energy.

**Operational data**
Given in the descriptions of the process above.

**Applicability**
These techniques are applicable to most installations.

**Economics**
None reported.

**Driving force for implementation**
Environmental impact and energy costs

**Example plants**
BE, ES, DE.

**Reference literature**
[ 227, IZA Report 2008 ]
*All the given information is from the existing BREF. The only amendment is that the former Section 5.3.1 Material storage, handling and pre-treatment processes is split in two sections 5.3.1 and 5.3.2 without any change. Thus the new reference [227] has not been used.*

## 5.3.3 Smelting processes

### 5.3.3.1 Primary lead smelting processes

**Descriptions**

The lead smelting processes to consider are shown in Table 5.32 [ 117, Krüger, J. 1999 ], [ 305, Ausmelt Lead and Copper processes 2009 ]:

- For lead concentrates and some secondary raw materials the blast furnace and the electric furnace after sintering or roasting or smelting of the concentrates. The direct smelting processes that use the Kaldo, Ausmelt/ISA Smelt, QSL or Kivcet processes.
- For mixed copper and lead concentrates the electric furnace after roasting the concentrate in a fluidised bed roaster.

| Furnace | Gas Collection | Advantages | Disadvantages | Comments |
|---|---|---|---|---|
| Blast Furnace<br>110000 t/yr Pb | Semi-sealed | Robust metallurgical performance | Older technology - needs modern process control. | Double bell seal in feed hopper or cold top operation |
| Imperial Smelting Furnace<br>100000 t/yr Zn<br>40000 t/yr Pb | Sealed | Robust metallurgical performance. Use of low calorific value gas | Older technology - needs modern process control<br>High operating cost | Double bell seal in feed hopper |
| Ausmelt/ISA Smelt<br>110000 t/yr Pb | Sealed or Semi-sealed | Primary and secondary raw materials | Operation in oxidation stage only | High $SO_2$ in off-gas |
| QSL<br>135000 t/yr Pb | Sealed | Primary and secondary raw materials. Process is now reliable. | Frequent tuyere replacement | Integrated process with energy recovery. High $SO_2$ in off-gas |
| Kivcet<br>90000 t/yr Pb | Sealed | Primary and secondary raw materials. | High lead content of slag. Process reliability not available | Integrated process with energy recovery. High $SO_2$ in off-gas |
| Kaldo Furnace<br>65000 t/yr Pb | Enclosed | Primary and secondary raw materials | Expensive | Mixed Cu/Pb materials |

**Table 5.32: Overview of primary lead smelting processes**
[ 117, Krüger, J. 1999 ]

*The figures in table 5.32 are more than 12 years old and can be considered as useless.*

The abatement system to consider for primary smelting processes is dust removal and the removal of other metals followed by the recovery of sulphur dioxide. This is usually achieved by conversion to sulphuric acid in a double contact process with four or more passes; sometimes a caesium-doped catalyst is used. The use of a single contact plant or WSA process is a technique to consider for weak sulphur dioxide gas streams (see Section LVIC-AAF BREF).

The gases are cooled (with heat/energy recovery) and cleaned before conversion. A combination of coolers and hot electrostatic precipitators or a combination of scrubbers (radial or jet) and wet ESPs are used. The separated dust is recycled internally or externally for metal recovery, sometimes a hydrometallurgical pretreatment for removal of cadmium and alkali metals is used. Mercury removal systems are employed using the techniques discussed in Section 2.20.7.

Steel belt, up-draught or fully enclosed down-draught sintering processes are techniques to be considered. Steel belt sintering has several advantages for certain metal groups and can minimise gas volumes, reduce diffuse emissions and recover heat.

### 5.3.3.2 Secondary lead smelters

The range of secondary materials and the variation in metal content and degree of contamination has lead to the development of a range of smelters for secondary materials. The blast furnace, QSL furnace, the Ausmelt/ISA Smelt furnace, the TBRC, the electric furnace and the rotary furnace are used for a wide range of materials [ 117, Krüger, J. 1999 ], [ 305, Ausmelt Lead and Copper processes 2009 ]. Secondary smelters such as the short rotary furnace are often designed for a certain material and are operated solely on this secondary material, the primary processes, i.e. the Ausmelt/ISA Smelt furnace and the QSL furnace, are optimised for productivity and flexibility so that besides primary concentrate, secondary material can be treated as well, usually mixed with primary material. Tin and lead can be separated from each other by vacuum distillation at high temperature. As a result of this, pure lead can be recovered. This technique is applied by some secondary copper or lead installations who also produce lead and tin. These furnaces are all techniques to consider in the determination of BAT.

Several of the techniques described in Sections 2.8, 2.4.3 and 2.9 are applicable to fume extraction and abatement and the process control systems used by these furnaces. These techniques are not routinely used by all installations. The process control system for some blast furnaces is considered to be suitable ~~-~~for development.

Gases from secondary smelters can contain some sulphur dioxide dependent on the source of the material. In particular the desulphurisation of battery paste may be needed unless paste is treated separately in a primary smelter or the sulphur can be fixed in a lead/iron matte or in the slag using a sodium-based flux or other fluxes that can perform the same function. If the sulphur is not fixed, a scrubber system may be needed. The gases can contain significant quantities of the more volatile metals such as antimony and cadmium, etc. The abatement stages for secondary smelting involve gas cooling (with heat/energy recovery), coarse particle separation and fabric filtration. Sulphur dioxide removal and afterburning may be needed depending on the composition of the furnace gases (e.g. VOCs and PCDD/F). The collected dusts are recycled to recover metals.

In several instances there may be significant concentrations of organic material (including PCDD/F) depending on the raw material used. For example EAF dust will have a high PCDD/F content and whole battery feed (or incomplete separation) will provide a significant load of organic carbon and chlorinated plastic material. Afterburning or carbon adsorption and high efficiency dust removal may be needed in these cases.

**Achieved environmental benefits**

Prevention and capture of emissions and improvement of the process dynamics.

**Cross-media effects**
Use of energy and raw materials.

**Operational data**
Table 5.33 gives an overview of the advantages and disadvantages of the secondary smelting furnaces for various materials.

| Furnace | Gas Collection | Advantages | Disadvantages | Comments |
|---|---|---|---|---|
| Rotary furnace | Sealed during operation. Charging area hooded | Robust, well established | Range of raw materials. Potential diffuse emissions | Integral feeding and tapping zone. Oxygen enrichment |
| Ausmelt/ISA Smelt | Integral hooding, sealed charging system | High smelting rate. Wide range of raw materials | Possible abrasion of lance | Oxygen enrichment |
| Blast furnace | Sealed via double bell or door | Robust process. Wide range of raw materials | Process control systems need development | Oxygen enrichment |
| Electric furnace | Sealed | Low gas volume | Only coarse or agglomerated material is useable | Afterburner for organic material and CO |
| TBRC | Enclosed system | Compact, high smelting rate. Rotation gives a high reaction rate | Expensive | Oxygen enrichment |
| NB: In all cases abatement systems need to take account of the raw materials and their pretreatment. Afterburning, sulphur dioxide removal, gas cooling and dust removal (fabric filter) will be used in various combinations depending on the pretreatment applied. | | | | |

**Table 5.33: Overview of secondary smelting furnaces**
[ 117, Krüger, J. 1999 ]

**Applicability**
These techniques are applicable to most installations

**Economics**
None reported.

**Driving force for implementation**
Environmental impact and energy costs

**Example plants**
BE, ES, DE, UK.

**Reference literature**
[ 117, Krüger, J. 1999 ], [ 227, IZA Report 2008 ].

#### 5.3.3.3 Reduction of dust and metal emissions in secondary lead production

*In [229] is mentioned that in Beerse, Belgium a new filter for the dusts from the refining stage will be used aiming to achieve 0.2 mg dust/Nm3. The company wanted to provide data as soon as the filter went into operation. Check about the status.*

**Description**
Dust and metals are emitted at different process steps, the smelting process is however the main stack emission source. ~~One site in France uses a finishing filter downstream of the fabric filter~~

~~in order to achieve very low dust concentrations. The filter consists of an absorbent media (made of polyester fibres) contained in a compartment. This compartment is changed once saturation occurs. Clogging should be avoided to prevent any pressure drop in the filter. Therefore, while using this technique, the input gas should be well defined and controlled. This technique leads to very low dust concentrations.~~

Four secondary lead production sites participated in a survey conducted by the French Agency for Environment and Energy Management (ADEME) and provided emission data. They all use fabric filters to clean flue-gases from the refining step. Three of them use fabric filters to clean flue-gases from the furnace. One has implemented a wet scrubber because of the characteristics of the raw material which is processed: as the raw material often contains paints and tars, pyrophoric dust may be produced. Two sites also use a wet scrubber in conjunction with the preprocessing of raw material step (including battery breaking).

Several techniques are used to minimise diffuse emissions:

- Enclosed buildings. Each production process building is enclosed: battery breaking, smelting and refining stages.
- Floor sweeping and washing. Regular washing is carried out (at least two or three times a week) in order to recover diffuse dust emissions that have settled on the floor.
- Hooding systems are used in conjunction with almost every process unit.

The production of secondary lead requires high quantities of energy. All of the French secondary lead production sites are natural gas-fired. As a consequence, very limited amounts of dust are produced by combustion and optimal operating conditions in the furnace are used to ensure lower emissions.

The end-of-pipe dedusting techniques are:

- Wet scrubbers used in conjunction with the battery crushing process. In one case, they are also used to clean flue-gases from the furnace where dust may be pyrophoric.
- Cyclones are as a pre-cleaning device and always in conjunction with fabric filters.
- Fabric filters more frequently used in France in conjunction with almost every smelting furnace. They are also used to clean flue-gases from the refining step.
- Finishing filters are used in one case downstream of fabric filters to further reduce the ~~clean residual~~ dust emissions from the refining furnace. The filter consists of an absorbent media (made of polyester fibres) contained in a compartment. This compartment is changed once saturation occurs. Clogging should be avoided to prevent any pressure drop in the filter. Therefore, while using this technique, the input gas should be well defined and controlled. This technique leads to very low dust concentrations.

**Achieved environmental benefits**

The emission ranges originate from the differences in the data provided by the production sites, the monitoring period and sampling point see Table 5.34. On the whole, reported dust concentrations are very low and are always lower than 5 mg/m$^3$. 90 % of dust stack emissions come from smelting furnaces.

Emission factors based on the stack emissions were calculated and were:

- dust: 13 - 52 g/t of lead produced
- Pb: 0.7 - 7 g/t of lead produced

According to the plant operators, diffuse emission factors can be as high as 1 to 1.5 times the stack emission factors. Such diffuse emission factors are still very difficult to assess.

**Cross-media effects**

Use of energy and raw materials.

*(Use of raw materials is a strange cross-media effect.)*

**Operational data**

Measurement results have been provided by the 4 sites which have participated in the ADEME survey. Table 5.34 gives reported dust, lead and cadmium concentrations, ~~the lowest figures refer to the use of a finishing filter~~ *(the information about low figures for dust when using finishing filters is not justified by the relvant reference [302].*

| Emission point | Dust (mg/Nm$^3$) | Pb (mg/Nm$^3$) | Cd (mg/Nm$^3$) |
|---|---|---|---|
| Main stack | 0.1 - 4.4 | 0.02 - 1.2 | <0.025 |
| Smelting furnace | 0.27 - 4.4 | 0.02 - 1.2 | <0.025 |
| Refining furnace | 0.006 - 0.5 | 0.0015 - 0.018 | <0.0001 |

**Table 5.34: Dust, Pb and Cd emissions from French secondary lead production**
[ 302, French Report on PM and HM 2007 ]

The ranges in the table are rather large. The applied techniques for the main stack and the smelting furnaces comprise fabric filter and wet scrubbers while for the refining furnace only fabric filters are applied and in addition in one case a finishing filter is used. For some plants the data refers to annual averages whereas for other to min-max ranges. Moreover, emissions values may differ depending on the measurement location and the the time when the measirment takes place. For instance, higher concentrations are observed during furnace charging.

| Plant | Dust | | Comment |
|---|---|---|---|
| | Inlet (g/Nm$^3$) | Outlet (mg/Nm$^3$) | |
| Bergsöe | | < 1 | ?? |
| ~~Beerse~~ | | ~~???~~ | ~~??~~ |
| Shaftfurnace | 1,5 – 2.0 | 0.5 – 2 | No battery preparation |
| QSL | 200 | < 1 | after sulphuric acid plant |
| Sirusmelt process | 7 – 200 | < 0.5 | after sulphuric acid plant |
| Short rotary furnaces:<br>Plant A<br>Plant B<br>Plant C (BMG AT) | <br>2 – 5<br>3 – 10 | <br>< 1 – 10<br>0.1 ~~–~~– 1<br><0.5 – 3.2 | Upstream battery preparation |
| Short rotary furnaces:<br>Plant A<br>Plant B<br>Plant C | <br>2 – 4<br>1<br>7 – 10 | <br>< 5<br>0.5<br>5 – 10 | No battery preparation |

*A lot of important co-information is mssing, i.e. $O_2$ concentration, off-gas sflow*

**Table 5.35: Performance data reported for bag filter systems at secondary lead smelter**
[ 346, SO2 - Lime injection FINAL 4.2. 2010 ] [254, VDI 2597] [ 237] [518]

| Plant | Dust | | Comment |
|---|---|---|---|
| | Inlet (g/Nm$^3$) | Outlet (mg/Nm$^3$) | |
| QSL | 0.5 – 3 | 1 – 3 | Secondary hoods, Refining, other |
| Sirosmelt process | 0.5 – 3 | 0.005 – 3.8 | Secondary hoods, Refining, other |
| Short rotary furnace Plant A | 0.1 – 2 | 0.1 – 3 | Secondary hoods, Refining, other |
| Short rotary furnace Plant B | 0.1 – 2 | 0.5 – 2 | Secondary hoods, Refining, other |

| | | | |
|---|---|---|---|
| Short rotary furnace Plant C (BMG AT) | | 0.5<br>< 0.5<br><br>< 0.5<br>< 0.5 | Batterie preparation<br>Secondary emissions from rotary furnace (hall_extraction)<br>Refining<br>Secondary emissions from refining (hallextraction) |
| Electric furnace | < 2 | < 2 | Secondary hoods |
| *A lot of important co-information is mssing, i.e. $O_2$ concentration, off-gas sflow* | | | |

**Table 5.36: Performance data reported for bag filter systems at secondary lead plant secondary emissions and auxiliary plants**
[254, VDI 2597] [518] [520]

**Applicability**
~~Use of a finishing filter is only applicable when the input gas is well defined, does not contain sticky material and is controlled.~~ *The finishing filter is just one exceptional case for refining furnace in conjunction with FF. The consideration on applicability should include FF and wet scrubber. Fabric filters and wet scrubbers are considered to be generally applicable.*

**Economics**
The main operational cost is due to the fan electrical consumption. Assuming 1 $m^3$ flow requires 0.001 kWh, this cost would be EUR 80000 - 200000 /year.

Other operational costs are:

Substitution of used fabric membranes (fabric filter): EUR 10000/year
Substitution of used cartridge (finishing filter): EUR 1500/year
Standard maintenance for mechanical devices

Cost data have been provided by one plant operator, as indicated in Table 5.37.
~~The investment costs are given in Table 5.35.~~

| Technique | Flow | Investment costs | Year |
|---|---|---|---|
| Cyclone + fabric filter + finishing filter | 80000 $Nm^3/h$ | EUR 600000 (before tax) | 2005/2006 |

**Table 5.37: Investment cost for an abatement technique configuration**
[ 302, French Report on PM and HM 2007 ]

**Driving force for implementation**
Improvement of environmental performance.

**Example plants**
France.

**Reference literature**
[ 302, French Report on PM and HM 2007 ]~~.~~ [ 346, SO2 - Lime injection FINAL 4.2. 2010 ] [254, VDI 2597] [ 237] [518].

### 5.3.3.4 Prevention of sulphur emissions from lead acid battery recovery

**Description**

Lead acid battery paste contains different lead compounds and some of them are sulphurised, such as $PbSO_4$ and $Pb_2OSO_4$.

To avoid the $SO_2$ formation during the paste smelting, there are two approaches [ 266, Italy Report on Desulphurisation 2008 ]:

1. the addition of additives to fix the sulphur into the slag
2. the removal of sulphur before feeding the paste to the furnace[rr47]. [266]

The desulphurisation of the paste where the sulphurised compounds can be converted in oxides or carbonates contacting the paste with an alkali salt solution according to the following simplified reactions:

$PbSO_4 + Na_2CO_3 \rightarrow PbCO_3 + Na_2SO_4$

$PbSO_4 + 2\ NaOH \rightarrow PbO + Na_2SO_4 + H_2O$

The sodium sulphate produced by this reaction is recovered in the form of a solution. From this solution it is possible to crystallise a saleable salt. In this section is also possible to process the exhausted electrolyte neutralising and converting it to sodium sulphate as well.

The reactions are quite fast and the conversion efficiency can be very close to 100 %. The scheme of this unit is very simple and is shown in the block diagram in Figure 5.13:

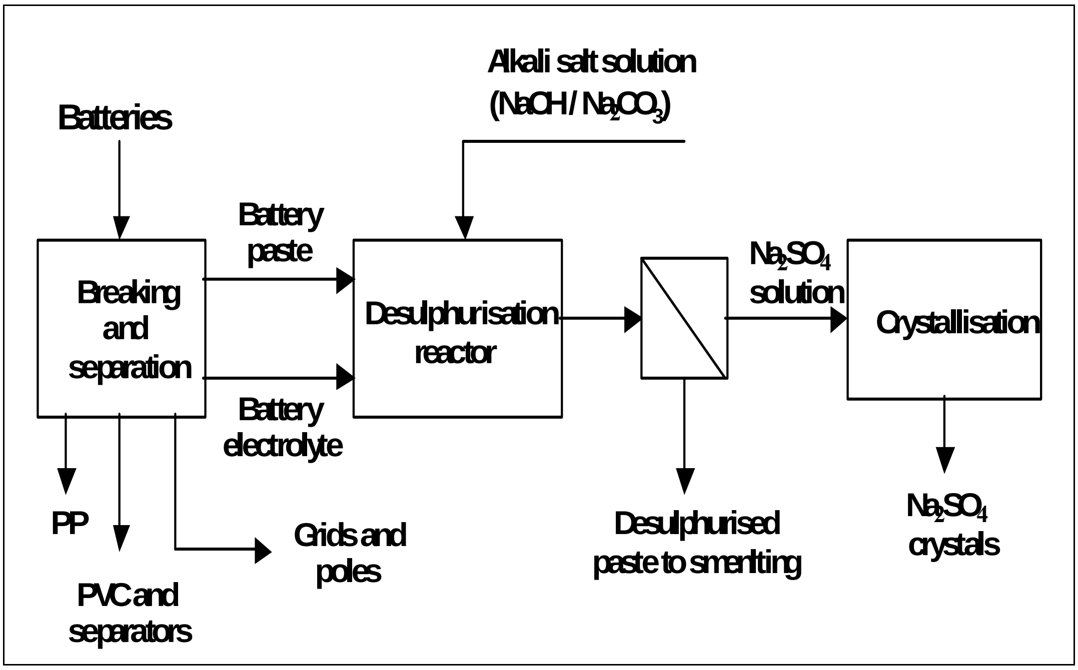


**Figure 5.13: Desulphurisation of battery paste**
[ 266, Italy Report on Desulphurisation 2008 ].

**Achieved environmental benefits**
The introduction of the desulphurisation unit introduces a lot of advantages over a traditional system without desulphurisation in the smelting and refining unit:

- reduced sulphur emissions by reducing the sulphur concentration in the paste
- strong reduction of smelting additives request
  - less sulphur to be fixed into the slag

  - reduced production of slag
    - less Pb in the slag
  - less ash to be recycled
  - possible production of non-hazardous slag
- reduced fuel consumption (30 to 40 %)
  - reduced emission of CO and $NO_X$
  - less slag to be heated
- higher furnace productivity (+ 20 to 30 %) and further reduction of emissions
- better management of the baghouse
- easier regulation of the furnace environment
  - optimisation of the smelting process
  - easier formation of the slag.

The water going into the process is used and no liquid effluents will be generated. The crystalliser takes care not only of the $Na_2SO_4$ production but also of the water balance.

**Cross-media effects**

No cross media effects reported.

**Operational data**

~~a)~~ The reaction is run at a very low temperature, in a wet process where the paste slurry is fed to a water solution producing a wet cake. For this reason no dust is produced in this unit.

As far as the consumption of reactant is concerned and considering a paste with a standard composition, about 220 kg of $Na_2CO_3$ per t of lead produced from batteries (also considering the acid neutralisation) is required to produce about 280 kg of $Na_2SO_4$ per tonne of lead. Under these conditions the sulphur removal is >90 %.

In this unit there are no problems relevant to the emissions and in any case all the equipment are under aspiration and the air is sent to a scrubber.

The reaction control can be achieved by simple pH measurement.

All the streams leaving this unit will be converted to products.

**Applicability**

The paste desulphurisation is applicable to existing battery treatment plants.

**Economics**

Saving are connected with:

- reduction of slag quantity
- a reduction of slag hazardousness
- a reduction of smelting times
- better handling of the exhaust gas system
- a reduction of recycled dusts.

Such saving can be between 10 and 20 % of the total smelting costs.

**Driving force for implementation**

Improvement of environmental performance especially a sharp reduction and better control of $SO_2$ and $NO_X$ emissions.

**Example plants**

Italy, Germany, Austria, Switzerland, Poland, Estonia, US, Canada.

**Reference literature**

***M. Olper, B. Asano;*** *Improved Technology in Secondary Lead Processing. Engitec Lead Acid Battery Recycling System;* ***1st International Seminar on Battery Waste Management, Florida, US, 6 - 8 November 1989.***

[237, UBA Austria 2004] [ 266, Italy Report on Desulphurisation 2008 ], [ 346, SO2 - Lime injection FINAL 4.2. 2010 ], [ 117, Krüger, J. 1999 ].

*M. Olper, B. Asano;* ***Improved Technology in Secondary Lead Processing. Engitec Lead Acid Battery Recycling System ;*** *1st International Seminar on Battery Waste Management, Florida, USA, 6-8 November 1989*

*E. K. Hudson, R. M. Reynolds, M. Olper;* ***The Engitec CX Lead-Acid Battery Recovery Technology;*** *Lead-Zinc '90, Anaheim, California, USA, 18-21 February 1990*

*M. Olper;* ***Recycling of Lead Acid Batteries with Desulphurisation Process;*** *Metal Bulletin's 4th International Scrap and Secondary Metal Conference, La Napoule, France, 21-23 November 1993*

*M. Olper, M. Maccagni;* ***Total Recycling of Lead Acid Batteries. The Environmental Friendly Route;*** *International Battery Exhibition, Beijing, China, June 2001*

### 5.3.3.5 Reduction of dust and sulphur emissions from secondary lead production

*Do we have to distinguish between Sec. Lead plants where the whole battery is processed or the ones where 5.3.3.4 is applied and additional end-of pipe techniques are applied???*

**Description**

In one case a~~A~~n existing continuous lead smelting process with varying $SO_2$ concentrations uses~~ing~~ lime injection in the afterburner of a lead smelter -[ 346, $SO_2$ - Lime injection FINAL 4.2. 2010 ]. The main process is designed to capture $SO_2$ through the addition of iron to the furnace and the formation of an iron matte. The capture rate by producing matte is approximately 90 %. Further 5 % $SO_2$ removal is achieved by the dry injection of lime (~ 60 kg/h) at the afterburner outlet at 1100 °C. The gas flow is 24000 $Nm^3$/h[rr48]..

Water injection is not possible because of clogging and blocking in pipes and the possible condensation problems in the fabric filters. Higher yields would be possible at the expense of a higher lime injection rate, but lime causes clogging and blocking of the tubes at high injection rate. Due to the lead content of the filter dust, it is recycled to the furnace after dechlorination and the lime content aids slag forming. The cost for the treatment of filter dust is relatively low.

**Achieved environmental benefits**

When using existing gas-cleaning equipment with a fabric filter that is designed to remove process dust, it can be used to capture gypsum if the filter capacity allows for this. When a filter is already used, direct injection is possible when temperature, moisture content and contact time are sufficient. An existing filter installation might be not sufficient because the amount of dust increases drastically and thus might need to be replaced.

The performance data for some secondary lead smelting plants is shown in **Error! Reference source not found.**.

| Plant | $SO_2$ mg/$Nm^3$ | | Dust mg/$Nm^3$ | | Comment |
|---|---|---|---|---|---|
| | Inlet | Outlet | Inlet | Outlet | |
| Bergsöe (Lead smelter) | 3000 | Average 400 (170 – 790) | | < 1 | 2.5 g lime addition/$Nm^3$ |
| Beerse (Lead smelter) | 3000 | 650 | | ??? | 300 g lime addition/$Nm^3$ |
| BMG ([1]) | | 260 – 666 | | <1 – 3.2 | |

| | | | | | |
|---|---|---|---|---|---|
| Other examples???<br>Varta Germany | ???? | 300 – 800 | 1,5 – 2.0 | 0.5 – 2 | |
| ***NB: Continuous measurments***<br>*A lot of important co-information is mssing, i.e. $O_2$ concentration, off-gas sflow* | | | | | |

**Table 5.38: Performance data for the example plant**
[ 346, SO2 - Lime injection FINAL 4.2. 2010 ] [237, UBA Austria 2004] [518, Umwelterklärung BMG, 2007]

**Cross-media effects**
This technique treats dust and $SO_2$ emissions simultaneously and may also have a positive impact on dioxin abatement.
~~Use of energy and raw materials.~~

**Operational data**
*~~The performance data for the example plant is shown in Table 5.36.~~Insert data for additive addition. Type, amounts, etc.*

| ~~Plant~~ | ~~$SO_2$ mg/Nm$^3$~~ | | ~~Dust mg/Nm$^3$~~ | | ~~Comment~~ |
|---|---|---|---|---|---|
| | ~~Inlet~~ | ~~Outlet~~ | ~~Inlet~~ | ~~Outlet~~ | |
| ~~Bergsöe (Lead smelter)~~ | ~~3000~~ | ~~400~~ | | ~~< 1~~ | ~~Sulphur removed as iron matte and 650 kg/hr lime addition to afterburner. Dust is used in process~~ |

~~**Table 5.36: Performance data for the example plant**~~
~~[ 346, SO2 - Lime injection FINAL 4.2. 2010 ]~~

**Applicability**
Optimum conditions can be incorporated in new installations.

**Economics**
Simultaneous injection of water decreases the quantities of lime needed as the reaction between $SO_2$ and lime takes place at the surface of the lime particles, a relatively high amount of lime is needed. The quantities that are needed can be reduced by using a lime with a high specific surface and/or by recirculation of the fabric filter dust. Lime cost ranges from EUR 60/ton for calcium hydroxide to EUR 200/ton for expanded calcium hydroxide.

**Driving force for implementation**
Improvement of environmental performance especially a sharp reduction and better control of $SO_2$ and $NO_X$ emissions

**Example plants**
Sweden.

**Reference literature**
[ 346, SO2 - Lime injection FINAL 4.2. 2010 ], [ 117, Krüger, J. 1999 ].

In this Section a lot of information from [346] is missing which could be added.

### ~~5.3.3.5~~5.3.3.6 Use of an afterburner in a shaft furnace without battery preparation

*The given example is limited to shaft furnaces and this should be indicated in the heading. Try to get grip of the data for other shaft furnaces processing whole Batteries.*

**Description**

The use of an afterburner, cooling system and fabric filter to remove VOC, metals and dust from a furnace off-gas is used in several processes. The example below is part of a lead acid battery recovery system that uses the pyrolysis products of the plastic content as fuel in the afterburner. The abatement system incorporates an afterburner to destroy VOCs. The process is shown in Figure 5.14.

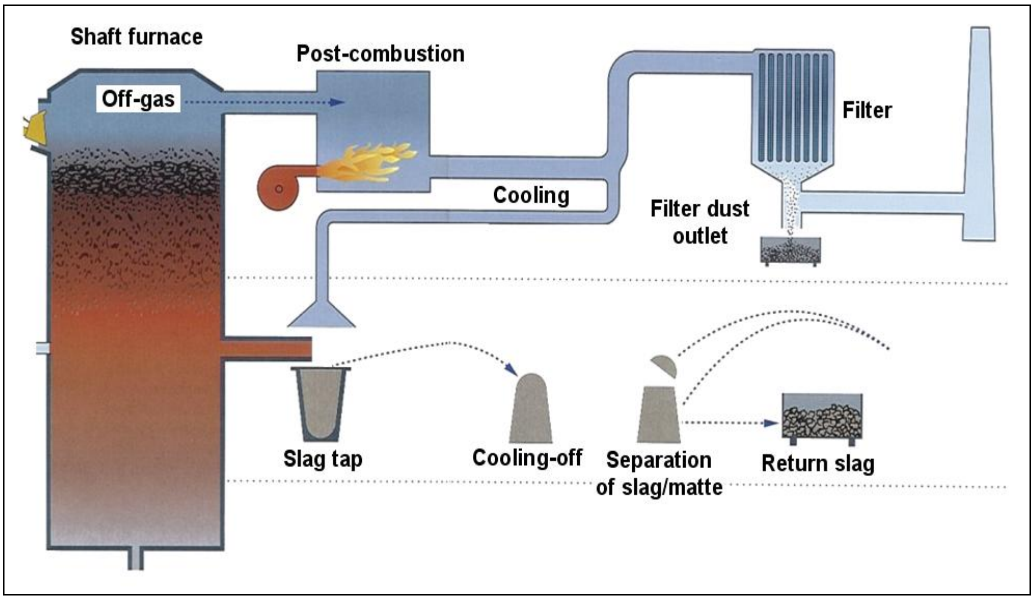


**Figure 5.14: Afterburner system used with a whole battery smelter (VARTA process)**
[ 117, Krüger, J. 1999 ], [ 229, Umicore etc 2007 ] *The reason why this reference appears here is may be that the plant in Beerse uses the VARTA process as well.*

**Achieved environmental benefits**

Destruction of VOCs and recovery of energy from the off-gases. Removal of dust and metals from the off-gas allows the filter dust to be returned to the furnace. ~~In the RTO, destruction of VOC with low additional energy. Dust is recovered by fabric filters and recycled in the furnace.~~ *How is the energy recovered from the off-gas? Why are two sentences added to this paragraph compared to the existing BREF when no RTO is applied and the last sentence is redundant?*

**Cross-media effects**

The loss of recyclable plastic and energy cost of replacement.

**Operational data**

Performance data for afterburning is given in Table 5.39.

| Parameter | Unit | Content |
|---|---|---|
| Waste gas flow | m$^3$/h | 65000 |
| Dust | mg/Nm$^3$ | 0.5 to 2.0 |
| Lead | mg/Nm$^3$ | <0.1 to 0.5 |
| Cadmium | mg/Nm$^3$ | <0.01 |
| Antimony | mg/Nm$^3$ | <0.01 |
| Arsenic | mg/Nm$^3$ | <0.01 |
| Carbon$_{total}$ | mg/Nm$^3$ | <10 |
| Sulphur dioxide | mg/Nm$^3$ | 300 to 800 |
| Nitric oxide ($NO_X$ as $NO_2$) | mg/Nm$^3$ | <50 |
| Carbon monoxide | mg/Nm$^3$ | <50 |
| Hydrogen chloride (HCl) | mg/Nm$^3$ | <20 |
| Hydrogen fluoride (HF) | mg/Nm$^3$ | <0.5 |
| PCDD/PCDF | ng I-TEQ/Nm$^3$ | <0.1 |

**Table 5.39: Performance data for afterburning**

~~[ 117, Krüger, J. 1999 ]~~ This is the wrong reference. The data are from the VDI 2597, [254] [254, VDI 2597] This is the shaftfurnace from VARTA, Germany. Try to get real measured recent data! In particular for SO2.

The off-gas amounts to 65000 Nm³/h. Emissions of dust, carbon monoxide and sulphur dioxide are monitored continuously. Calcium hydroxide additive can be injected into the off-gas channel, to prevent peaks of sulphur dioxide emissions. The fabric filter dust has a lead content of up to 65 wt- % and can be recycled back to the smelting furnace as input material after chlorine removal. In order to achieve this, the filter dust is treated externally in a hydro-metallurgical process to produce lead carbonate. The lead carbonate is returned and fed as raw material to the shaft furnace.

**Applicability**

~~The comparison of battery processing techniques has been made to assess the main process types. There is a balance between the recovery of polypropylene from the battery cases and the use of the plastic content as a fuel in the process. The most obvious comment is that the energy content of the battery case should be compared to the energy cost of making the plastic and moulding it. There are however local effects such as the existence of a local outlet for PE and other plastics and potential local uses of acid and heat and long-range factors such as the potential effects of sulphur dioxide. These factors must be assessed on a site-specific basis.~~

~~The other factor that should be determined at a local level is the desulphurisation of battery paste, the potential for sulphur fixing in Pb-Fe matte or in the slag and the possible facilities for smelting battery paste in another installation. White slag produced by using soda-based fluxes may not be suitable for disposal locally. Other fluxes are available to fix the sulphur in the slag and avoid soluble components but the details are not available.~~*Try to find out what is the current status of these slags. Are they used or disposed off.*
Generally applicable.

**Economics**

No data has been reported ~~but data for a similar system in the copper sector are in the annex on costs.~~ ~~-~~Several plants are operating viably. *How can we state that it is viable if there are no data? And what does it mean that several plants ar eoperating viable? There are only 3 plants in Europe as far as I know. Are there others not operating viable??*

**Driving force for implementation**

Destruction of PCDD/F and VOCs.

**Example plants**

~~Austria for RTO,~~ Germany, Belgium, Netherlands and Sweden. *Where is the information for the other examples. The information in the whole section has been taken from one example only and this is the German VARTA shaft furnace. Try to get infor about other shaft furnaces with whole battery processing and afterburner. Campine, Beerse; Boliden, Bergsoe*

**Reference literature**

[ 99, Hähre, S. 1998 ], [ 117, Krüger, J. 1999 ], [ 254, VDI 2004 2004 ].

### ~~5.3.3.6~~5.3.3.7 Use of a regenerative afterburner

**Description**

The off-gas from the short rotary furnace is cleaned by a fabric baghouse and then sent to an RTO. The rotary furnace treats the products of the CX battery separation plant (grid metal and desulphurised paste). For reduction coke and separators are used. After the baghouse, the VOC content is controlled. When the VOC concentration rises, the off-gas is sent to the RTO. Autothermal operation is achieved and no additional gas is needed and the gas consumption is minimised.

Emissions are continuously monitored in the stack for dust, $SO_2$, VOC and volume.

**Achieved environmental benefit**

The destruction of VOC with low additional energy is an achieved environmental benefit, furthermore dust is recovered by fabric filters and recycled in the furnace.

*Ask Ms. Winter for Dioxin data. Maybe there are some in the meantime.*

Table 5.34 shows the achieved emission concentration values for some organic pollutants prior to the after burning at the main stack.

| Emission point | Year | Total C (mg/Nm$^3$) | Benz(a)pyren (mg/Nm$^3$) | VOC (mg/Nm$^3$) |
|---|---|---|---|---|
| Main stack prior to afterburning | 2000 | 15.8 | 0.0016 | n/a |
| | 2003 | 11.4 | n/a | n/a |
| | 2007 | 7.9 | 0.00685 | n/a |
| NB: Continuous measurments | | | | |

**Table 5.40: Total carbon and Benzo(a)pyren emissions at the main stack**

[ 518, Umwelterklärung BMG 2007 ] [237, UBA Austria 2004]

*From the figure 5.15 it can be seen that VOC is measured after the stack. So try to get the data!*

**Cross-media effects**

No data has been reported.

**Operational data**

Polypropylene is separated in the CX breaker and can be recycled or be used as a secondary fuel. The process is shown in Figure 5.15.

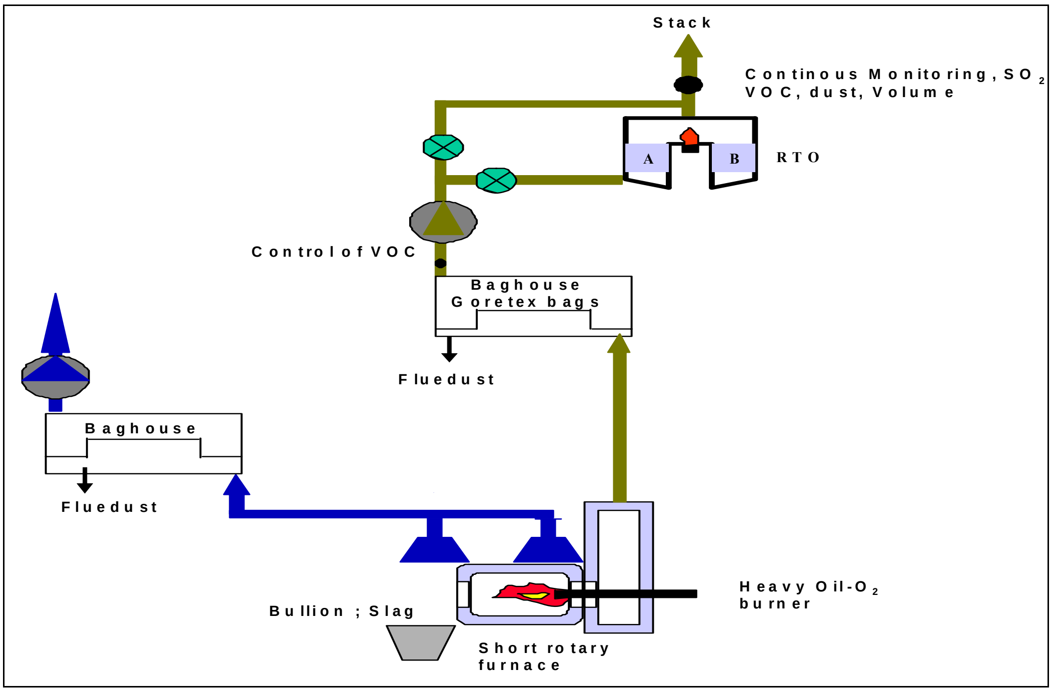


**Figure 5.15: General plant layout with RTO**
[ 325, Austrian RTO for secondary lead smelter 2009 ]

**Applicability**
This technique is applicable to furnaces with ~~that produce generate~~ high residual VOC concentrations~~ of VOC~~.

**Economics**
No data has been reported. Approximately EUR 1 million including foundation and construction. Either no data are reported or an estimation of the costs is included. On which reference this statement relies?

**Driving force for implementation**
Environmental regulation.

**Example plants**
BMG Metall und Recycling GmbH, Arnoldstein, Austria~~AT.~~

**Reference literature**
[ 325, Austrian RTO for secondary lead smelter 2009 ].
[237]

## 5.3.4 Other lead process stages

### 5.3.4.1 Slag treatment

*All what is mentioned here and in section 2.9 is useless in the sense that it will not provide permit writers with information which can help to write permits.*
*What is needed are special abatement techniques applied during slag treatment in the secondary lead industry. Slag from Lead smelter are sometimes further processed after cooling. Is cooling promoted in a way and if so, how? Ask TWG. If no information is available than this section should be deleted. Also the crossreference to section 2.9!!*

**Description**
Slag fuming and slag reduction stages that were discussed earlier as available techniques are the techniques to consider in the determination of BAT. The specific feed materials will influence

the final process choice. The techniques discussed in Section 2.9 that are appropriate to the process are also techniques to consider.

**Achieved environmental benefits**
The environmental benefits are the prevention of diffuse emissions of metals, dust and other compounds.

**Cross-media effects**
None are reported.

**Operational data**
None are available.

**Applicability**
The processes and the techniques are suitable for use with new and existing installations.

**Economics**
None was provided but the processes are operating economically.

**Driving force for implementation**
The reduction of emissions and saving raw materials.

**Example plants**
Plants in DE, AT, FR, BE, PL.

**Reference literature**
[ 229, Umicore etc 2007 ], [ 274, Farrell Mission in DE 2008 ].
*Umicore wanted to provide data, also ask for slag treatment and abatement techniques.*

### 5.3.4.2 Refining of lead

*All what is mentioned here and in section 2 is useless in the sense that it will not provide permit writers with information which can help to write permits.*
*What is here needed are special abatement techniques applied during lead refining in the secondary lead industry If no additional information will be found or provided by TWG insert all usefull infos from here into section 5.3.3.3.*

**Description**
The processes that were discussed ~~earlier~~ earlier *(where???)* as available techniques are all techniques to consider in the determination of BAT. The specific content of other metals will influence the final process choice. The techniques discussed in Chapter 2 should also be considered in conjunction with these processes, in particular, temperature control of the kettles and fume collection and abatement systems. Refining kettles are not considered suitable for melting scrap lead that is contaminated with organic materials.

**Achieved environmental benefits**
Prevention of emissions of metals and dust and improvement of the process dynamics. Recovery of other metals.

**Cross-media effects**
None reported.

**Operational data**
Given in the descriptions of the process above and in Section 5.1.3.

**Applicability**
These techniques are applicable to most installations.

**Economics**
None reported.

**Driving force for implementation**
Environmental impact and energy costs.

**Example plants**
BE, ES, DE.

**Reference literature**
[ 227, IZA Report 2008 ], [ 117, Krüger, J. 1999 ].

## 5.3.5 Techniques to consider in the determination of BAT for primary zinc production

### 5.3.5.1 Use of optimised pyrometallurgical (and hydrometallurgical) processes

*This would be the right heading for this section. But it hardly can be applied because the nine subheading can not be applied to such kind of a heading.*
*I propose to delete the complete section since the amount of useful information is limited. Maybe a good example for ISF can be given.*

~~5.3.5 Primary zinc~~

**Description**
The New Jersey distillation column is a technique to consider for the pyrometallurgical production of primary zinc used in conjunction with the ISF for mixed lead and zinc concentrates and washed Waelz oxide [ 230, FF Mission report 2007 ]. An overview of the Imperial Smelting Furnace is given in Table 5.41.

| Furnace | Gas Collection | Advantages | Disadvantages | Comments |
|---|---|---|---|---|
| Imperial Smelting Furnace | Sealed | Robust metallurgical performance.<br>Use of LCV gas.<br>Campaigns used to treat sulphidic and oxidic materials | Older technology - needs modern process control and fabric filters and efficient gas collection from the sinter plant. | Double bell seal in feed hopper |

**Table 5.41: Overview of the Imperial Smelting Furnace**
[ 117, Krüger, J. 1999 ]

The hydrometallurgical processes (both calcine leaching and direct concentrate leaching) are very important in the production of zinc. The processes that were discussed earlier as available techniques are all techniques to consider in the determination of BAT [ 117, Krüger, J. 1999 ]. The specific feed materials will influence the final process choice. As reported earlier the Goethite process relies on a low iron content of the calcine (or ZnO) used for precipitation while the jarosite process is able to give good zinc recoveries even with a high iron content (up to 10 %) [ 136, Fugleberg, S. 1999 ]. In both cases effective washing of the precipitated iron is needed. The techniques discussed in Chapter 2 should also be considered in conjunction with these processes and an overview of primary zinc hydrometallurgical processes is given in Table 5.42.

| | |
|---|---|
| **Technique** | Zinc roast, leach, electrowinning. 65000 - 482000 t/yr Zn |
| **Gas Collection** | Sealed roaster |
| **Advantages** | Proven performance |
| **Disadvantages** | Iron precipitate |
| **Comments** | Concentrate with low iron content produces lower quantities of iron residue |

**Table 5.42: Overview of primary zinc hydrometallurgical processes**

Because the hydrometallurgical processes involve leaching and electrolytic stages, adequate treatment and re-use or disposal of leaching residues and electrolyte bleed respectively and the solid residues arising from treatment of the electrolyte bleed need to be considered. The connection of reactors and filters to suitable scrubbers or demisters should be considered to prevent the emission of aerosols. The techniques discussed in Section 2.12 to prevent emissions to water for example by containing drainage systems are relevant. Techniques to render the jarosite or goethite residues inert should be used if possible. The techniques are being used to prevent the production of iron residues or to render them acceptable for land reclamation.

**Achieved environmental benefits**
The environmental benefits are the prevention of diffuse emissions of metals, dust and other compounds.

**Cross-media effects**
None are reported.

**Operational data**
None are available.

**Applicability**
The processes and the techniques are suitable for use with new and existing installations.

**Economics**
None was provided but the processes are operating economically.

**Driving force for implementation**
The reduction of emissions and saving raw materials.

**Example plants**
Plant in PL.
*For what kind of process is the Polish plant included? Pyrometallurgical or hydrometallurgical production? ISF is applied in Europe at:*

Poland ZGH Boleslaw, HC Miasteczko Slaskie
Romania, Mytilineos

**Reference literature**
[ 230, FF Mission report 2007 ], [ 117, Krüger, J. 1999 ]

### ~~5.3.5.1~~5.3.5.2 Use of concentrate with low iron content

Concentrate from the Century Mine in Australia, has a high zinc content of 58 %. The concentrate consists mainly of zinc sulphide and also contains small quantities of iron, lead, silica, carbon and silver (Zn 54.18 to 58.69 %; Fe 0.76 to 2.17 %) [ 240, NI Input on Zn production 2008 ]. There are limited quantities of this concentrate available and the availability might not extend beyond 2015.

In 2000, major changes to the production process enabled Nyrstar, Budel Zink to convert to Century Mine zinc concentrate. In 2007, 80 % of the input of the installation was this concentrate and 20 % was waste material. Calcination is carried out conventionally and zinc from calcine is dissolved in dilute sulphuric acid in two leaching stages.

In addition to zinc, the iron, silica, cadmium, copper and cobalt content are also dissolved from the calcine. In the first leaching stage (neutral leaching), the calcine is mixed with spent acid from the electrolysis department. As the solution is only slightly acidic, most of the zinc oxide is dissolved, however the zinc ferrites and zinc silicates are not affected. Thickeners are used to separate the undissolved solids from the zinc sulphate solution, after which the solution is pumped to the purification stage.

The undissolved solids proceed to a second leaching stage (hot acid leaching). At a high acid concentration and temperature, zinc ferrites and zinc silicates dissolve. Subsequently, the dissolved silica, the bulk of the iron together with undissolved components such as lead sulphate are precipitated from solution. These precipitated solids are separated in thickeners.

With a throughput of 240000 tonnes of concentrate the amount of this saleable solid is about 70000 tonnes per year and total waste produced is quoted as 500 to 2000 tonnes [ 228, IZA plant data 2008 ].

The solution is partially purified in an iron precipitation step and returned to the neutral leaching step. The solids are filtered and washed in two separate filtration steps and are sold as a lead-silver product.

*The text in the box has been copied from Section 5.1.5.2.3. It should be merged with the following text.*

**Description**

A concentrate with a high zinc content (58 %) is produced at a mine located in Northern Queensland in Australia. The concentrate consists mainly of zinc sulphide and also contains small quantities of iron, lead, silica, carbon and silver. The concentrate is roasted in a conventional process but the subsequent leaching of the calcine is a much simpler process due to the composition of the concentrate [ 240, Nl Input on Zn production 2008 ], [ 228, IZA plant data 2008 ].

~~.~~

In addition to zinc, other metals are also dissolved from the calcine. In the first leaching stage (neutral leaching) the calcine is mixed with spent acid from the electrolysis department. As the solution is only slightly acidic, most of the zinc oxide is dissolved, however the zinc ferrites and zinc silicates are not affected. Thickeners are used to separate the undissolved solids from the zinc sulphate solution, after which the solution is pumped to the purification stage.

~~-~~The undissolved solids proceed to a second leaching stage (hot acid leaching). At high acid concentration and temperature, zinc ferrites and zinc silicates dissolve. Subsequently the dissolved silica and the bulk of the iron together with undissolved components such as lead sulphate precipitate again from solution. These precipitated solids are separated in thickeners.

The solution is partially purified in an iron-precipitation step and returned to the neutral leaching step. The solids are filtered and washed in two separate filtration steps and are sold as a lead-silver product.

This combined output of iron, silicates and metals such as lead and silver in one valuable product is only possible when there is an exceptionally low iron content in the raw material. For smelters using feed with a higher iron content, a combined output would result in a residue that is too diluted by iron precipitates and so separate outputs of the iron residue and the lead/silver residue are required.

### Achieved environmental benefits

The change-over to this concentrate was made in 2000 along with the construction of the new waste water treatment plant that treats groundwater as well as process effluent.

The low iron concentrate allows the calciner to be operated under steady-state conditions and this, combined with very low variation in the sulphur content, allows an even concentration (6 to 7 %) of $SO_2$ to be produced. This constant gas strength assists the operation of the associated sulphuric acid plant at a high conversion efficiency. The monthly average of $SO_2$ emissions in 2006 was in the range of 33 to 70 mg/Nm$^3$, (the annual average for 2006 was 55.4 mg/Nm$^3$) [ 240, Nl Input on Zn production 2008 ], [ 228, IZA plant data 2008 ].

In the waste water treatment plant, $H_2S$ is produced biologically using a sulphate reducing bacteria and the gas transported to the precipitation stage with a carrier gas [ 319, Biotechnology for Sustainable Hydrometallurgy 2003 ]. Sulphide precipitation can result in much lower concentrations in the cleaned effluent for certain metals depending on the pH and temperature and the metal sulphide produced can be returned to the smelting stage. Ferric sulphate can be added after precipitation to remove the excess sulphide.

The electrolyte bleed solutions are treated in a biological conversion stage using hydrogen as an electron donor which is produced by converting natural gas and steam [ 320, Biologically produced Sulphide 2004 ]. Zinc sulphide is produced at a rate of 10 tonnes per day and is recycled back to the smelter.

The process is now virtually free of solid wastes. Only very minor amounts of process waste arise now such as 75 t/yr of a sludge that contains mercury, and calcium fluoride from waste water treatment, 200 t/y) which are both processed off site.

### Cross-media effects

Use of energy.

### Operational data

The operational data for the materials produced for the plant are given in Table 5.43 and Table 5.44 for the waste water treatment plant.

| Product | 2003 | 2004 | 2005 | 2006 |
|---|---|---|---|---|
| Zinc metal | 223752 | 225382 | 227565 | 238274 |
| Cadmium metal | 495 | 549 | 423 | 575 |
| Sulphuric acid (96 %) | 333655 | 312806 | 309453 | 302966 |
| Leach Product | 64722 | 62801 | 66589 | 70395 |

**Table 5.43: Annual production of products in tonnes**
[ 240, Nl Input on Zn production 2008 ], [ 228, IZA plant data 2008 ].

| **Design capacity** | **$H_2S$ production**<br>**Volume of influent** | **3200 kg/d**<br>**40 m$^3$/h** | |
|---|---|---|---|
| Production | ZnS<br>$CaF_2$ | 10 t/d<br>0 - 9 t/d | |
| Effluent quality | | **In** | **Out** |
| | $SO_4^{2-}$ | 15000 | <300 |
| | Zn | 10000 | <0.2 |
| | $F^-$ | 500 | <50 |

**Table 5.44: Effluent treatment plant performance**
[ 240, Nl Input on Zn production 2008 ], [ 228, IZA plant data 2008 ].

*What means effluent quality? What are these values? Units??*

**Applicability**

This technique is applicable to installations that have access to this concentrate but there is a limited time when this will be available and because of insufficient capacity for treatment of the residue. Some installations however use a small percentage of this concentrate in their normal mix.

**Economics**

No data has been reported but the installation is operating under commercial conditions.

**Driving force for implementation**

Environmental regulations that did not allow further deposits of untreated iron residues on land.

**Example plants**

NL

**Reference literature**

[ 240, Nl Input on Zn production 2008 ], [ 228, IZA plant data 2008 ], [ 320, Biologically produced Sulphide 2004 ].

### ~~5.3.5.2~~5.3.5.3 Jarofix process

**Description**

In the Jarofix process, jarosite precipitates formed during the leaching of zinc ferrites are mixed with preset ratios of Portland cement, lime, and water. The reaction generates a chemically and physically stable-_material, reducing the long-term liability associated with iron residue disposal while offering concomitant processing advantages. Supporting mineralogical studies of aged Jarofix products indicate that jarosite reacts with the alkaline constituents of the cement to form various stable-_phases that incorporate zinc and other soluble metals. The persistence of alkaline phases in the Jarofix product helps to ensure its long-term environmental stability [ 228, IZA plant data 2008 ], [ 289, USEPA Method 1311 and 1312 2008 ].

**Achieved environmental benefits**

Production of an inert residue that is classified as non-hazardous waste allows the elimination of the long-term storage of jarosite in lagoons and the production of a material that has low leachability. It should be noted that while the metals do not leach when the waste is fixed, the process does increase the volume of material produced to approximately 1.15 tonnes of Jarofix per tonne of zinc produced. The material is used to reclaim land that will be used for recreational or commercial purposes.

**Cross-media effects**

None reported.

**Operational data**

For quality control purposes, the Jarofix material is leached using an acidic or buffered solution. The resulting extract is analysed and compared to a leachate criteria list. If the resulting concentration is equal to or in excess of the concentration specified for that contaminant in the applicable schedules, the material is considered leachate toxic and may not be suitable for recovery. The results obtained, however, show that the Jarofix produced has a very low leachable metal content. The results shown in Table 5.45 were reported for Jarofix produced over a two year period in a Canadian plant. US EPA methods 1311 and 1312 for the leaching of metals from residues were used.

| Component | Extraction at pH 4.93 with acetic acid | Extraction at pH 4.2 with nitric/sulphuric acids |
|---|---|---|
| Al | <0.1 - 0.2 | 0.2 - 0.2 |
| As | 0.03 - 0.04 | 0.01 - 0.03 |
| Be | <0.01 | <0.01 |
| Cd | <0.005 - 0.006 | <0.005 |
| Co | 0.09 - 0.10 | 0.03 - 0.04 |
| Mn | 0.05 - 0.20 | 0.01 |
| Ni | <0.01 | <0.01 |
| Pb | <0.05 | <0.05 |
| Zn | <0.01 - 0.12 | <0.01 |

**Table 5.45: Jarofix leaching tests using US EPA test methods**
[ 264, Jarofix 1999 ], [ 289, USEPA Method 1311 and 1312 2008 ].
*What are the units for the data in the table 5.42?*

**Applicability**
This technique is applicable to all iron residues from zinc production.

**Economics**
No data has been reported but a review of the processes available to eliminate jarosite residue concluded that the Jarofix process was the most economical. This report is confidential.

**Driving force for implementation**
Environmental regulation that did not allow further deposits of untreated iron residues on land.

**Examples**
Canada and Spain.

**Reference information:**
[ 228, IZA plant data 2008 ], [ 289, USEPA Method 1311 and 1312 2008 ], [ 264, Jarofix 1999 ].

### ~~5.3.5.3~~5.3.5.4 Use of the Waelz kiln and the Ausmelt/ISA Smelt furnace to treat zinc ferrites

**Description**
In the conventional roast-leach-electrowin process, the neutral leaching stage is followed by a hot acid leaching stage to dissolve zinc ferrites from the solid residue from the neutral leaching. Iron is also dissolved in this stage and should be removed. Several methods of iron elimination exist including the jarosite, goethite and hematite processes which produce an iron residue for disposal or further treatment (e.g. the Jarofix process). An alternative to the conventional process is to stop at the neutral leaching stage and send the residue to the Waelz kiln process.

At the Polish company ZGH Bolesław approximately 90 % of the zinc is recovered in the neutral leaching stage. The residual ferrites account for 20 to 25 % of the total calcine mass. They contain,: Zn,17.5 to 19.5 %; Pb, 8.0 to 10.5 %; Fe, 20.0 to 23.0 %; $SiO_2$, 1.8 to 2.0 %; S, 8.0 to 9.0 %; S (as $SO_4$), 5.5 to 6.5 %; Cd, 0.35 to 0.45 %; As, 0.2 to 0.3 %; Mn, 0.4 to 0.6 %; Cu, 0.15 to 0.25 %; and $H_2O$, 18.0 %.

The zinc ferrites are treated in two Waelz kilns (of length 40 m in length and an inner diameter of 2.6 m) operating with three zones. The charge material is composed of a mixture of ferrites with 10 % sand and 40 % anthracite.

Furnace gases carry the zinc-rich dust produced in the kiln through a dust chamber, then a mixing chamber and into a tubular cooler with forced airflow and finally a fabric filter. The Waelz oxide product is collected at the outlet section of the cooler and fabric filter. The dedusted gases are finally desulphurised in a wet FGD process, where limestone reacts with $SO_2$ and oxygen to produce gypsum.

The Waelz oxide contains 48.0 - 54.0 % Zn; 13.0 - 15.0 % Pb; 2.0 - 4.5 % Fe; 0.6 - 0.8 % Cd, 0.15 - 0.25 % As; 0.3 - 0.8 % $SiO_2$; 1.8 - 2.7 % S; 0.08 - 0.15 % Mn; 2.8 - 3.7 % Cl; 0.10 - 0.12 % F with the zinc recovery efficiency of 85 - 87 %. The Waelz oxide is then returned to the neutral leach stage.

The slag from the kiln contains: 2.6 - 3.5 % Zn; 1.0 - 1.5 % Pb; 25.0 - 30.0 % Fe; 0.004 - 0.006 % Cd; 0.01 - 0.1 % As; 13.4 - 14.0 % $SiO_2$. The leachate tests show that material is suitable-_for construction and road building [ 280, Polish Report 2008 ].

*(We should be careful with such statements because in other countries waelz kiln slag is disposed of and can not be used)*

The Ausmelt/ISA Smelt furnace is used in Korea to produce a non-leachable slag and recoverable metal oxides from a variety of lead and zinc-containing residues from primary lead and zinc smelting [ 305, Ausmelt Lead and Copper processes 2009 ].

**Achieved environmental benefits**
The use of a Waelz process to treat the neutral leach residue results in the elimination of long-term storage of jarosite in lagoons. It produces a slag that can be further treated to recover valuable metals [ 354, F Farrell Mission in Bulgaria July 2009 2009 ].

**Cross-media effects**
Use of energy and potential dust emissions.

**Operational data**
The emissions from Waelz kiln process are:

- $SO_2$ - 1 kg/t of the product, 20 t/year
- $NO_X$- 2.5 kg/t of the product, 50 t/year
- CO - 40 kg/t of the product, 800 t/year
- Dust $PM_{10}$ - 0.3 kg/t of the product, 6.0 t/year
- Slag - 1.7 t/t of the product
- Synthetic gypsum from FGD plant - 200 kg/t of the product
- Effluents (slag cooling) - 0.007$m^3$/t of the product, treated in the ETP onsite

The Waelz kiln installation treating hydrometallurgical slimes consumes:

- Reducing agent (coke, anthracite) - 1 t/t of the product
- $SiO_2$ - 0.3 t/t of the product
- Natural gas - 70 $Nm^3$/t of the product
- Electric energy - 240 kWh/t of the product
- Compressed air - 330 $Nm^3$/t of the product

[ 228, IZA plant data 2008 ].
*Without further information about the waste gase flow these data can hardly be used.*

**Applicability**
This technique is applicable to all iron residues from the neutral leach stage of zinc production.

*This statement might be a bit misleading. The idea behind this alternative technique is to stop the leaching at the neutral leaching stage and send the residue to the Waelz kiln process.*
*The question is if this technique can be applied to other existing leaching stages in hydrometallurgical zinc processing.*

**Economics**
No data available but the process is operating successfully.

**Driving force for implementation**
Eliminating hazardous waste (jarosite) to be stored is the main driving force.

~~The processes can be used for secondary zinc bearing materials treatment (EAF dust).~~*This is not the idea behind the propsed techniques to consider.*

**Example plants**
Treatment of neutral leach residue, Poland 'ZGH Bolesław', Korea Zinc and Bulgaria.
Other Waelz processes treating EAF dust only where the Waelz residue is used for construction materials, FR, DE, IT, ES.

**Reference literature**
[ 228, IZA plant data 2008 ], [ 280, Polish Report 2008 ], [ 305, Ausmelt Lead and Copper processes 2009 ], [ 354, F Farrell Mission in Bulgaria July 2009 2009 ].

### ~~5.3.5.4~~5.3.5.5 Compacting iron residue

**Description**
Compacting is a technique to increase the capacity of a storage area for iron residue. The classical way to store goethite and jarosite is pumping the slurry into a pond (with a plastic liner at the bottom and walls) for settling, and then pumping the cleared solution at the surface back to the plant for zinc recovery while the settled solid material remains at the bottom of the pond. The pond is gradually filled with cake until it is completely full with cake. At the end of its life, the pond is covered.

The compacting technique involves filtering the goethite by means of a high pressure press filter (15 to 30 bars) possibly combined with the addition of lime or other agents to decrease the inherent leachability for metals. The filter cake is transported into a basin, similar to the type used for classical storage (or an existing emptied pond), and each layer of the cake is then further compacted by means of a specific heavy vehicle. The final moisture content of the stored iron-rich residue is significantly lower than in a classical pond (reduced from about 65 % to 35 %) and due to the firm nature of the cake, it can be formed into a mound and so increases the storage capacity by a factor 2 to 4 depending on the final height.

**Achieved environmental benefits**
The production of a more dense iron residue requires less storage volume (optimal use of land). There is a reduced risk for accidental leakage because the permeability of the stored material is extremely low and is in the same order as clay. There is no aqueous solution above the solid material. The leachability of metals can be decreased by adding lime or other additives.

**Cross-media effects**
Use of energy.

**Operational data**
The final moisture content of compacted goethite at the Nyrstar plant in Balen (Belgium) is approximately 35 % compared to 60 % for the uncompressed material. Specific permeability can be decreased to <10 - 9 m/s.
*Sorry, but this is impossible. Perhaps is should be <10$^{-9}$ m/s.*

**Applicability**
This technique is applicable to all goethite residues from zinc production. It has not yet been tried for jarosite residues.

**Economics**
It is reported that the costs are comparable to hydraulic storage. There is a shift from capital (pond area) to operating costs (filtering/handling).

**Driving force for implementation**
Optimal use of land and an increased lifetime of existing ponds.

**Example plants**
Belgium, France.

**Reference literature**
[ 274, Farrell Mission in DE 2008 ].

### 5.3.5.6 Emissions reduction in c~~C~~hemical purification~~refining~~

The processes based on cementation and chemical treatment that were discussed earlier as available techniques are all techniques to consider in the determination of BAT. The specific feed materials will influence the final process choice. The techniques discussed in Chapter 2 should also be considered in[rr49] conjunction with these processes for example the removal of arsine and stibine by scrubbing gases from the chemical treatment stages with an oxidising agent such as potassium permanganate 0.5 mg/Nm$^3$ as As is achievable [ 136, Fugleberg, S. 1999 ], [ 234, UBA Copper, lead, zinc and aluminium 2007 ].

**Achieved environmental benefits**
The environmental benefits are the prevention of diffuse emissions of metals, dust and other compounds. *This statement is misleading.Chemical purification is conducted by the use of arsine which can cause arsine emissions. The use of strong oxidising agents such as potassium permanganate is a solution to reduce As emissions.*

**Cross-media effects**
None are reported.

**Operational data**
None are available.

**Applicability**
The processes and the techniques are suitable ~~-~~for use with new and existing installations.

**Economics**
None was provided but the processes are operating economically.

**Driving force for implementation**
The reduction of emissions and saving raw materials.

**Example plants**
Plants in DE, AT, FR, BE, PL and NL.

**Reference literature**
[ 274, Farrell Mission in DE 2008 ], [ 136, Fugleberg, S. 1999 ], [ 234, UBA Copper, lead, zinc and aluminium 2007 ].

### ~~5.3.5.6~~5.3.5.7 Purification by solvent extraction

**Description**

Solvent extraction can be used to selectively concentrate a zinc containing solution that is produced from either primary or secondary raw materials. SHG zinc can be produced after electrolysis or it is also possible to produce pure zinc sulphate, zinc oxide or other zinc chemicals. One solvent extraction cycle is used with D2EHPA as the complexing agent and kerosene as the solvent. The process comprises the stages of leaching, solvent extraction and electrowinning [ 327, Highlights and hurdles in Zinc production by solvent extraction 2008 ].

When applied to primary zinc ores and concentrates, the process involves atmospheric leaching of the raw material , upgrading and purification of the pregnant leach solution by solvent extraction (SX), and zinc recovery by electrowinning (EW), the process diagram is shown in Figure 5.8. The SX stage is also used to recover zinc from dirty secondary raw materials such as batteries.

Main stages included in solvent extraction (SX) unit are extraction, washing, stripping, and organic regeneration. The aim of the solvent extraction system is to produce an ultra-pure zinc loaded electrolyte capable to produce SHG zinc by electrowinning with full confidence.

The net result of the extraction stage is the selective transfer of zinc from the pregnant leach solution (PLS) to the organic phase and the corresponding transfer of the acidity in the opposite direction. The extractant Di-2-ethylhexyl phosphoric acid (DEHPA) dissolved in kerosene is used for selective extraction of zinc ions versus the other constituents of the PLS as shown in reaction ($^1$).

$$2RH + Zn^{2+} = R_2Zn + 2H^+ \qquad (^1)$$

The aqueous acid zinc raffinate leaving the extraction stage is recycled to the leaching section after organic entrainments are removed. A small proportion is sent to bleed treatment section to balance the components of the circuit.

The zinc-loaded organic phase leaves extraction stage and flows to the washing stage. In this stage, impurities (due to aqueous entrainment and co-extraction) are removed from the zinc loaded organic phase in a counter-current washing stage with diluted spent electrolyte coming from the tank house. The organic phase that leaves the washing stage is sent to the stripping stage.

The washed organic phase enters into the stripping stage where it is counter-currently contacted with spent electrolyte coming from the electrowinning section. At the end there is a selective transfer of zinc ions from the zinc loaded and washed organic phase to the spent electrolyte, which becomes a zinc loaded electrolyte, and the corresponding transfer of the acidity in the opposite direction, as shown in reaction ($^2$).

$$R_2Zn + 2H^+ = 2RH + Zn^{2+} \qquad (^2)$$

The aqueous phase is pumped to the tank house after organic entrainments are removed. The stripped organic raffinate is collected and recycled back to the SX system. A very small organic phase regeneration facility is provided to prevent iron building-up in the organic phase solution.

**Achieved environmental benefits**

The SX technology can reduce the production of solid residues and liquid effluents due to iron co-leaching. Energy saving in the electrolytic process are achieved because lower cell voltage can be used with the purer electrolyte produced by the SX processes.

**Cross-media effects**

None reported.

**Operational data**

Typical composition of SX process streams are shown in Table 5.46 including the acidic aqueous solution with a low zinc content (acid raffinate) that leaves the extraction stage and is recycled to the leaching section. Table 5.47 shows the reagents and utilities consumption for the SX process.

| Parameter | PLS | Acid raffinate | Loaded electrolyte |
|---|---|---|---|
| Flowrate m$^3$/h | 830 | 960 | 280 |
| Zinc g/l | 38 | 13 | 117 |
| Iron g/l | 0.02 | 0.02 | <0.005 |
| Magnesium g/l | 1.0 | 1.0 | 0.030 |
| Chloride g/l | 1.0 | 0.9 | 0.050 |
| Fluoride g/l | 0.04 | 0.04 | 0.070 |
| Nickel mg/l | 0.3 | 0.2 | 0.00008 |
| Cadmium mg/l | 0.3 | 0.3 | 0.00001 |
| Copper mg/l | 0.5 | 0.5 | 0.00009 |
| Calcium mg/l | 0.7 | 0.6 | 0.050 |
| Silicon mg/l | 0.07 | 0.06 | |
| Aluminium mg/l | 0.08 | 0.07 | 190 |
| Manganese mg/l | 2.1 | 2.0 | 2.2 |
| Sulphuric acid g/l | | 36 | 80 |

**Table 5.46: Typical composition of the main SX process streams**
[ 327, Highlights and hurdles in Zinc production by solvent extraction 2008 ]

| Component | Unit | Consumption per tonne of zinc produced |
|---|---|---|
| NaCl ~~kg~~ | kg | 16 |
| Active charcoal ~~kg~~ | kg | 0.9 |
| D$_2$EHPA ~~kg~~ | kg | 0.7 |
| Kerosene ~~kg~~ | kg | 8 |
| Demineralised water ~~m$^3$~~ | m$^3$ | 3 |
| Electricity ~~kWh~~ | kWh | 115 |

**Table 5.47: Main reagent and utilities consumption in the modified Zincex Process.**
[ 327, Highlights and hurdles in Zinc production by solvent extraction 2008 ]

**Applicability**
The process is applicable to all RLE processes and to the recovery of zinc from secondary raw materials.

**Economics**
A reduction of 10 % of the operating costs are reported. The total investment costs for an SX plant were EUR 240 per tonne installed annual capacity for a plant producing 15000 t/yr SHG zinc.

**Driving force for implementation**
Reduced energy use, ability to treat a wider range of raw materials.

**Example plants**
Namibia.
*Are there any other plants applying this process, preferably in Europe?*
*What about [309] , Pekkala (2007)."Performance Highlights of a Modern VSF™ SX Plant"*
*Are there plants in Finland or Australia?*

**Reference literature**
[ 327, Highlights and hurdles in Zinc production by solvent extraction 2008 ]

### ~~5.3.5.7~~5.3.5.8 Electrowinning

Electrowinning processes that feature optimised cell dimensions (spacing, number of cells, etc.) and use aluminium cathode blanks are techniques to be considered. Mechanised (and automatic) harvesting and stripping of the cathodes as well as more elaborate short circuit detection for example by using infra-red sensors to monitor cell temperatures is also worth considering depending on the scale of the operation.

Electrowinning produces gases that are evolved at the anode and will produce an acid mist. This should be collected and removed, extraction and mist elimination are used and collected mist returned to the process. Scrubbing the collected gases does not allow re-use of the mist and contributes to waste water[rr50]. Foaming agents produce an effective covering to the cells and can be used to reduce the amount of mist formed. Organic or plastic bead layers can also be used.
*Try to get more information and examples about electrolysis.*

### ~~5.3.5.8~~5.3.5.9 Collection and treatment of electrolyte mist

*Combine with section 5.3.5.8 if appropriate.*

**Description**
Two systems exist and are generally accepted for the collection of electrolyte mist:
a) combined: the cellhouse air is ventilated by the atmospheric cooling towers, the air from the building is used as cooling agent in the coolers;
b) non-combined: the cellhouse air is ventilated (forced or natural-draught) independently from the electrolyte cooling; the cooling towers make use of air from outside the building.

Demisting the air from the cooling towers is best practise for both the combined and non-combined option.

Aerosol formation can be prevented by the use of additives.
*Which additives. Is this a technique to be considered itself?*

**Achieved environmental benefits**
The removal of acid mist that would be otherwise emitted to the local environment and an improvement in the workplace conditions.

**Cross-media effects**
Energy costs of operating fans.

**Operational data**
Electrolyte cooling is practised and the heat may be recovered. C~~c~~ell gases or cell-room ventilation air are collected so that they can be demisted. Demisting of the cooling air is carried out. Sealed tank house drainage systems, the recovery of electrolyte bleed are used. Subjective comparison with non modified plants shows a significant improvement inside and outside of the plants [ 228, IZA plant data 2008 ]. Achievable emission level for acid mists is 10–35 mg/Nm$^3$.
*The higher end of this range is proposed by comment No 893 and refers to LVIC-AAF BREF table 4.25. At least a cross reference would be needed here. Better try to get some good data.*

**Applicability**
This technique is applicable to all electrowinning processes.

**Economics**
Not assessed but this technique is economically viable in a number of installations.

**Driving force for implementation**
Health and safety issues and local environmental impact.

**Example plants**
ES, BE, FR, NL.

**Reference literature**
[ 103, Farrell, F. 1998 ], [ 228, IZA plant data 2008 ].

### 5.3.6 ~~S~~Techniques to consider in the determination of BAT for secondary zinc production

The processes that were discussed earlier as available techniques are all techniques to consider in the determination of BAT. The specific feed materials will influence the final process choice. The techniques discussed in Chapter 2 should also be considered in conjunction with these processes.

#### 5.3.6.1 Slag fuming furnaces

*Unclear: Copper, zinc, lead are mentioned. Crosscheck with [99] and other references. Copper recovery is not mentioned in [99]. The description seems to be more suitable for other slags.*

**Description**
The slag from the electric copper matte smelting furnace, together with dust that contains zinc from EAFs of the steel industry, are treated for metal recovery in a fuming plant. The copper lead and zinc values are recovered by coal reduction. Zinc is fumed while copper is obtained as a matte.

The thermal treatment of jarosite and goethite has been demonstrated commercially in Korea and Japan using the Ausmelt/ISA Smelt furnace. Zinc and other volatile metals are fumed off and recovered. The slag produced could be suitable for construction processes.

**Achieved environmental benefits**
Reduction of the amount of waste generated and the recovery of zinc from residues

**Cross-media benefits**
None reported.

**Operational data**
The fuming plant consists of two main process units: the fuming furnace and the electrically heated settler. The fuming furnace gases that contain the zinc (and lead) volatilised, are re-oxidised and cooled in a waste heat boiler; after temperature adjustment in an evaporative cooler, the metal oxide dust is separated in electrostatic precipitators (two in parallel plus one in series) before release to the atmosphere via the stack. The heat from the fuming furnace cooling water is recovered and used for district heating.

The fuming furnace is operated batch wise. The melt is transferred into the electrically heated settler where matte and alloy are separated and tapped. The slag is granulated and sold for different applications.

The secondary gases from fuming including the gases of the settler are collected in a ventilation system and combined with the electric furnace gases; the gas stream is cleaned in a baghouse and released to atmosphere via stack, (see Table 5.48).

| Fuming furnace | |
|---|---|
| Size: | L 8.1 m; W 2.4 m. |
| Capacity: | 105 tonnes. |
| Fuming agent: | Preheat air and coal |
| Cycle: | approximately 120 min. |
| Steam generation: | approximately 55 t/h |
| District heating: | 4 - 8 MW |
| Settler: | |
| Size: | L 11.3 m; W 3.5 m; H 3 m |
| Capacity: | 250 tonnes |

**Table 5.48: Fuming Plant Data for a lead fuming process**
[ 238, ECI Copper Installations 2008 ]
*Check whether this is the correct reference.*

**Applicability**
This technique is applicable to all plants recovering zinc and copper from residues.

**Economics**
No data has been reported.

**Driving force for implementation**
Waste minimisation and the recovery of metals.

**Example plants**
Boliden Rönnskär, SE; Boleslaw, PL; Plovdiv, BG.

**Reference literature**
[ 238, ECI Copper Installations 2008 ], [ 305, Ausmelt Lead and Copper processes 2009 ].

### 5.3.6.2 Slag Fuming Process using a plasma arc

**Description**
This fuming process can be used to treat metal oxides, such as baghouse dust from electric arc steelmaking furnaces or secondary materials such as complex slags containing Zn and ZnO. The materials are fed into the slag bath of a plasma arc furnace where the reactions take place producing ZnO. Coke or similar material is used as the reducing agent. A slag former is added if needed, to the feed. The different metal oxides are reduced according to the equilibrium determined by slag temperature and oxygen potential [ 350, Arc Fume process 2009 ].

The slag temperature is controlled by the plasma power and slag composition. The power consumption is about 1.2 MW/tonne of fed EAF dust. The oxygen potential is adjusted by the coke feed rate and liquefied natural gas flow in the tuyères. Coke is used only as a reducing agent and not for heating; it is possible the process can be controlled accurately to reduce zinc and lead oxides to the metals, while maintaining the iron as the oxide in the slag.

Reduced metals with a high vapour pressure such as lead and zinc leave the furnace as metal vapour. The off-gas exits the furnace at temperature about 1300 °C. Off-gases are reoxidised by air to produce ZnO and PbO. If re-oxidation takes place in the furnace, then about one third of the heat generated can be recovered by heating up the slag, therefore reducing the power consumption of the plasma generator. The general flow sheet of the process is illustrated in Figure 5.16.

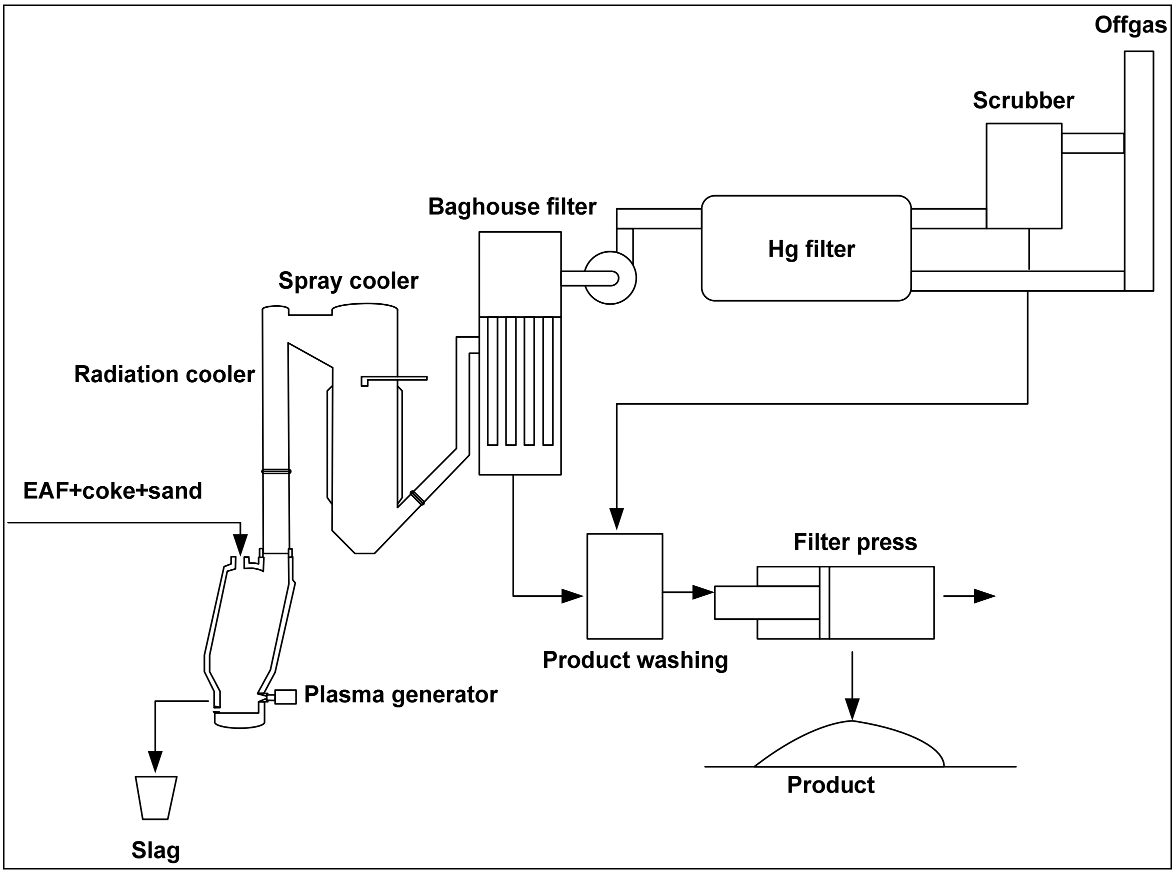


Figure 5.16: Flow sheet of the plasma arc fuming process.

The off-gases produced by the process have to be cooled and cleaned. Elements such as F and Cl are stripped by injecting NaOH into the spray cooler and scrubber. Hg is removed in an active carbon filter. Reoxidised Zn and Pb are removed from the off-gases in the baghouse filters from where they are then collected for washing. Water with additions of $Na_2CO_3$ is used for product washing to reduce the amount of Cl, F in the final product. Metals such as Cd, Pb and Zn are present in the wash water and the pH in the washing tanks is adjusted in the range between 9.5 and 11 to minimise the concentration of Cd, Zn and Pb. The wash water is monitored and is treated before discharge to the environment by the addition of $Na_2S$.

### Achieved environmental benefits

Higher yield of zinc, lower $CO_2$ emissions and use of slag. Reduction of the amount of waste generated.

### Cross-media effects

There is an increase in the use of energy and reducing agents.

### Operational data

The recovery rate of Zn is about 92 %. The ZnO content is about 88 % and F and Cl contents are below 0.2 %. A stable non-soluble slag with Pb content about 0.1 % is produced as a by-product. The slag basicity (CaO+MgO)/SiO is around 1. The slag is used in various industries such as concrete manufacturing and/or construction. Table 5.49 shows the material balance of the process.

| Input (kg) | | Output (kg) | |
|---|---|---|---|
| EAF dust | 1000 | Slag | 426 |
| Coke | 80 | Gas | 7505 |
| Sand | 90 | Product | 494 |

| | | | |
|---|---|---|---|
| Compressed air | 5915 | | |
| Water | 1286 | | |
| LNG and oil | 54 | | |
| **Total** | **8425** | | **8425** |

**Table 5.49: Material balance of the plasma arc fuming process (calculated for 1 tonne of EAF dust)**
[ 350, Arc Fume process 2009 ]

Cleaned off-gases consist mainly of $CO_2$, $H_2O$ and $N_2$ Table 5.50 shows the main gaseous components of the off-gases.

| **Component** | **(%)** | **(kg)** |
|---|---|---|
| $CO_2$ | 4.0 | 300 |
| $H_2O$ | 29.4 | 2207 |
| $N_2$ | 56.4 | 4233 |
| $O_2$ | 10.1 | 758 |
| Other | 0.1 | 8 |

**Table 5.50: Main gaseous components of the plasma arc fuming process.**
[ 350, Arc Fume process 2009 ]
*These data are of low significance.*
*What about pollutants? Are there any data from measurments about pollutants?*

#### Applicability
Due to the efficient separation of elements in the process residues that are normally recovered in for thermal processes can be recovered.

#### Economics
The investment cost for a plasma arc plant of 50000 tonne per year capacity is approximately EUR 13 million.

#### Driving force for implementation
Waste minimisation and the recovery of metal.

#### Example plants
Høyanger (Norway), Hofors (Sweden).

#### Reference literature
[ 350, Arc Fume process 2009 ].

### 5.3.6.3 THE SDHL ~~and other Waelz~~ kiln processes

#### Description
The aim of the SDHL process is to increase the throughput of the zinc recovery accompanied by a decrease of energy requirements. Additionally, the technique is capable of being installed at existing Waelz units. By blowing air into the lower end of the furnace, it becomes possible to use the energy of the metallic iron content in the Waelz slag and to run the process at substoichiometric conditions [ 234, UBA Copper, lead, zinc and aluminium 2007 ], [ 246, French Report on SDHL process 2008 ]. Oxidation of the iron content brings several advantages:

- lower residual carbon content <1 %;
- no additional natural gas input is needed at normal operation;
- 40 % reduction of coke breeze input;
- higher throughput;

- higher zinc recovery;
- reduction of $CO_2$ emissions.

Implementing the basic slag system has resulted in a PCDD/F reduction by a factor of 10. A longer lifetime of the refractory lining is achieved.

Neutral leach and other residues from the roast-leach-electrowin process to produce zinc are also recovered in Waelz kilns along with other residues containing zinc [ 351, Farrell 2009 ]. The slag chemistry is controlled but the slag is treated further to recover copper and other metals that are not leached in the neutral or soft acid leaching stages.

**Achieved environmental benefits**
Fixation of impurities in the furnace slag or in the salt residues. Reduced energy use and emissions of process.

**Cross-media effects:**
No data has been reported.

**Operational Data:**
See Table 5.51.

| Parameter | Unit | Common Waelz process | SDHL-process |
|---|---|---|---|
| Throughput | (t/d | 146 | 200 - 210 |
| Zinc recovery | (%) | 84 | 91 - 93 |
| $Fe_{met}/Fe_{total}$ | - | 80 - 90 | 10 |
| Coke consumption | (kg/t) | 380 | 160 - 170 |
| Natural gas consumption at normal operation mode | ($m^3$/h) | 180 | 0 |

**Table 5.51: Effect of implementation of the SDHL process**
[ 234, UBA Copper, lead, zinc and aluminium 2007 ]

The plant operating in France reported emissions before and after the implementation of the SDHL process. Table 5.52 gives a comparison of the SDHL process (from mid 2004 when the process was commissioned) with the traditional Waelz kiln process that was operating prior to this time.

| Component | Annual mean | Before | After |
|---|---|---|---|

| | value | 2003 | 2004 | 2005 | 2006 | 2007 |
|---|---|---|---|---|---|---|
| $SO_2$ | (kg/h) | 22148 | 7.390 | 0.584 | 0.424 | 0.199 |
| $NO_X$ | (kg/h) | 2.140 | 1.143 | 0.946 | 2.467 | 1.407 |
| VOC - non methane | (kg/h) | 2.000 | 4.237 | 3.057 | 2.104 | 7.711 |
| Dust | (kg/h) | 0.070 | 0.129 | 0.204 | 0.181 | 0.193 |
| HCl | (kg/h) | 0.069 | 0.123 | 0.261 | 0.070 | 0.051 |
| HF | (kg/h) | | 0.124 | 0.027 | 0.346 | 0.065 |
| Sum of metals | (kg/h) | 0.0491 | 0.0317 | 0.0177 | 0.0257 | 0.0327 |
| Pb | (kg/h) | 0.0054 | 0.0133 | 0.0076 | 0.0102 | 0.0204 |
| Zn | (kg/h) | 0.0372 | 0.1191 | 0.0730 | 0.1065 | 0.2446 |
| Hg | (kg/h) | | 0.00445 | 0.00079 | 0.00148 | 0.00608 |
| As | (kg/h) | | 0.00053 | 0.00076 | 0.00089 | 0.00129 |
| Cd | (kg/h) | 0.0013 | 0.0011 | 0.0012 | 0.0007 | 0.0007 |
| | | | | | | |
| PCDD/F | (µg ITEQ/h) | 9.653 | 7.235 | 1.141 | 2.567 | 1.292 |
| Airflow | (Nm$^3$/h) | 113706 | 133977 | 131056 | 140781 | 148329 |

**Table 5.52: Air emissions associated with the SDHL process before and after conversion**
[ 246, French Report on SDHL process 2008 ]

| Component | Annual mean 2007 Value | |
|---|---|---|
| $SO_2$ | mg/Nm$^3$ | 1.34 |
| $NO_X$ | | 9.49 |
| VOC - non methane | | 51.99 |
| Dust | | 1.3 |
| HCl | | 0.34 |
| HF | | 0.44 |
| Sum of metals | | 0.22 |
| Pb | | 0.14 |
| Zn | | 1.65 |
| Hg | | 0.041 |
| As | | 0.0087 |
| Cd | | 0.0047 |
| PCDD/F | ng I-TEQ/Nm3 | 0.0087 |
| Airflow | (Nm$^3$/h) | 148329 |

**Table 5.53: Air emission concentrations associated with the SDHL process after conversion for the year 2007**
[ 246, French Report on SDHL process 2008 ]

**Applicability**
This technique is applicable to most conventional Waelz kilns.

**Economics**
Cost of implementing SDHL process are given as EUR 1300000.

**Driving force for implementation**
Recovery of additional components from EAF dust.

**Example plants**
Germany (Freiburg, Duisburg), Spain (Asua Erandioko) and France (Fouquieres lez Lens)

**Reference literature**
[ 234, UBA Copper, lead, zinc and aluminium 2007 ], [ 246, French Report on SDHL process 2008 ], [ 351, Farrell 2009 ].

### 5.3.6.4 Washing of Waelz oxide

**Description**
Waelz oxide can also be washed with water in a two or three-stage process, using sodium bicarbonate, sodium carbonate or sodium hydroxide in all stages, to remove chloride, fluoride, sodium and potassium. The alkalis of the rich leach liquor from the first washing step are removed by a crystallisation step to produce a salt residue and an alkali-free condensate or are discharged after treatment. The salt residue is dumped or backfilled underground, the effluent is discharged to river or sea. The condensate of the crystallisation step is recycled; in this case the total process works without producing waste water. The purified final product is dried and can be used as the feed material for the zinc electrolysis process [ 234, UBA Copper, lead, zinc and aluminium 2007 ].

Figure 5.17 and Figure 5.18 show the overall processes for washing Waelz oxide [ 234, UBA Copper, lead, zinc and aluminium 2007 ].

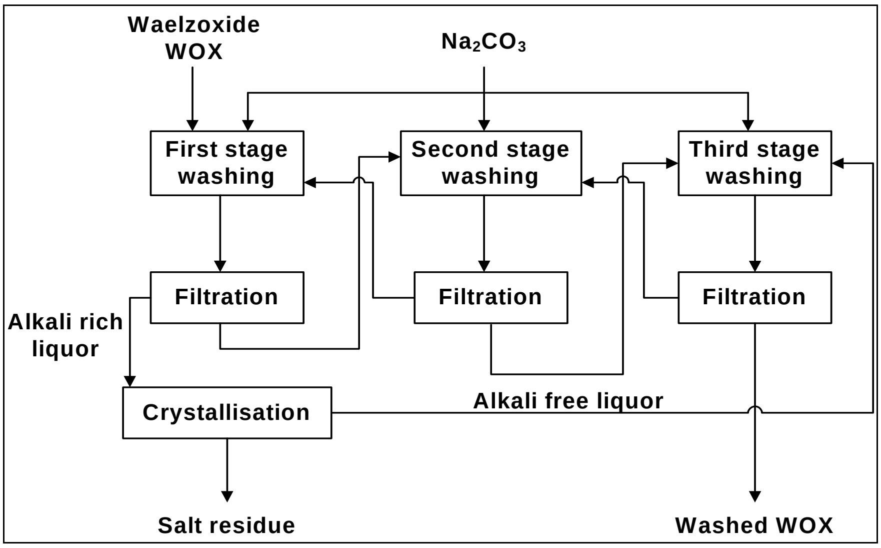


**Figure 5.17: Diagram of a Waelz oxide three stage washing circuit**
[ 234, UBA Copper, lead, zinc and aluminium 2007 ]

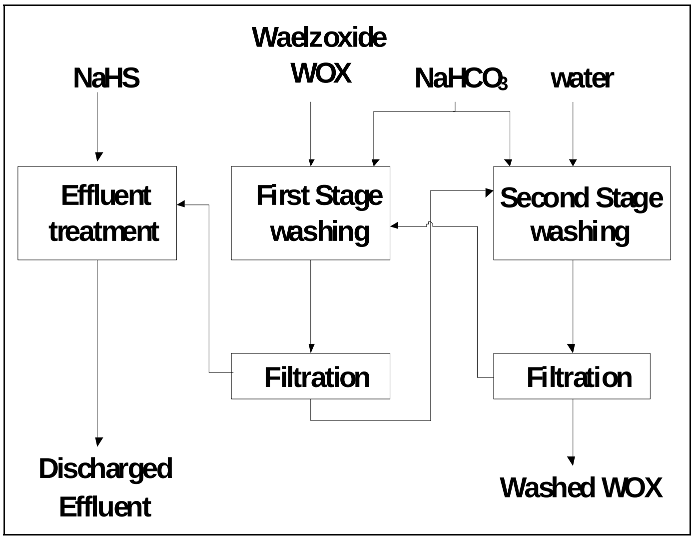


**Figure 5.18:** **Diagram of a Waelz oxide two-stage washing circuit**

*Both figures 5.10 and 5.11 are included in Section 5.3.6.4 and should be deleted either here or there.*

**Achieved environmental benefits**

Removal of impurities in the salt residues and efficient energy use for process.

**Cross-media effects**

Use of water, chemicals and energy.

**Operational data**

The effect of washing and the waste water from the washing process are given in Table 5.54 and Table 5.55.

| Component | Unwashed Waelz oxide | Washed Waelz oxide (triple or double stage washing) |
|---|---|---|
| Zn % | 58 - 63 | 63 - 68 |
| Pb % | 7 - 10 | 9 - 11 |
| S % | 0.5 - 1 | <0.15 |
| F % | 0.4 - 0.7 | 0.08 - 0.15 |
| Cl % | 4 - 8 | 0.05 - 0.15 |
| $K_2O$ % | 1.5 - 2 | 0.1 - 0.2 |

**Table 5.54:** **Effect of waelzoxide washing**

[ 234, UBA Copper, lead, zinc and aluminium 2007 ]

| Component (mg/l) | Waste water after treatment with NaHS |
|---|---|
| Zinc | 0.01 - 1.0 |
| Lead | 0.01 - 0.20 |
| Cadmium | 0.01 - 0.10 |

**Table 5.55:** **Waste water from the washing process**

[ 234, UBA Copper, lead, zinc and aluminium 2007 ]

**Applicability**

This technique is applicable to most new and existing Waelz kilns.

**Economics**

Not assessed but process is in use and is economically viable.

**Driving force for implementation**
Recovery of zinc and reduction in waste.

**Example plants**
ES, DE, FR.

**Reference literature**
[ 93, García-Agocheaga, B. 1998 ], [ 234, UBA Copper, lead, zinc and aluminium 2007 ].

### 5.3.6.5 Purification by solvent extraction

**Description**
Solvent extraction can be used to selectively concentrate a zinc containing solution that is produced from secondary raw materials (see also 5.3.5.6) [ 327, Highlights and hurdles in Zinc production by solvent extraction 2008 ].

When applied to secondary raw materials the process involves the upgrading and purification of the pregnant leach solution by solvent extraction (SX) to separate halides and metals from the zinc solution the process diagram is shown in Figure 5.8. The resulting purified electrolyte can fed to a conventional RLE process.

The SX stage is used to recover zinc from dirty secondary raw materials such as batteries. Other sources of zinc secondary materials include dusts and fumes from pyrometallurgical processes (e.g. copper smelters, steel electric arc furnaces, etc.); from combustion processes (e.g. domestic wastes incineration, spent tyres incineration, etc.); secondary zinc oxides from fuming processes like Waelz and Primus furnaces; etc.

**Achieved environmental benefits**
The SX technology can reduce the production of solid residues and liquid effluents. ~~Producing zinc from secondary raw materials uses about 20 % of the energy used by primary production.~~

**Cross-media effects**
None reported.

**Operational data**
Producing zinc from secondary raw materials uses about 20 % of the energy used by primary production.
*I do not understand if this is related to secondary Zn procuction in general or to the solvent extraction process.*

Table 5.56 and Table 5.57 show the expected composition and the consumption respectively of the main streams of the SX process being commissioned in Japan in 2010.

| Parameter | PLS | Acid rafinate | Loaded electrolyte |
|---|---|---|---|
| Flowrate $m^3$/h | 147 | 160 | 59 |
| Zinc g/l | 30 | 11 | 104 |
| Iron g/l | 0.05 | 0.01 | 0.004 |
| Magnesium g/l | 3.7 | 3.7 | 16 |
| Chloride g/l | 18 | 17 | 0.2 |
| Fluoride g/l | 1.8 | 1.7 | 0.01 |
| Cadmium mg/l | 0.7 | 0.6 | <0.001 |
| Copper mg/l | 2.6 | 2.4 | <0.001 |
| Calcium mg/l | 0.7 | 0.6 | 0.5 |

| | | | |
|---|---|---|---|
| Silicon dioxide mg/l | 0.2 | 0.2 | 0.2 |
| Aluminium mg/l | 0.8 | 0.7 | 0.1 |
| Manganese mg/l | 1.8 | 1.8 | 12 |
| Sulphuric acid g/l | | 31 | 127 |

**Table 5.56: Typical composition of the main SX process streams**
[ 327, Highlights and hurdles in Zinc production by solvent extraction 2008 ]

| Component | Consumption per tonne of zinc produced |
|---|---|
| Active charcoal kg | 0.9 |
| $D_2$EHPA kg | 1.0 |
| Kerosene kg | 5.0 |
| Demineralised water $m^3$ | 3 |
| Electricity kWh | 121 |

**Table 5.57: Main reagent and utilities consumption in the modified Zincex Process.**
[ 327, Highlights and hurdles in Zinc production by solvent extraction 2008 ]

**Applicability**
The process is applicable to purifying solutions of zinc produced from all secondary raw materials.

**Economics**
Operating costs for a plant in Japan are reported to be 25 to 75 $/t SHG zinc. The total investment costs for an SX plant were EUR 400 to 600 per tonne installed annual capacity for a plant producing 100000 t/yr SHG zinc.

**Driving force for implementation**
Reduced energy use, ability to treat a wider range of raw materials.

**Example plants**.
Japan, Spain.

**Reference literature**
[ 327, Highlights and hurdles in Zinc production by solvent extraction 2008 ].

#### 5.3.6.6 Use of flue gas desulphurisation in the lead/zinc industries

This technique is reported in Section 2.11.3.4.
*Where and to which process this should this be applied?*

### 5.3.7 Cadmium and other metals

The processes that were discussed earlier as available techniques are all techniques to consider in the determination of BAT. The specific feed materials will influence the final process choice and thallium separation practised. The techniques discussed in Chapter 2 should also be considered in conjunction with these processes. VOCs and odours may also be present during solvent extraction processes used for the production of Ga, Ge, etc.

### 5.3.8 Fume and gas collection and abatement

The techniques discussed in Sections 2.4.3 and 2.9 of this document for the removal of $SO_2$, VOCs, PCDD/F and dust are techniques to consider for the various process stages involved in the production of the metals in this group.

*What about the desulpurisation of secondary emissions as described in 2.11.3.6 for Bergöe, Sweden.*

### 5.3.8.1 Emissions of metals and other components

**Description**
The metal content of the dust varies widely between processes. In addition, for similar furnaces, there are significant variations due to the use of varying raw materials. It is therefore not possible to report specific achievable concentrations for all metals emitted to air in this document.

Low emission concentrations of metals are associated with the use of high performance, modern abatement systems such as a membrane fabric filter provided the operating temperature is correct and the characteristics of the gas and dust are taken into account in the design. Table 5.58 ~~and Table 5.55~~ give some indication of the ~~effects o~~metal~~n the~~ content ~~of metals in~~of dust that will be encountered from various processes. Table 5.59 shows some data about dust and metal emission concentration from various lead production stages.

There are several gases that can be produced by the processes in this sector, these are site-specific issues but the chemical treatment methods for gaseous components are shown in Table 5.60.

**Achieved environmental benefits**
The environmental benefits are the prevention of diffuse emissions of metals, dust and other compounds.

**Cross-media effects**
None are reported.

**Operational data**

| Component | Zinc fluidised bed roaster | Zinc refining | ISF process | Lead direct smelting processes | Secondary lead processes | Lead refining |
|---|---|---|---|---|---|---|
| Pb % | 0.2 - 2 | 0.15 - 0.86 | 10 - 15 | 30 - 50 | 20 - 55 | 14 - 83 |
| Zn % | 50 - 60 | 52 - 76 | 20 - 50 | 3 - 5 | 0.01 - 10 | 3 - 28 |
| Sb % | NA | NA | NA | - | 0.1 - 40 | NA |
| Cd % | 0.2 | 0.02 - 0.7 | 0.5 | 3 - 5 | 0.01 - 10 | NA |
| As % | 0.004 | 0.01 - 0.1 | NA | 5 - 10 | 0.01 - 3 | NA |
| NA - Means not available | | | | | | |

**Table 5.58: Metal content of dusts from various lead and zinc production processes**
[ 99, Hähre, S. 1998 ], [ 117, Krüger, J. 1999 ]

| Emission point | Dust ($mg/Nm^3$) | Pb ($mg/Nm^3$) | Cd ($mg/Nm^3$) |
|---|---|---|---|
| Main stack | 0.1 - 4.4 | 0.02 - 1.2 | <0.025 |
| Smelting furnace | 0.27 - 4.4 | 0.02 - 1.2 | <0.025 |
| Refining furnace | 0.006 - 0.5 | 0.0015 - 0.018 | <0.0001 |

**Table 5.59: Dust and m~~M~~etal emission con~~tent of other dusts~~centration from various lead production stages**
[ 234, UBA Copper, lead, zinc and aluminium 2007 ]

*Can't find them in [234]*
*The data are from→ [ 302, French Report on PM and HM 2007 ]*
*See Table 5.34: Dust, Pb and Cd emissions from French secondary lead production*

| **Reagent used.** | **Component in off - gas.** | **Treatment method.** |
|---|---|---|
| Solvents, VOCs, (for In, Ga, etc.) | VOC | Condensation. Activated carbon, Bio-filter |
| Chlorine, HCl (for In, Ga, etc.) | $Cl_2$ | Collection. Caustic scrubber system |
| Nitric Acid (for In, Ga, etc.) | $NO_X$ | Oxidise and absorb, recycle, scrubber system |
| Ammonia (for In, Ga, etc.) | $NH_3$ | Recovery, scrubber system |
| Antimony or arsenic oxides | Stibine or arsine | Oxidise and absorb in a scrubber system |

**Table 5.60: Chemical treatment methods for gaseous components**
[ 117, Krüger, J. 1999 ]

**Applicability**
The processes and the techniques are suitable for use with new and existing installations.

**Economics**
None was provided but the processes are operating economically.

**Driving force for implementation**
The reduction of emissions and saving raw materials.

**Example plants**
Plants in DE, AT, FR, BE, PL and NL.

**Reference literature**
[ 234, UBA Copper, lead, zinc and aluminium 2007 ], [ 99, Hähre, S. 1998 ], [ 117, Krüger, J. 1999 ].

### 5.3.8.2 Collection of fumes

**Description**
The use of secondary hoods is also a technique to consider. The design of the hooding system should take account of access for charging and other furnace operations and the way the source of process gases change during the process cycle [ 117, Krüger, J. 1999 ]. This can be achieved by using a system of intelligent control to target fume emissions automatically as they occur during the cycle without the high energy penalty of continuous operation.

The use of hoods for tapping and casting is also a technique to consider. Tapping fumes will consist mainly of oxides of the metals that are involved in the smelting process. An example of a co-incident hood for charging and tapping of a rotary furnace is shown in Figure 5.19.
*This is mentioned in the general chapter 2.4.5.1, 4.3.6.3 and in 6.3.3.1.. Either there or here. Avoid repetition.*

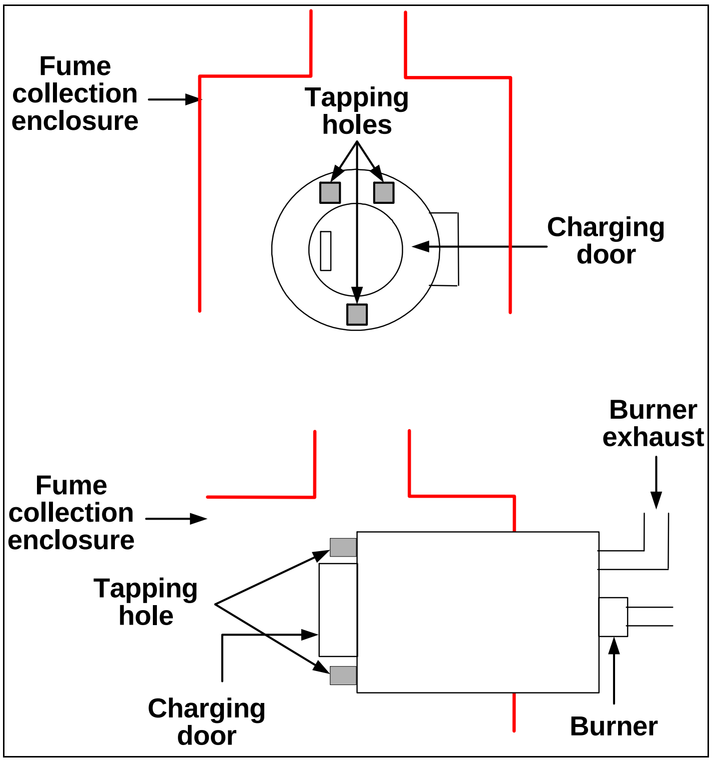


**Figure 5.19: Co-incident fume collection system for charging and tapping of a rotary furnace** [ 103, Farrell, F. 1998 ]
*This is called a diagram of an integral fume collection system in section 4.3.6.3*

Furnace lining wear may mean that door end tapping holes may not allow all of the metal to be tapped.

**Achieved environmental benefits**
Easier fume collection from a single point before treatment good collection efficiency with reduced power consumption.

**Cross-media effects**
No data has been reported.

**Operational data**
No data has been reported.

**Applicability**
This technique is applicable to all rotary furnaces.

**Economics**
There is a low cost of modification and several examples are operating viably.

**Driving force for implementation**
Fume and dust collection from diffuse emissions.

**Example plants**
France, UK, Germany

**Reference literature**
[ 103, Farrell, F. 1998 ], [ 117, Krüger, J. 1999 ]

## 5.3.9 Waste water

All waste water should be treated to remove dissolved metals and solids in some cases, a two-stage precipitation process is used with a hydroxide stage followed by a sulphide stage to ensure the removal of lead and cadmium [ 168, Steil, H.U. et al. 1999 ]. The techniques listed in Section 2.10 are the techniques to consider. In a number of installations, cooling water and treated waste water including rainwater is re-used or recycled within the processes.

#### 5.3.9.1.1 Treatment of weak acid, process effluent and groundwater

**Description**

One plant uses a biological process to produce sulphide ions. Weak acid which is the bleed from the wet gas-cleaning, has a high sulphate concentration (10 - 25 mg/l). The sulphate is reduced to sulphide ions with hydrogen gas and sulphate-reducing bacteria in a biological waste water treatment plant [ 320, Biologically produced Sulphide 2004 ].

$$SO_4^{2-} + 8H^{2+} \xrightarrow{SRB} S^{2-} + 4H_2O$$

The hydrogen is produced out of natural gas and steam in a reformer unit. The zinc and other metals react with $S^{2-}$ and precipitate as a metal sulphide.

$$Me + S^{2-} \rightarrow MeS$$

Sulphate and metal concentrations after this treatment are still too high to be discharged directly and the water is treated in another step together with other waste water from production and groundwater. This also uses sulphate-reducing bacteria to precipitate metals with sulphide, but in this case ethanol, is used as electron donor instead of hydrogen.

The metal sulphides and biomass slurry is re-used as concentrate in the roasting stage.

**Achieved environmental benefits**

The metal contents of the effluent of such a biological process are similar to those of the cleaned water of the best-performing waste water treatment based on inorganic sulphide addition (NaHS, $Na_2S$), mainly as the chemistry behind both processes is fundamentally the same (based on the low solubility of metal sulphides). The biological process has a positive effect because the sulphate content of the treated water is reduced but there are the significantly higher investment and operational costs [ 320, Biologically produced Sulphide 2004 ].

**Cross-media effects**

No data has been reported.

**Operational data**

Operational data is described in the description.

**Applicability**

The technique is applicable to weak acid where there are no other recovery options and for waste waters from the RLE process in admixture with contaminated groundwater.

**Economics**

No data has been reported but one plant s operating viably.

**Driving force for implementation**

Clean up of historical environmental problems.

**Example plants**

NL

**Reference literature**
[ 320, Biologically produced Sulphide 2004 ], [ 319, Biotechnology for Sustainable Hydrometallurgy 2003 ]

### 5.3.10 By-products, process residues and waste

The processes that were discussed earlier as available techniques are all techniques to consider in the determination of BAT. The specific feed materials will influence the final process choice but environmental pressures are causing companies to move away from using special lagoons for iron residues. Alternative techniques such as the Jarofix process, compacting or the recovery of zinc after the neutral leach stage in a pyrometallurgical process are being used [ 228, IZA plant data 2008 ]. The techniques discussed in Chapter 2 should also be considered in conjunction with these processes.

## 5.4 Best Available Techniques

In understanding this section and its contents, the attention of the reader is drawn back to the Preface of this document and in particular the fifth section of the Preface: ‘How to understand and use this document’. The techniques and associated emission and/or consumption levels, or ranges of levels, presented in this chapter have been assessed through an iterative process involving the following steps:

- identification of the key environmental issues for the sector which for the production of lead zinc and cadmium are dust, metal fume, VOCs (including PCDD/F), odours, $SO_2$, $NO_x$ , other acid gases, waste water, residues such as sludge, filter dust and slag;
- examination of the techniques most relevant to address these key issues;
- identification of the best environmental performance levels, on the basis of the available data in the European Union and worldwide;
- examination of the conditions under which these performance levels were achieved; such as costs, cross-media effects, and the main driving forces involved in implementation of the techniques;
- selection of the best available techniques (BAT) and the associated emission and/or consumption levels for this sector in a general sense, all according to Article 2(12) and Annex IV to the Directive.

Expert judgement by the European IPPC Bureau and the relevant Technical Working Group (TWG) has played a key role in each of these steps and in the way in which the information is presented here.

On the basis of this assessment, best available techniques, and as far as possible emission and consumption levels associated with their use, are presented in this section that are considered to be appropriate to the sector as a whole and in many cases reflect the current performance of some installations within the sector. Where emission and consumption levels “associated with best available techniques” are presented, this is to be understood as meaning that those levels represent the environmental performance that could be anticipated as a result of the application, in this sector, of the techniques described, bearing in mind the balance of costs and advantages inherent within the definition of BAT. However, they are neither emission nor consumption limit values and should not be understood as such. In some cases, it may be technically possible to achieve better emission or consumption levels but due to the costs involved or cross-media considerations, they are not considered to be appropriate as BAT for the sector as a whole. However, such levels may be considered to be justified in more specific cases where there are special driving forces.

The emission and consumption levels associated with the use of BAT have to be seen together with any specified reference conditions (e.g. averaging periods).

The concept of ‘levels associated with BAT’ described above is to be distinguished from the term ‘achievable level’ used elsewhere in this document. Where a level is described as ‘achievable’ using a particular technique or combination of techniques, this should be understood to mean that the level may be expected to be achieved over a substantial period of time in a well maintained and operated installation or process using those techniques.

Where available, data concerning costs have been given together with the description of the techniques presented in the previous sections. These give a rough indication about the magnitude of the costs involved. However, the actual cost of applying a technique will depend strongly on the specific situation regarding, for example, taxes, fees, subsidies, and the technical characteristics of the installation concerned. It is not possible to evaluate such site-specific factors fully in this document. In the absence of data concerning costs, conclusions on economic viability of techniques are drawn from observations on existing installations.

The BAT (including the associated emission and consumption levels) given in this section are 'BAT in a general sense' (i.e. considered to be appropriate to the sector as a whole). It is intended that they are a reference point against which to judge the current performance of an existing installation or to judge a proposal for a new installation. In this way, they will assist in the determination of appropriate 'BAT-based' conditions for the installation or in the establishment of general binding rules under Article 9([8]) of the IPPC Directive. It is foreseen that new installations can be designed to perform at or even better than the BAT levels presented in this section. It is also considered that existing installations could move towards the BAT levels presented in this section or do better, subject to the technical and economic applicability of the techniques in each case.

While the BAT reference documents do not set legally binding standards, they are meant to give information for the guidance of industry, Member States and the public on achievable emission and consumption levels when using specified techniques. The appropriate permit conditions for any specific case will need to be determined taking into account the objectives of the IPPC Directive and the local considerations.

**Recommendation to help users/readers of this document:**

It is strongly recommended that this section on BAT be read in conjunction with the sections of this document that describe the techniques to consider in the determination of BAT. The applicability of the techniques and measures are reported in these sections and should be taken into account at a local level. To help the reader, references to the appropriate sections are included in the description of BAT.

If not otherwise mentioned, BAT associated emission and consumption levels given in this section are expressed as follows:

- for pollutants emitted to air (except dioxins): expressed on a daily average basis with standard conditions of 273 K, 101.3 kPa, measured oxygen content and dry gas with the plant operating normally under steady-state conditions and no dilution of the gases;
- for dioxins: expressed as the average over the sampling period which should preferably be a minimum of 6 hours;
- for waste water: based on qualified random samples or 24 hour flow proportional composite samples.

As described in the Preface, this document does not propose emission limit values. The best available techniques and the ranges of emission or consumption levels associated with best available techniques (BAT-AEL ranges) are related to installations with different sizes, different kinds of operation and different raw materials. In this document, special local considerations cannot be taken fully into account. The determination of appropriate permit conditions will involve taking account of local, site-specific factors such as the technical characteristics of the installation concerned, its geographical location and the local environmental conditions. In the case of existing installations, the economic and technical viability of upgrading them also should be taken into account. Even the single objective of ensuring a high level of protection for the environment as a whole will often involve making tradeoff judgements between different types of environmental impact, and these judgements will often be influenced by local considerations.

Although an attempt is made to address some of these issues, it is not possible for them to be considered fully in this document. The techniques and emission and consumption levels presented here will therefore not necessarily be appropriate for all installations. On the other hand, the obligation to ensure a high level of environmental protection including the minimisation of long-distance or transboundary pollution implies that permit conditions cannot be set on the basis of purely local considerations. It is therefore of the utmost importance that the information contained in this document is fully taken into account.

Section 2.20 to this document reports BAT for the following common processes and the following sections should be referred to for those techniques that are BAT:

- environmental management systems (EMS) (Section 2.20.1)
- material handling and storage (Section 2.20.2)
- process control (Section 2.20.3)
- fume and gas collection (Section 2.20.4)
- the prevention and the destruction of PCDD/F (Section2.20.5)
- sulphur dioxide removal (Section 2.20.6)
- the removal of mercury (Section 2.20.7)
- effluent treatment and water re-use (Section 2.20.8)
- energy efficiency (Section 2.20.9)
- intermediate products, process residues and wastes (Section 2.20.10)
- emission monitoring (Section 2.20.11)
- prevention of the formation of $NO_X$ (Section 2.20.12)
- removal of dust and particles (Section 2.20.13)

BAT for the production of lead and zinc is the combination of the generally applicable techniques reported in Section 2.20 and the specific techniques indicated in this section.

## 5.4.1 Prevention and control of emissions to air

### 5.4.1.1 Primary lead smelting

**a) BAT is to prevent diffuse emissions and optimise the use of energy in primary lead smelting by using one of the techniques listed in Table 5.61 (see Section 5.3.3.1).**

| Technique | Raw Materials | Comments |
|---|---|---|
| Kaldo process<br>TBRC (totally enclosed) | Pb concentrate and secondary material (most grades) | Dry feed, variable sulphur dioxide. Operated in a complex installation with a Cu smelter |
| QSL | Pb concentrate and secondary material | Moist feed |
| Kivcet furnace | Cu/Pb concentrate and secondary material | Dry feed |
| Kaldo Furnace | Pb concentrate and secondary material | Moist, pelletised feed |
| Ausmelt/ISA Smelt Furnace | Pb concentrate and secondary material | Moist, pelletised feed |

**Table 5.61: BAT for primary lead smelters**

*What is the difference between Kaldo process and Kaldo furnace?*

**b) BAT is to prevent and control emissions of dust, metals and sulphur dioxide from the smelter gases produced during primary lead production using one of the techniques reported in Section 2.11.3.1.**

### 5.4.1.2 Lead refining processes

**a) BAT is to prevent diffuse emissions and recover other metals by using a combination of the following lead refining techniques (see Section 5.~~3.4.2~~1.3).**

*In section 5.3.4.2 nothing of all the following techniques is eincluded. How can one refer to this without including any information into the document????*

- Separation of copper as a sulphide dross.

- The removal of arsenic, antimony and tin by oxidation with a mixture of sodium nitrate and caustic soda, followed by mechanical skimming to remove the oxide dross. Air/oxygen can also be used.
- Desilvering by the Parkes process.
- The removal of zinc by vacuum distillation.
- The removal of bismuth by treatment with a mixture of calcium and magnesium in the Kroll-Betterton process.
- The separation of tin and lead from each other by vacuum distillation at high temperature.

**b) BAT is to prevent the formation of lead fume in the lead refining stage by controlling the temperature of the refining kettles to a maximum of 480° C and by using indirect heating (see Section 5.3.4.2).** *First of all this figure 480° C can not be found in section 5.3.4.2 and secondly this figure can not be found in the whole document!*

**c) BAT is to prevent and control emissions of dust and metals to air from the lead refining stage by using all of the techniques shown in Table 5.62.**

**The emission levels given in Table 5.62 are the BAT-AELs**

| Pollutant | Techniques | BAT-AELs | Comments |
|---|---|---|---|
| Dust | Fabric or ceramic filter,<br>Wet ESP for gases from slag granulation or wet gas quenching | <1 to 5 mg/Nm$^3$ | Dust should be monitored continuously with a bag burst detection system.<br>(See Sections 2.9.2.2.2, 2.9.2.2.4 and 2.20.13) |
| Metals | Fabric or ceramic filter<br>Wet ESP for gases from slag granulation or wet gas quenching | see Section 5.3.8.1 | The concentration of metals is linked to the concentration of dust and content of the metals in the dust (see Section 5.3.8.1) |
| NB: Collected emissions only. BAT-AELs are given as daily averages based on steady-state operation or, in cases where continuous monitoring is not practicable as the average over the sampling period. | | | |

**Table 5.62: BAT and BAT-AELs to prevent and control emissions to air from lead refining**

### 5.4.1.3 Primary zinc

**a) BAT is to prevent and control emissions of dust, metals and sulphur dioxide from the roaster gases produced during primary zinc production using one of the techniques reported in Section 2.11.3.1.**
*This is only for the primary emissions. What about secondary emissions?*

**b) BAT is to prevent and control emissions from the electrowinning cells by purifying the electrolyte for zinc production by using one of the techniques listed in Table 5.63 (see Section 5.1.5.2.4**[rr51]**).**

| Components removed | Techniques | Comments |
|---|---|---|
| Metals and halides | Solvent extraction<br>(see Section 5.1.5.2.3) | Can also be used to concentrate the electrolyte |
| Metals<br>(Cu, Ni, Co, Cd, Tl etc.) | Cementation and chemical treatment to remove metals<br>See Section 5.1.5.2.4) | Zinc powder, As or Sb oxides. barium hydroxide and dimethylglyoxime are used as reagents |

**Table 5.63: Techniques for electrolyte purification**

**The emission levels given in Table 5.64 are the BAT-AELs.**

**c) BAT is to prevent and control emissions of acid mists, arsine, stibine and VOC to air from the leaching, chemical refining, electrowinning and electrolyte purification stages of primary zinc production by using the techniques listed in Table 5.64 or a combination of them (see Section 5.3.5.7).** *(The cross reference to 5.3.5.7 is not correct. This section only deals with solvent purification but table 5.64 includes leaching, refining, electrowinning which are included in other sections in 5.3.5. )*

**The emission levels given in Table 5.64 are the BAT-AELs.**

| Pollutant | Techniques | BAT-AEL | Comments |
|---|---|---|---|
| Acid mists | Demister<br>Wet alkaline scrubber. | <10 – 35 mg/Nm³ | A demister will allow the collected acid to be re-used.<br>(See Section 5.3.5.9) |
| Arsine, stibine | Oxidising scrubber | <0.5 mg/Nm³ | Oxidising agent such as potassium permanganate (See section 5.3.5.6) |
| VOC as C | Containment, condenser, carbon or biofilter | <5 mg/Nm³ | (See Section 2.9.2.6) |
| NB: Collected emissions only. BAT-AELs are given as daily averages based on steady-state operation or, in cases where continuous monitoring is not practicable as the average over the sampling period. | | | |

**Table 5.64: BAT and BAT-AELs to prevent and control emissions to air from leaching, chemical refining, electrolyte purification and electrowinning**

*What about SO2 emissions from electrolysis. In Table 5.16 is mentioned that these emissions are significant.*

*As mentioned in Section 5.2.2 VOC occurs during roasting and sintering and casting.. I don't know if this is really valid for primary zinc production. I don't think it is a good idea to have one table for lead and zinc. VOC emissions are different from both plants. Emissions from roasting and sintering are both treated in sulphuric acid plants and thus the techniques mentioned under 5.4.1.3 are not applied for VOC treatment.*

*If these emissions occur and are being treated we need some examples in the techniques to consider section. A general crossreference to section 2.9.2.6 is not sufficient.Until now no values are included.*

### 5.4.1.4 Secondary lead and zinc

**a) BAT is to prevent diffuse emissions and optimise the use of energy in secondary lead smelting by using one of the techniques given in Table 5.65 for the raw materials that are available (see Section 5.3.3.2 and 5.3.6 and Section 5.1.2).**

| Technique | Raw Materials | Comments |
|---|---|---|
| Sealed submerged arc electric furnace | Cu/Pb materials | Sealed furnace, lower gas volumes. |
| Ausmelt/ISA Smelt. | Pb concentrate and secondary materials (most grades). | May be operated continuously or as a batch process including slag reduction |
| Rotary furnace | Most secondary materials. | Batch process, can offer flexibility for various materials. |
| QSL furnace | Pb concentrate and secondary material | Wide range of materials can be treated |
| TBRC (totally enclosed). | Secondary lead/copper material (most grades) | Operated in a complex installation with a Cu smelter. Tin and lead are separated by vacuum distillation. |
| Blast furnace. | Drained batteries | Suitable for coarse material, afterburner makes energy recovery possible. |
| Melting crucibles and | Clean lead and clean | Temperature control of kettles is needed. |

| | | |
|---|---|---|
| kettles | scrap only | |
| Imperial Smelting Furnace | Lead/zinc sulphidic concentrates and oxidic materials (Waelz oxide) on a campaign basis | Older technology which needs modern process control and fabric filters and efficient gas collection from the sinter plant. |

**Table 5.65: BAT for secondary lead smelters**

*The Imperial Smelting furnace is also used for zinc as indicated by the blue text in the last row. This should be included in the caption and the BAT itself.*

**b) BAT is to prevent and control emissions of dust, metals, sulphur dioxide, nitrogen oxides, TOC and PCCD/F to air and optimise the use of energy in secondary zinc production by using one of the techniques described in Section 5.3.6 with good process control, gas collection and abatement systems (see Section 5.3.6).** *(referring to 5.3.6 is not helpful because it includes 6 different processes)*

**c) BAT is to prevent and control emissions of dust, metals, sulphur dioxide, nitrogen oxides, TOC and PCCD/F to air from the materials pretreatment, secondary smelting, thermal refining, melting, slag fuming, Waelz kiln operation, the melting of clean material, alloying and zinc dust production in the lead and zinc sector by using the techniques shown in Table 5.66 or a combination of them (see Sections 5.3.3, 5.3.6, 2.9.2.4.1 and 2.9.2.4.2).** *(referring to 5.3.6 is not helpful because it includes 6 different processes)*

**The emission levels given in Table 5.66 are the BAT-AELs**

| **Pollutant** | **Techniques** | **BAT-AELs** | **Comments** |
|---|---|---|---|
| Dust | Fabric or ceramic filter<br>Wet ESP for gases from slag granulation or wet gas quenching | <1 to 5 mg/Nm$^3$ | A bag burst detection system should be used.<br>(See Sections 2.9.2.2.2, 2.9.2.2.4 and 2.20.13) |
| Metals | Fabric or ceramic filter<br>Wet ESP for gases from slag granulation or wet gas quenching | See Section 5.3.8.1 | The concentration of metals is linked to the concentration of dust and content of the metals in the dust (see Section 5.3.8.1) |
| $SO_2$ | Wet limestone or alkaline scrubber<br>Alkali semi-dry scrubber and fabric filter<br>Desulphurisation of battery paste | <50 to 400 mg/Nm$^3$ | (See Section 2.11.3.4)<br>What about 2.11.3.6????? |
| $NO_X$ | Low-$NO_X$ burner or<br>Oxy-fuel burner | <100 to 300 mg/Nm$^3$[rr52] | (See Sections 2.9.2.4.3, 2.20.12 and 5.2.2.2) |
| Total organic carbon as C | RTO, afterburner<br>Optimised combustion. | 1 – 10 mg/Nm$^3$ | Pretreatment of secondary material is needed to remove organic coatings.<br>(See Sections 2.9.2.6[rr53]) |
| PCDD/F | High efficiency dust removal or<br>Afterburner or RTO followed by quenching or<br>Absorption on activated carbon or<br>Carbon/lime injection. | <0.1 ng I-TEQ/Nm$^3$ | (See Sections 2.10.2.1, 2.20.5 and 5.3.3.6~~5.3.3.5~~[rr54]) |

NB: Collected emissions only. BAT-AELs are given as daily averages based on steady-state operation or, in cases where continuous monitoring is not practicable as the average over the sampling period. For PCDD/F, the BAT-AEL is the average over the sampling period which should preferably be a minimum of six hours.

**Table 5.66: BAT and BAT-AELs to prevent and control emissions to air from materials pretreatment, secondary smelting, thermal refining, melting, slag fuming, Waelz kiln operation, the melting of clean material, alloying and zinc dust production**

### 5.4.1.5 Cadmium and other metals

**a) BAT is to prevent and control emissions of dust and metals to air and optimise the use of energy in the recovery of cadmium and other metals by using a combination of the following techniques (see Section 5.1.10).**

- recovery from the flue dust from the gas-cleaning section that precedes the sulphuric acid plant by leaching with sulphuric acid and then stripping it from this liquor;
- cadmium cementate leaching in a sulphuric acid medium and electrowinning;
- recovery as cadmium chloride liquor in an ion exchange process followed by production of a cementate in an exchange reaction with high grade zinc;
- distillation at high temperatures or under vacuum followed by melting of cadmium with caustic soda and sodium nitrate to remove residual zinc.

### 5.4.1.6 Other process stages

**a) BAT is to prevent diffuse emissions and optimise the use of energy in other processes by using one of the techniques given in Table 5.67. (See Sections 5.1.2.1, 5.3.5.7 and 5.3.6.1).**

| Process Stage | Technique | Comments |
|---|---|---|
| Electrowinning | Permanent cathode, reduction of mist formation at the cell | Mist collection returns the acid to the process. |
| Zinc fuming | Slag fuming furnace and Waelz kiln (see Section 5.3.6). | Destruction of PCDD/F |
| Battery crushing | 2 stage process to allow stage separation and minimise contamination of plastic fraction | Collection and re-use of battery acid.<br>Collection of acid mists. |

**Table 5.67: BAT for other process stages**

## 5.4.2 Effluent treatment and water re-use

**a) BAT is to prevent and control emissions of metals, solids and oils/tars to waste water by using the techniques given in Section 2.20.8. (Also see Section 5.2.3)**

**The emission values given in Table 5.68 are the BAT-AELs.**

| BAT-AEL (mg/l) | | | | | |
|---|---|---|---|---|---|
| **Process** | **Pb** | **As** | **Hg** | **Cd** | **Zn** |
| Process water from a zinc process | <0.2 | <0.1 | <0.01 | <0.05 | <1.0 |
| Waelz oxide washing process | <0.2 | <0.1 | - | <0.1 | <1.0 |
| NB: BAT-AELs are based on qualified random samples or twenty four hour flow proportional composite samples. | | | | | |

**Table 5.68: BAT-AELs for emissions to water from lead and zinc processes**
*(But these values are just for zinc production, lead is not included)*

## 5.4.3 By-products, process residues and waste

Specific techniques for the lead and zinc sectors are given here. The specific feed materials that are available to the operator will influence the final process choice, particularly the way in which iron is precipitated. The use of a concentrate that contains low amounts of iron can minimise the quantity of iron residue that is produced [ 240, Nl Input on Zn production 2008 ] but this concentrate has very limited availability. Other techniques can be used to reduce or treat the iron residues [ 228, IZA plant data 2008 ].

**a) BAT is to re-use or recycle slags, slimes and filter dusts as far as possible in the processes or after leaching tests as construction material using the following techniques (see Sections 2.20.10 and 5.3.11). If recycling or re-use is not economically possible, secure disposal should be used.**

- re-use or recycle of slags, slimes and filter dusts as far as possible in the processes or after leaching tests as construction material;
- monitoring of the solubility of metals in the residue using a standard leachate test.

**b) BAT is to treat the iron residue produced during the roast-leach-electrowinning process for zinc production using the following techniques (see Sections 5.1.5.2.3, 5.3.5.1, 5.3.5.2, 5.3.5.3 and 5.3.5.4):**

- use of an iron precipitation method (goethite or jarosite) depending on the composition of the concentrate (see Section 5.1.5.2.3) and meet the requirements for the disposal area set out in the Landfill Directive.
- use of the Waelz kiln, zinc fuming, Jarofix or compaction processes or a low iron concentrate described in Section 5.3.5.1, Section 5.3.5.2, Section 5.3.5.3 and Section 5.3.5.4 to minimise the amount of iron residue for disposal and meet the requirements for the disposal area set out in the landfill directive.

## 5.5 Emerging techniques

- SX/EW system for zinc recovery of EAF dust has been reported.

*(Where can this be found? This abbreviation appears only here!*

- Leaching processes based on chloride for zinc and lead recovery are reported as being at the demonstration stage [ 202, Fundación Entorno, Empresa y Medio Ambiente 1999 ].

- The use of a plasma burner for secondary zinc materials.

- The thermal treatment of jarosite and goethite has been demonstrated in the Outotec process, [ 98, Lijftogt, J.A. et al 1998 ]. Zinc and other volatile metals are fumed off and recovered, the slag produced could be suitable for construction processes. The processes have not been shown to be economically viable as a general residue treatment method.

- The injection of fine material via the tuyères of a blast furnace has been successfully used and reduces the handling of dusty material and the energy involved in returning the fines to a sinter plant.

- The EZINEX process is based ammonia/ammonium chloride leaching followed by cementation and electrolysis. It was developed for the direct treatment of EAF dusts and one plant is operational. It may be used for richer secondary zinc feed [ 117, Krüger, J. 1999 ].

- The Outotec Flash Smelting Furnace has been used on a demonstration basis for the production of lead by direct smelting. The use of Waelz kilns for this purpose has also been reported. The literature contains many other potential examples that have not yet been developed beyond the pilot scale.

- Processes are being developed in order to optimise the recycling of batteries by treating only certain battery parts in a closed loop recycling. The known processes are all still in the development phase.

- A process to desulphurise lead battery paste using a solvent (amine)-based system has been developed on a pilot scale in Poland. The process avoids the use of sodium carbonate and the production of white slag. The process separates the acid/sulphate phase from the lead phase and clean gypsum is produced that is suitable for sale. The solvent is regenerated and there are no other wastes.

- The CLEP process is operated as a pilot plant in Italy. The process is the production of lead carbonate or oxide and sodium sulphate from spent battery paste in a wet process. There are no emissions to air and lead oxide is re-used in the production of battery paste.

- The application of reverse osmosis for the purification of used process and cooling water from lead production is under investigation in an industrial scale demonstration plant. The aim is the reduction of waste water to be disposed of, leading to a reduced emission of metals and a reduced demand for fresh water. The waste waters arising and the recovered metals are returned to the smelter.

- A process is investigated to recycle lead alloys and lead compounds from spent batteries and to produce new battery grids in a single process. The innovative technology is based on the coupling of an electrochemical dissolution process with a galvanic deposition process of lead and lead alloys in a single bath near room temperature. The technology is free of direct $CO_2$ emission and is claimed to be highly energy efficient because of the combination of two processes in only one electrochemical cell.

- The treatment of slags arising from pyrometallurgical zinc and lead production in a submerged arc furnace for recovery of zinc and lead and production of a useable and environmentally friendly slag is investigated.

- The recirculation of electric arc furnace dust within the fabric filter agglomerates the dust. This results in an increase in the Zn content of the dust collected in the baghouses.

# 6 PROCESSES TO PRODUCE PRECIOUS METALS

## 6.1 Applied processes and techniques

Precious metals can be conveniently placed into three groups; silver, gold and platinum group metals (PGMs). The most significant sources are precious metal ores, by-products obtained from the processing of other non-ferrous metals (in particular anode slimes from copper production, leach residues and crude metal from zinc and lead production) and recycled material. Many raw materials are subject to the Hazardous Waste Directive and this has an impact on the transport, handling and notification systems.

Production processes are common for primary and secondary raw materials and they are therefore described together. For a given refinery, the scale of operation reflects the relative quantities of each metal present. Typically there is much more silver and gold than PGMs.

A variety of processes have been developed which exploit the chemical properties of these metals. Although they are relatively inert, their reactivity varies and the various oxidation states of the metal in their compounds allows a variety of separation techniques to be used [ 5, B R Lerwill et al. 1993 ], [ 18, HMIP (UK) 1994 ]. For example, the tetroxides of ruthenium and osmium are volatile and can be separated easily by distillation. Many of the processes use very reactive reagents or produce toxic products, these factors are taken into account by using containment, fail safe systems and sealed drainage areas. This is further driven by the high value of the metals.

Many of the processes are commercially confidential and outline descriptions only are available. The processes are usually carried out in various combinations to recover the precious metals that are present in a particular feedstock. The other feature of the industry is that generally, the precious metals are recovered on a toll basis, which can be independent of the metal value. Much of the processing is therefore designed to accurately sample and assay the material as well as recover it. Sampling is carried out after the material has been processed physically or from side-streams during normal processing. There are over 200 types of raw materials available to the industry and they are normally characterised into five homogenisation ~~types~~ categories as shown in Table 6.1.

| Homogenisation category | Type of raw material | Comment |
|---|---|---|
| Original | Catalysts, prepared sweeps, solutions~~.~~ | Direct to process |
| Sweeps | Mineral + metal, non-fusible carbon catalysts | Incineration, roasting and pre-enrichment |
| Scrap | Fusible material | |
| Material to be shredded | Photographic material~~Film~~, electronic scrap | |
| Materials for dissolution | Material that is dissolved in acid, CN, NaOH, etc~~.~~*(does this mean dissolved in HCN, dissolved in NaOH?)* | |

**Table 6.1: Homogenisation categories for sampling**
[ 18, HMIP (UK) 1994 ]
*Either insert comments for all raw materials or delete this column.*

The raw material characterisation is based on the most suitable ~~-~~entrance point into the processing flow sheet (see Figure 6.1) and is independent of the precious metals that the material contains. The raw materials are usually sampled according to this characterisation and it is reported that most companies use this scheme. The samples are subject to treatment to dissolve the precious metal content or produce a form capable of analysis. Some times this involves all or part of the actual recovery process and so abatement systems are used during the sampling process.

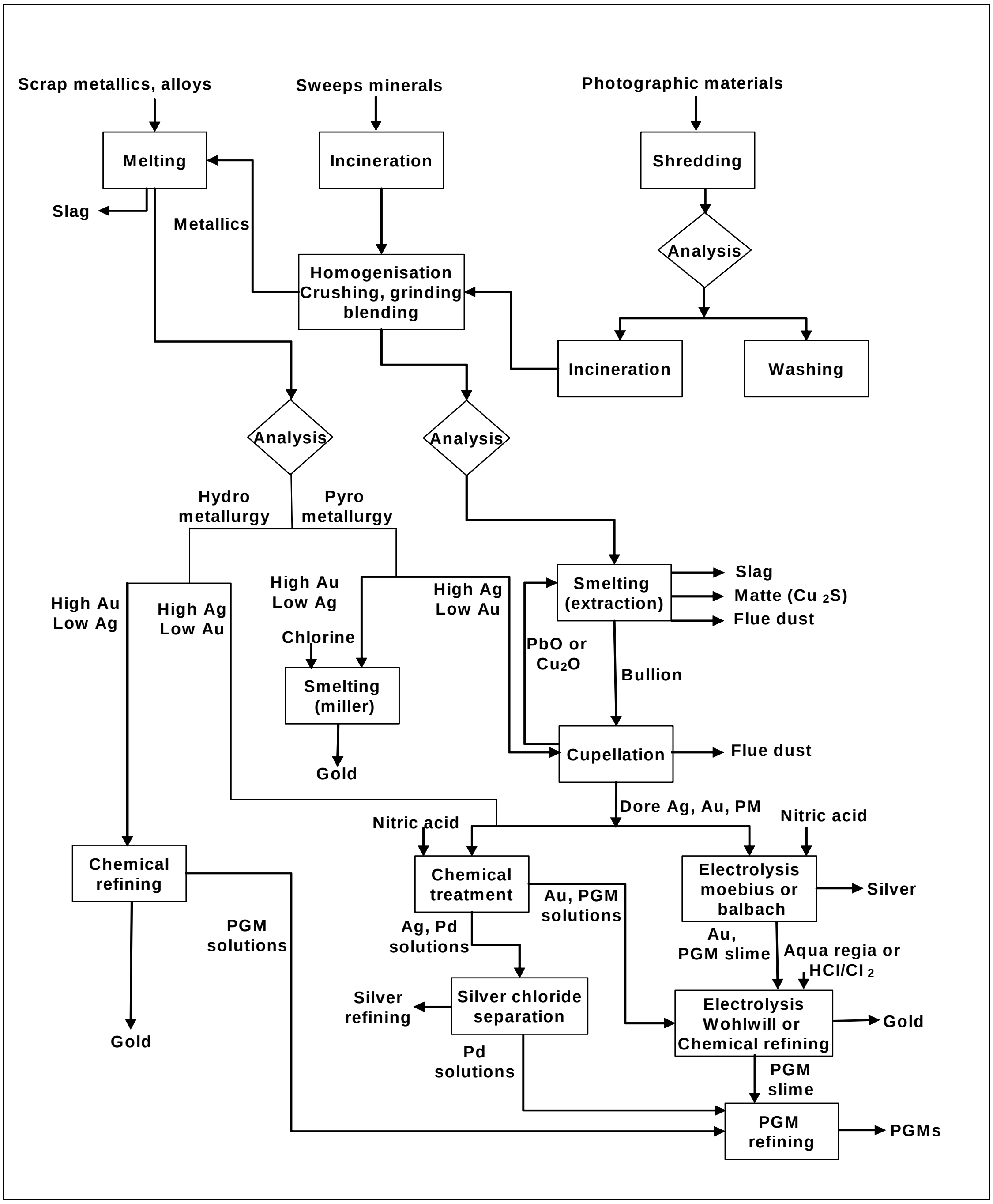


**Figure 6.1:** **Example of a general flow sheet for precious metal recovery**

*In Section 6.1.2.1 is explained that the product s either gold or anodes consisting of 98% gold which are further processed and electrorefined. This should be introduced in the flow chart.*

There is also a need to process these materials rapidly and this is reflected in the intentional over capacity of production in this sector. The extensive sampling and analysis also allows the optimum choice of process combinations to be made.

Anode slimes from electrolytic copper refining are a significant source of precious metals and they are treated to remove and recover the precious metals together with other metals such as selenium and tellurium. The process details depend on the proportion of metals that are present. Pyrometallurgical or hydrometallurgical routes are used and solvent extraction stages are also incorporated in some cases~~,~~. Figure 6.2 gives as a general example the flow sheet for anode slime treatment.

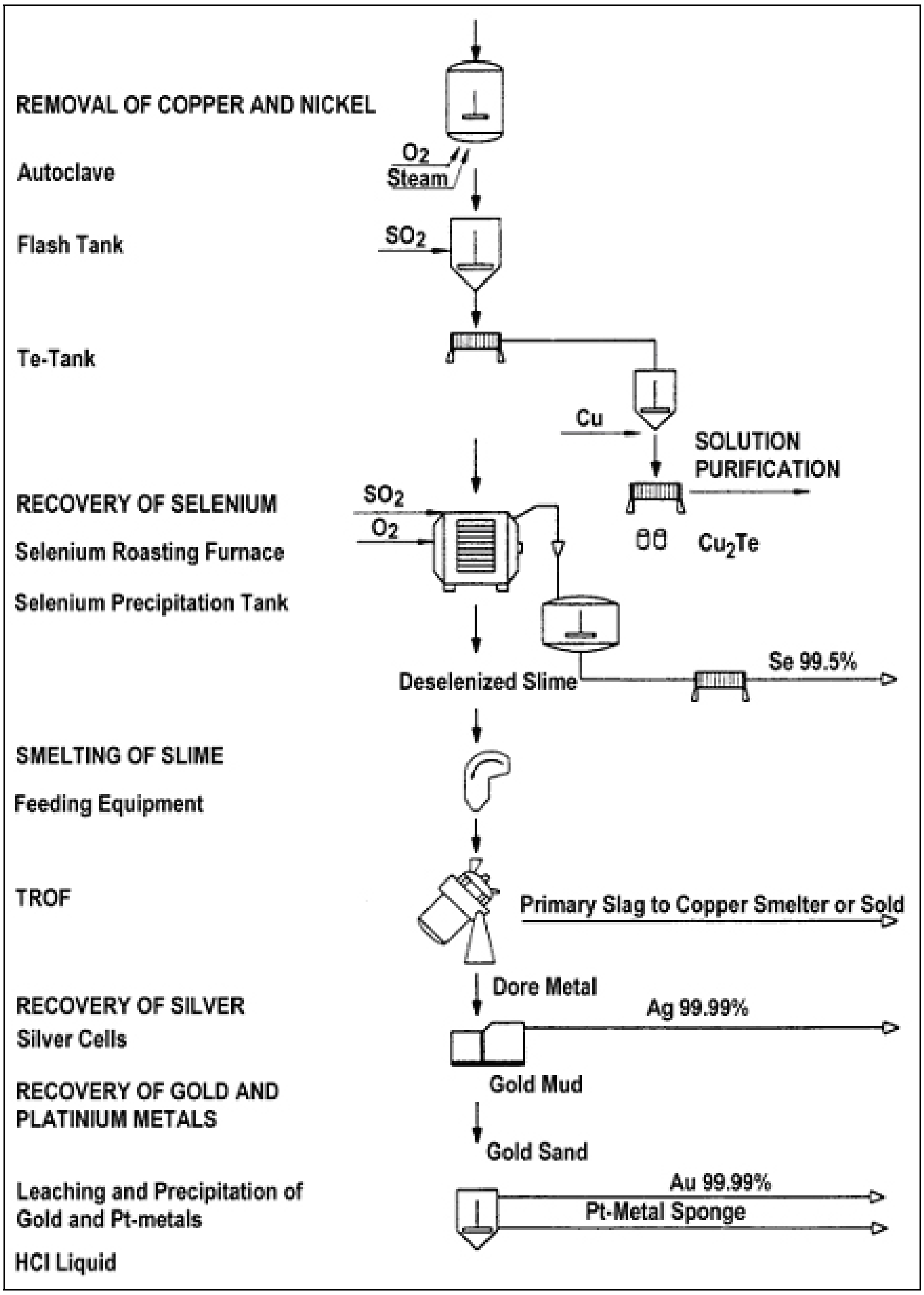


**Figure 6.2: Example flow sheet for anode slime treatment**

## 6.1.1 Silver

The principal sources of silver are scrap (e.g. jewellery, coins and other alloys) concentrates, anode (or tank house) slimes, photographic ~~films~~materials, papers and sludges, and ashes, sweeps as well as other residues [ 102, Hasenpusch, W. 1998 ], [ 5, B R Lerwill et al. 1993 ], [ 18, HMIP (UK) 1994 ].

#### 6.1.1.1 Photographic materials

Photographic film, papers and sludges are incinerated on a batch basis in single hearth furnaces, or on a continuous basis in rotary kilns, to produce a silver-rich ash. Smaller recyclers use box furnaces. The calorific value of the feed is such that fuel is only required during start-up. A fired afterburner, located in a separate chamber, is used to combust the partially burned products in the waste gas as well as filter and caustic scrubber systems. The ash is recovered and treated with other silver-bearing material, the gases are filtered and the dust that is collected is also treated to recover silver.

A chemical stripping process in which the silver salts are leached from the emulsion layer is also used. This process treats waste photographic film with a thiosulphate solution that can also contain enzymes. The silver is recovered from the leach liquor by electrowinning and the depleted electrolyte is recycled to the leaching stage. The plastic backing of the photographic film can be recovered in theory but the feed material usually includes quantities of paper such as envelopes and this can inhibit recovery and results in a waste stream [ 5, B R Lerwill et al. 1993 ].

Silver is also recovered from waste solutions from the photographic and other industries by chemical precipitation as sulphide to form a powder which is dried, melted and refined.

~~Alternatively, silver thiosulphate solutions are electrolysed at two volts to produce silver sulphide, which is insoluble (in practice, 5 - 10 ppm Ag in solution is achieved).~~*Doesn't this belong to the second last paragraph ?*

#### 6.1.1.2 Ashes, sweeps, etc.

Ashes, sweeps, printed circuit boards, agglomerated fines, sludges and other materials that contain copper and precious metals are blended and smelted in Ausmelt/ISA Smelt, electric, blast, rotary and reverberatory furnaces or top blown rotary converters (TBRC). Lead or copper is used as a collector for the silver and other precious metals; electric power, coke, gas or oil are used as fuel and to generate a reducing atmosphere. In some cases, selected plastic waste can be used as a fuel or a reducing agent and in these cases appropriate afterburning is used to prevent the emission of organic compounds such as VOCs and PCDD/F. Fluxes are added to collect the non-metallic components of the feed materials, which are removed as a slag. Periodically the furnace is run with a slag charge to recover any precious metals in the slag before it is granulated or cast prior to disposal, treatment for depletion or use.

The silver and other precious metals produced in the smelting furnace are collected into molten lead or copper. The lead alloy is transferred to a cupellation furnace where the lead is oxidised to litharge (lead oxide) using air or oxygen. The copper alloy is treated in a similar manner as that used to produce copper oxide [ 102, Hasenpusch, W. 1998 ].

These precious metal-bearing materials may also be treated in base metal smelters. The metals are then recovered from the lead, Cu or Ni processes.

#### 6.1.1.3 Recovery from base metal production

The electrolytic refining of copper anodes produces slimes whose composition is dependent on the feed materials and processes used in the copper smelter. Anode slimes generally contain significant quantities of silver, gold and PGMs and they are sold for their precious metals values [ 46, Dr. M. Guindy 1996 ], [ 47, Järvinen, O 1995 ], [ 48, Järvinen, O 1994 ], [ 49, Hyvärinen, O. et al. 1989 ] or recovered at the site of the smelter [ 90, Traulsen, H. 1998 ].

Treatment processes vary according to the composition of the slimes, an example is shown above in Figure 6.2 which includes the recovery of selenium. The stages can include the removal of copper and nickel (and a major portion of tellurium) by acid leaching (atmospheric or under pressure using $O_2$), or roasting to remove selenium unless it has been removed by volatilisation during smelting. In some cases, lead residues are produced which are recovered from dedicated lead processes. Smelting is carried out with silica and sodium carbonate fluxes to produce Dore metal in reverberatory, electric, Kaldo, TBRC or bottom blown oxygen cupel (BBOC) furnaces. Dore (silver or gold) is metal that has been concentrated to a form that contains more than 60 % of the metal [ 102, Hasenpusch, W. 1998 ]. Hydrometallurgy and solvent extraction stages are also used for the recovery of precious metals from anode slimes for example the Kennecott and Phelps Dodge processes.

In the hydrometallurgical production of zinc, the precious metals, if present in the concentrate are enriched in the Pb/Ag leach residue, which can be processed further in a lead smelter. During lead smelting and refining, the precious metals are concentrated in a Pb-Zn-Ag alloy (see Figure 6.3).

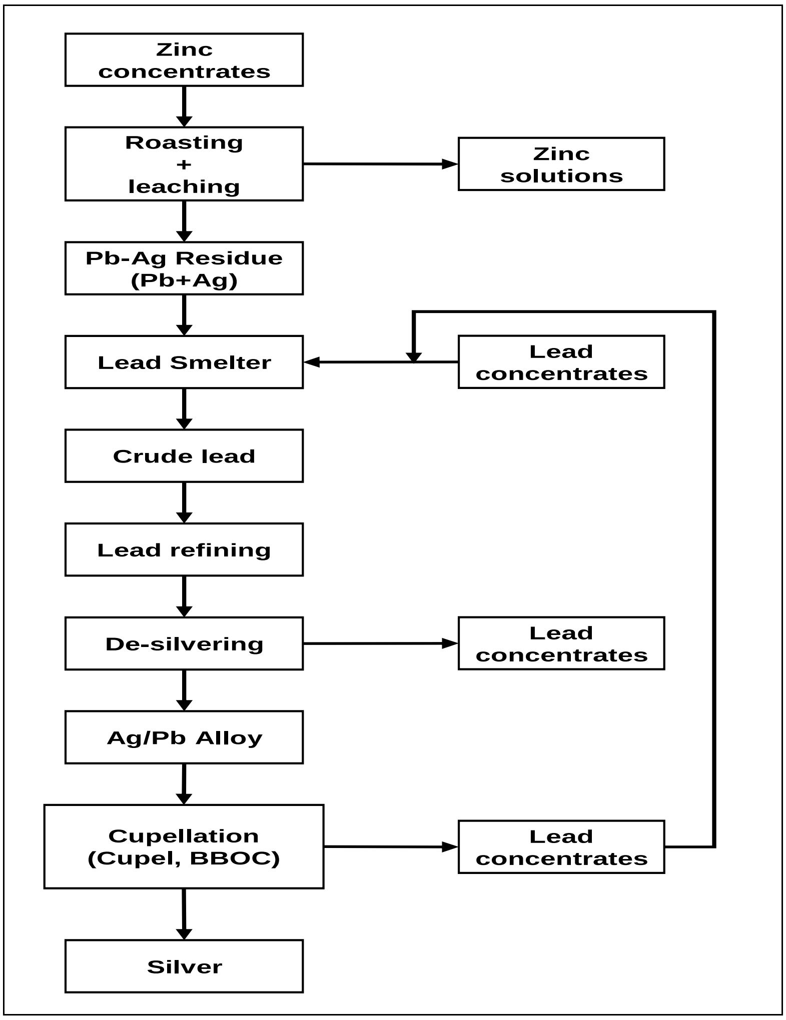


**Figure 6.3: Recovery of silver from zinc and lead production**

Further treatment can include the removal of the bulk of the lead and zinc by liquation and vacuum distillation and finally cupellation in a reverberatory furnace, TBRC, TROF, cupel or a BBOC. Lead is oxidised to litharge (lead oxide) using air and oxygen. Some installations that operate copper and lead refineries combine the precious metal-enriched phases from the lead and copper lines during the cupellation stage.

In the refining of nickel, the precious metals are recovered from the copper by-product. In the refining of zinc in a zinc-lead shaft furnace, the precious metals may be recovered from the lead product. Precious metal recovery processes vary according to the amount of desired metals and other associated metals, e.g. selenium.

#### 6.1.1.4 Refining

The anodes[r55] are refined in Moebius or Balbach-Thum electrolytic cells using titanium or stainless steel cathodes in an acidified silver nitrate electrolyte. A direct current applied between the electrodes causes silver ions dissolved from the anode to migrate and deposit as crystals of silver on the cathodes. The crystals are continuously scraped off the cathodes, removed from the cells, filtered and washed. The slimes from the electrolytic cells are treated for their gold and PGM content.

The silver crystals may be melted in a crucible furnace and batch cast into market ingots or grains for rolling down. They can be continuously cast into market bars for rolling down to sheet and strip. Silver is also cast into billets for extrusion into rods for subsequent drawing into wire.

Silver produced by smelting, and high-grade silver residues from manufacturing processes can be further refined by dissolution in nitric acid. The resulting solution is purified either by recrystallisation as silver nitrate suitable for use in the photographic industry or by electrolysis to fine silver for melting and casting into bullion bars.

### 6.1.2 Gold

The principal sources of gold are impure gold from mining operations, industrial, jewellery, sweeps and dental scrap. Gold is recovered along with silver from the anode slimes from copper electrorefining and other materials using processes described above. Gold is present in the anode slimes from the silver electrolysis stage and is recovered by leaching the slimes with hot hydrochloric acid and chlorine gas and is then precipitated from the solution [ 282, KGHM 2008 ]. Scrap materials may contain significant proportions of zinc, copper and tin.

#### 6.1.2.1 The Miller process

The Miller process can be used to pretreat the material. In this process, the feed materials are melted in an indirectly heated crucible or electric induction furnace while chlorine gas is injected into the melt. At the operating temperature of about 1000 ºC, gold is the only metal present that does not react to form a stable- molten or volatile chloride. Molten silver chloride rises to the surface of the melt. A borax flux is used to assist collection and skimming of the metal chlorides. Zinc in the feed is converted to zinc chloride which, together with volatile metal chlorides, is exhausted to a gas scrubbing system [ 5, B R Lerwill et al. 1993 ], [ 102, Hasenpusch, W. 1998 ].

The Miller process is operated to produce either 98 % gold, which is cast into anodes for electrorefining, or 99.5 % gold that is cast into bullion bar.

#### 6.1.2.2 Electrorefining

Gold anodes are refined in Wohlwill cells that contain gold foil or titanium cathodes. The electrolyte used is an acidic gold chloride solution maintained at about 70 °C. A D.C. electric current applied between the electrodes causes gold ions dissolved from the anodes to migrate and deposit on the cathodes yielding a product that contains 99.99 % gold. Chlorine is evolved at the anode and is collected in an integral enclosure.

### 6.1.2.3 Other processes for gold recovery

Gold is also recovered and refined by dissolving the feed materials in aqua regia or in hydrochloric acid/chlorine. This is followed by the precipitation of high purity gold suitable for melting and casting. Where the feed material contains significant quantities of metallic impurities, a solvent extraction step may be introduced before the gold precipitation stage. Solvent extraction processes and precipitation are also used to recover gold from liquors arising during the production of platinum.

Gold is also removed from solid and[r56] liquid cyanide solutions such as plating baths. Solutions of sodium or potassium cyanide can be used to remove gold from surface coated material such as electronic contacts or plated materials. Gold is recovered from the cyanide solutions by electrolysis. Cyanides react with acids to form HCN and therefore careful segregation of these materials is practised. Oxidising agents such as hydrogen peroxide or sodium hypochlorite as well as high temperature hydrolysis are used to destroy cyanides.

## 6.1.3 Platinum group metals (PGM)

PGMs comprise platinum, palladium, rhodium, ruthenium, iridium and osmium. The principal raw materials are concentrates produced from ores, mattes and slimes from nickel and copper operations. Secondary materials such as spent chemical and auto exhaust catalysts, electronic and electrical component scrap are also significant sources. PGMs can be present in the anode slimes described above and are separated from the gold and silver by a variety of hydrometallurgical processes. Low grade feedstock may be crushed and blended while metallic feed materials are generally melted to provide a homogeneous product for sampling.

The main stages in the recovery of PGMs are [ 102, Hasenpusch, W. 1998 ], [ 5, B R Lerwill et al. 1993 ], [ 18, HMIP (UK) 1994 ]:

- pretreatment of the feedstock, sampling and assay~~;~~
- concentration and separation of PGM. by pyrometallurgical and hydrometallurgical techniques such as chemical precipitation, chemical dissolution, liquid/liquid extraction, distillation of tetroxides, ion exchange and electrolytic processes~~;~~
- pyrolysis or reduction of metallic chloro compounds to pure metal sponges.

Specific processes have been developed for carbon-based catalysts, using incineration prior to the dissolution stage. Powder-based catalysts and sludges are treated in batches, often in box section furnaces. Direct flame heating is applied to dry and then ignite the catalyst that is allowed to burn naturally. The air ingress to the furnace is controlled to modify the combustion conditions and an afterburner is used.

Reforming or hydrogenation catalysts can be treated by dissolution of the ceramic base in sodium hydroxide or sulphuric acid. Prior to leaching, the excess carbon and hydrocarbons are burnt off. PGMs from automotive catalysts can be collected separately in Cu or Ni in plasma, electric or converter furnaces [ 102, Hasenpusch, W. 1998 ]. Small operators use open trays to burn off catalysts by self-ignition or roasting, these processes can be dangerous and fume collection and afterburning can be used to treat the fume and gases.
Organic-based homogenous spent catalysts from, e.g. chemical or pharmaceutical industries can be treated by distillation and precipitation. The gaseous emissions are treated in an afterburner.

PGM refining is complex and individual process stages may have to be repeated to achieve the required purity. The number and order of the stages also depends on the contaminants to be removed and the specific mix of PGMs to be separated from any one batch of feedstock. The processing of secondary materials such as spent chemicals and auto catalysts, electrical and electronic scrap in base metal smelters or specific equipment finally produces PGM-rich residues or precipitates.

## 6.2 Current emission and consumption levels

*Can we create a mass stream overview for the PM sector?*

Precious metal refineries are complex networks of main and subsidiary processes. The raw materials used vary greatly in quality and quantity and therefore the equipment used has a variety of capacities and uses. Multi-purpose reactors and furnaces are used extensively and processing steps are often repeated. It is therefore not possible to identify single process steps and their contribution to emissions and consumption.

Some general principles apply to the emissions and consumptions of this sector:

- On average a 10-fold quantity of material should be treated to isolate precious metals. The concentrations vary from <1 % to nearly pure metal.
- High-energy techniques are used, e.g. ~~Electric~~ electric furnaces. Energy recovery is practised if appropriate.*Examples are needed!!*
- Residues that contain base metals are sold for recovery.
- Many chemical treatments involve the use of cyanide, chlorine, hydrochloric acid and nitric acid. These reagents are re-used within the processes but eventually require oxidation or neutralisation with caustic soda and lime. Sludges from waste water treatment are closely monitored for metals and are recovered if possible.
- A variety of organic solvents are used for liquid-liquid extraction.
- A variety of oxidising and reducing agents are used.
- Acid gases such as chlorine or nitrogen oxides are recovered for re-use.
- Gas volumes vary greatly between cycles. The small scale of the processes usually allows for good containment. Local exhaust ventilation is used.

*Most of what is mentioned above is to general and should be deleted.*

### 6.2.1 Material loops in the precious metal recycling industry

*Reconsider if and where these material loops should appear.*
One of the characteristics of the PM industry is the need to keep solution volumes small to diminish the losses of precious metals or their compounds. Consequently there are several closed cycles in operation to reclaim materials and these are shown below.

#### 6.2.1.1 The non-metallic cycles

Hydrochloric acid and nitric acid are mainly used for the dissolution of metals. Sulphuric acid is used to a lesser extent as part of scrubber solutions for ammonia absorption and electrolyte in silver powder baths. Other materials are used as reagents or are present in the feed materials [ 102, Hasenpusch, W. 1998 ].

a) The hydrochloric acid loop
For processes involving dissolution, hydrochloric acid, HCl, is used in combination with excess chlorine. By using evaporation and collection in water, an azeotropic acid (in concentrations of about 20 wt-% ~~w/w~~) is obtained. This is used in different parts of the refinery.

b) The nitric acid loop
Silver and palladium are often dissolved in nitric acid, $HNO_3$. A significant quantity of nitrogen oxide off-gases (NO and $NO_2$) can be captured with oxygen or hydrogen peroxide in special scrubber cascades. The long residence time needed to oxidise small quantities of NO and the reduction of gas absorption by exothermic reactions can produce problems. Therefore cooling and combined scrubbers are necessary to reach the limit values and avoid brown fumes from the stack. The resulting nitric acid from the first scrubber usually has concentrations of about 45 wt-% ~~w/w~~ and can be re-used in several processes.

c) The chlorine loop
Chlorine is used in wet processes to dissolve metals and in dry chlorination steps at elevated temperatures to refine them. In both cases, closed systems are used, e.g. using U-tubes with water to produce hypochlorite solutions. Hypochlorite is also used as an oxidising agent in scrubber solutions for various refining processes.

d) The ammonium, sodium or potassium chloride loop
Ammonia and ammonium, sodium or potassium chloride are used in the recovery of PGMs. The relatively small solubility of ammonium chloride, $NH_4Cl$, in evaporated solutions at room temperature makes it possible to re-use crystalline precipitates of this salt.

e) The alumina loop
Heterogeneous catalysts based on alumina, $Al_2O_3$, are treated in the PM refineries in large quantities for example the reforming catalysts from the oil refining industry. The catalysts are dissolved in caustic soda above 200 °C under pressure and the resulting aluminate solution is sold after separation of the PM as a precipitation aid in water treatment. Alternatively it can be returned to the alumina industry via the BAYER process (dissolution of bauxite). Similar external cycles are possible with aluminium sulphate solutions, which result when the catalysts are dissolved in sulphuric acid.

### 6.2.1.2 The non-PM loops

PM refineries process a lot of materials that contain copper, lead, tin, tungsten, rhenium, cadmium, mercury and other special metals. For the separation of all these metals special processes are established which produce concentrates for external non-PM metallurgical plants [ 102, Hasenpusch, W. 1998 ].

a) Copper
The use of copper as the carrier material for precious metals is becoming more important and copper oxides remain after smelting processes. In hydrometallurgical stages, copper can be precipitated by caustic soda, NaOH, and/or lime, CaO. Copper residues can be recovered in a copper refinery or converted to the sulphate and electrowon if the volume justifies it.

For removing traces of copper, especially in the presence of chelates like ammonia, precipitation with sulphides or mercapto compounds (e.g. TMT 15, a 15 wt-% solution of trimercaptotriazine) is necessary.

b) Lead
Lead cycles have been known since the middle ages in the refining of silver. The process is still used in the sweep extraction. Liquid lead is a good solvent for the PMs, especially in an excess of silver. The PM-enriched lead is oxidised in furnaces or converters by oxygen, producing a nearly quantitative separation of lead and other non-PMs. The resulting oxides are reduced by carbon, e.g. in a blast furnace, and lead is produced and is used again in the process. Excess lead is sold to lead refineries.

c) Tin
Tin is separated as the metal in solution or as a hydroxide precipitate.

d) Tungsten and other metals
For some metals coming from galvanic processes, the base metals such as nickel alloys, tungsten and molybdenum can be recycled by cyanide stripping.

e) Rhenium
For rhenium, ionic exchangers are used. After purification and precipitation the ammonium salt, $NH_4ReO_4$ is produced.

f) Cadmium
The cadmium concentration of special alloys, e.g. solders and brazes has decreased over the last years. Cadmium is enriched in flue dusts of special campaigns and sent to external metallurgical plants.

g) Mercury
Mercury may form part of some special materials in small concentrations, e.g. dental amalgam, powders or slimes, residues from battery plants and special Polaroid films. For this kind of material, high temperature distillation, perhaps combined with low vacuum, is the first step of recovery. Average concentrations of the distilled scraps and sweeps are less than 0.1 wt-% ~~w/w~~ of mercury concentration limits.

These loops and the separation of non-PM compounds contribute to the avoidance of contamination and optimisation of profitability.

## 6.2.2 Environmental issues for the precious metal production processes

Precious metal production processes are primarily a source of particulate and gaseous emissions to air and emissions to water. Generally, the information given in Section 6.2.2.1 to 6.2.2.3 below describe the most relevant environmental issues for precious metals production.

### 6.2.2.1 Emissions to air

The sources of emissions ~~from the process~~ are:

- incineration
- other pretreatment
- smelting and melting furnaces
- leaching and purification
- solvent extraction
- electrolysis
- final recovery or transformation stage.

The main emissions to air from precious metal production are:

- sulphur dioxide ($SO_2$) and other acid gases (HCl)
- oxides of nitrogen ($NO_X$) and other nitrogen compounds
- metals and their compounds
- dust
- chlorine
- ammonia and ammonium chloride
- VOCs and PCDD/F.

Odour may be present as a result of some of the compounds listed above. The relevance of potential ~~the~~ ~~substances~~ emissions to air~~emitted~~ from the major sources in precious metals production is given in Table 6.2. ~~,~~ ~~Table 6.3 and Table 6.4.~~

| Component | Incineration or smelting | Leaching and purification | Electrolysis | Solvent extraction | Distillation |
|---|---|---|---|---|---|
| Sulphur dioxide and HCl | •• | • | • | | |
| VOC | • | ••• | | ••• | ••• |

| | | | | | |
|---|---|---|---|---|---|
| PCDD/F | •• | | | | |
| Chlorine | | ••• | •• | | |
| Nitrogen oxides | •• | •• | | | |
| Dust and metals | •••([1]) | • | • | • | • |

NB: ••• More significant – • less significant
([1]) Diffuse or non-captured emissions are also relevant for these sources.
*Source: [ 527 ]*

**Table 6.2: ~~Significance~~ Relevance of potential emissions to air from major sources in precious metals production**

| ~~Installation~~ | ~~Production (tonnes)~~ | ~~Dust (kilograms per tonne of metal)~~ | ~~Nitrogen oxides (kilograms per tonneof metal)~~ | ~~Sulphur dioxide (kilograms per tonne of metal)~~ |
|---|---|---|---|---|
| ~~A~~ | ~~2155~~ | ~~58~~ | ~~154~~ | ~~232~~ |
| ~~B~~ | ~~1200~~ | ~~4.5~~ | ~~68~~ | ~~3.1~~ |
| ~~C~~ | ~~2500~~ | ~~2~~ | ~~7~~ | ~~9~~ |
| ~~D~~ | ~~1110~~ | ~~18~~ | | |
| ~~C~~ | ~~102~~ | ~~127~~ | ~~21~~ | |

~~**Table 6.3: Emissions to air from a range of precious metal production processes**~~
~~[ 282, KGHM 2008 ], [ 238, ECI Copper Installations 2008 ]~~

| ~~Parameter~~ | ~~Incineration processes~~ | ~~Pyrometallurgical processes~~ | ~~Hydrometallurgical processes~~ |
|---|---|---|---|
| ~~Production range~~ | ~~200 – 1000 kg/d~~ | ~~150 – 1200 t/yr~~ | ~~20 – 600 t/yr~~ |
| ~~Dust mg/Nm$^3$~~ | ~~2 – 10~~ | ~~4 – 10~~ | |
| ~~Nitrogen oxides mg/Nm$^3$~~ | ~~50 – 150~~ | ~~~200~~ | ~~1 – 370~~ |
| ~~Sulphur dioxide mg/Nm$^3$~~ | ~~1 – 25~~ | ~~10 – 100~~ | ~~0.1 – 35~~ |
| ~~CO mg/Nm$^3$~~ | ~~10 – 50~~ | ~~80 – 100~~ | |
| ~~Chloride mg/Nm$^3$~~ | ~~2 – 5~~ | ~~<30~~ | ~~0.4 – 5~~ |
| ~~$Cl_{2\ mg}$/Nm$^3$~~ | | ~~<5~~ | ~~2 – 5~~ |
| ~~Fluoride mg/Nm$^3$~~ | ~~0.03 – 1.5~~ | ~~2 – 4~~ | |
| ~~TOC mg/Nm$^3$~~ | ~~2 – 5~~ | ~~2 – 20~~ | |
| ~~PCDD/F ng ITEQ/Nm$^3$~~ | ~~<0.1~~ | ~~<0.1~~ | |
| ~~HCN mg/Nm$^3$~~ | | | ~~0.01 – 2~~ |
| ~~$NH_{3\ mg}$/Nm$^3$~~ | | | ~~0.2 – 4~~ |

~~**Table 6.4: Emissions to air from a range of small processes**~~
~~[ 161, Bobeth, A. 1999 ]~~

## ~~6.2.2.1~~6.2.2.1.1 Dust and metals

Dust and metals can generally be emitted from any pyrometallurgical process such as incinerators, smelting, melting and cupellation furnaces ~~and cupels~~ as diffuse or collected and abated emissions. Furnace sealing and secondary collection from launders is an important factor in preventing diffuse emissions. Some electric furnaces use hollow electrodes for material additions to allow improved furnace sealing. Ash from incinerators is usually quenched and the maintenance of the water seal is an important factor in reducing diffuse emissions. Batch incinerators using open trays or boxes present dust and ash containment problems. Collected emissions are usually treated in ceramic or fabric filters, ESPs or wet scrubbers [ 161, Bobeth, A. 1999 ] (See ). *Is there any example of a ceramic filter??*

| ~~Component~~ | ~~Annual average (mg/Nm$^3$)~~ |
|---|---|

| | | |
|---|---|---|
| ~~Dust~~ | ~~2.6~~ | |
| ~~Cu~~ | ~~0.24~~ | |
| ~~Pb~~ | ~~0.2~~ | |
| ~~As~~ | ~~0.01~~ | |
| ~~Cd~~ | ~~0.001~~ | |

~~**Table 6.5: Emissions from a precious metal recovery plant sharing the acid plant of a smelter**~~
~~[ 282, KGHM 2008 ]~~

*What is the difference of this table compared with table 6.7? Why is it not included in the other table? Where are these data?? They are not in [282]!!*

*I found the information now: It is a contribution of the European precious Metals Federation. It has the new reference [525] . But the dust concentration is 2.9 mg/m$^3$.*

### ~~6.2.2.2~~6.2.2.1.2 Sulphur dioxide

These gases are formed from the combustion of sulphur contained in the raw material or the fuel or are produced from acid digestion stages. Control of the feedstock can be used to minimise emissions and wet or semi-dry scrubbers are used when the concentrations justify it. Electrode mists and gases can be produced during electrowinning. Gases can be collected and re-used and mists can be removed by demisters and returned to the process. Some installations operate on the site of primary smelter and the off-gases are treated in the sulphuric acid plant [ 282, KGHM 2008 ], [ 238, ECI Copper Installations 2008 ].

### ~~6.2.2.3~~6.2.2.1.3 Chlorine and HCl

These gases can be formed during a number of digestion, electrolytic and purification processes. Chlorine is used extensively in the Miller process and in the dissolution stages using hydrochloric acid/chlorine mixtures. Chlorine is recovered for re-use wherever possible, e.g. using sealed electrolytic cells for gold and PGMs. Scrubbers are used to remove residual amounts of chlorine and HCl.

The presence of chlorine in waste water can lead to the formation of organic chlorine compounds if solvents, etc. are also present in a mixed waste water.

### ~~6.2.2.4~~6.2.2.1.4 Nitrogen oxides

This is produced to a certain extent during combustion processes and in significant amounts during acid digestion using nitric acid. High concentrations of nitrogen oxides are treated in scrubbers so that nitric acid can be recovered, various oxidising agents are used to promote conversion and recovery as nitric acid.

Residual nitrogen oxides from furnace off-gases can be removed by catalytic means such as selective or non-selective catalytic reduction if very high $NO_X$ concentrations occur continuously [ 161, Bobeth, A. 1999 ].

The choice of abatement techniques essentially depends on the variation of the $NO_X$ concentration.

### ~~6.2.2.5~~6.2.2.1.5 VOC and PCDD/F

VOCs can be emitted from solvent extraction processes. The small scale of the processes usually allows sealing or enclosure of reactors and good collection and recovery using condensers. Collected solvents are re-used [ 102, Hasenpusch, W. 1998 ].

If the hot gases produced during the smelting stages are not cooled rapidly, the organic carbon compounds that can be emitted might include PCDD/F resulting from the poor combustion of oil and plastic in the feed material and from de novo synthesis. Scrap treatment to remove organic contamination can be practised but more usually afterburners are used to treat the gases produced followed by rapid cooling. In cases where it is not possible to treat the gases from the furnaces in an afterburner, they can be oxidised by adding oxygen above the melting zone. It is also possible to identify organic contamination of secondary raw materials so that the most appropriate furnace and abatement combination can be used to prevent the emissions of smoke and fumes and the associated PCDD/F. Organic compounds, including PCDD/F can be decomposed by catalytic oxidation, often in joint reactors.

Examples for afterburners with rapid cooling and catalytic oxidation with suffient data are needed.

### ~~6.2.2.6~~6.2.2.1.6 Summary of emissions to air

gives the specific emissions for three major pollutants and shows the emission concentrations for three different processes in precious metals production.

| Parameter | Unit | Plant 1 | Plant 2 | Plant 3 | Plant 4 | Plant 5 |
|---|---|---|---|---|---|---|
| Production | t/yr | 2155 | 1200 | 2500 | 1110 | 102 |
| Dust | kg/t | 58 | 4.5 | 2 | 18 | 127 |
| $NO_X$ | | 154 | 68 | 7 | | 21 |
| $SO_2$ | | 232 | 3.1 | 9 | | |
| *Source:* [ 527 ] | | | | | | |

**Table 6.3: Specific emissions to air from a range of precious metal production processes**

| Parameter | Unit | Incineration processes | Pyrometallurgical processes | Hydrometallurgical processes |
|---|---|---|---|---|
| Production range | t/yr | 73 - 365 | 150 - 1200 | 20 - 600 |
| Dust mg/Nm$^3$ | mg/Nm$^3$ | 2 - 10 | 4 - 10 | |
| Nitrogen oxides | | 50 - 150 | ~200 | 1 - 370 |
| Sulphur dioxide | | 1 - 25 | 10 - 100 | 0.1 - 35 |
| CO | | 10 - 50 | 80 - 100 | |
| Chloride | | 2 - 5 | <30 | 0.4 - 5 |
| $Cl_2$ | | | <5 | 2 - 5 |
| Fluoride | | 0.03 - 1.5 | 2 - 4 | |
| TOC | | 2 - 5 | 2 - 20 | |
| PCDD/F | ng I-TEQ/Nm$^3$ | <0.1 | <0.1 | |
| HCN | | | | 0.01 - 2 |
| $NH_3$ | | | | 0.2 - 4 |
| *Source: [ 161, Bobeth, A. 1999 ]* | | | | |

**Table 6.4: Emission concentrations to air from three different process in precious metal production**

~~Six~~ Two plants have reported data for captured air emissions ~~data~~ for different process steps as summarised in Table 6.5 ~~and Table 6.7~~.

| **Pollutant** | **Unit** | **Plant 1** | | | | | | **Plant 2** | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Without sulphuric acid plant | With sulphuric acid plant | Furnace hall (furnace in operation) | Furnace hall (waiting for the charge) | Refinery | Slag crushing | Ag, Au process step | Pt scrubber | PtRh, Pd scrubber |
| Dust | mg/Nm$^3$ | 2.9 | | 0.5 | 0.3 | 1.1 | 1.1 | 0.097 | | |
| NOx | mg/Nm$^3$ | 520 | 230 | ~~NA~~ | 3 | 3 | | 17.1 | | 92 |
| SO$_2$ | mg/Nm$^3$ | 9400 | 280 | ~~9~~ | 6 | 2 | | | | |
| H$_2$SO$_4$ | mg/Nm$^3$ | NA | 70 | | | | | | | |
| CO | mg/Nm$^3$ | 830 | | | 21 | 1 | | | | |
| Cl$_2$ | mg/Nm$^3$ | NA | | | | | | | | 0.134 |
| HCl | mg/Nm$^3$ | NA | | | | | | | 3.12 | 0.926 |
| PCDD/F | ng I-TEQ/Nm$^3$ | NA | | | | | | | | 0.02 |
| Cu | mg/Nm$^3$ | 0.24 | | 0.0005 | | | 0.022 | | | |
| Pb | mg/Nm$^3$ | 0.2 | | 0.029 | | | 0.43 | | | |
| As | mg/Nm$^3$ | 0.011 | | 0.0005 | | | 0.003 | | | |
| Cd | mg/Nm$^3$ | 0.001 | | 0.00001 | | | 0.0002 | | | |

NB: All values are annual means NB: Daily averages.

*Source:* [ 282, KGHM] [525].

**Table 6.5: Captured e~~E~~missions to air from ~~six~~ two PM plants for different process steps**
[ 282, KGHM 2008 ] [525]

*I found the information now: It is a contribution of the European precious Metals Federation. It has the new reference [525] .* Plant 5 and 6 are Belgium plants. Reference [282] is the wrong reference and it refers to Polish plants only.
*Where are these data?? They are not in [282]!!*

| ~~Metals in dust~~ | ~~Plant 1~~ | ~~Plant 2~~ |
|---|---|---|
| ~~Dust mg/Nm$^3$~~ | ~~1.1~~ | ~~0.5~~ |
| ~~Cu mg/Nm$^3$~~ | ~~0.022~~ | ~~0.0005~~ |
| ~~Pb mg/Nm$^3$~~ | ~~0.43~~ | ~~0.029~~ |
| ~~As mg/Nm$^3$~~ | ~~0.003~~ | ~~0.0005~~ |
| ~~Cd mg/Nm$^3$~~ | ~~0.0002~~ | ~~0.00001~~ |

~~**Table 6.7: Metal content in filter dust from two PM plants**~~
[ 282, KGHM 2008 ]
*From the unit (mg/Nm$^3$) it can not be seen why the caption is about metal content in filter dust which should be mg/kg!*
*Clarify please.*
*Where are these data?? They are not in [282]!!*
*These data do not give any information on the reference time! (They are annual averages)*

##### ~~6.2.3~~6.2.2.2 Emissions to water

On sites handling a range of metals, common facilities are frequently employed to manage emissions to water. The techniques described below may therefore not relate just to precious metals.

Pyrometallurgical and hydrometallurgical processes use significant quantities of cooling water. Liquors from leaching cycles are normally recirculated in sealed systems. The source of potential emissions to water from precious metals production is shown in Table 6.6 below. Suspended solids, metal compounds and oils can be emitted to water from these sources.

All waste water is treated to remove dissolved metals and solids. Precipitation of metal ions as hydroxides or sulphides is used, a two-stage precipitation can also be used. Ion exchange is suitable for low concentrations and amounts of metal ions. In a number of installations, cooling water and treated waste water including rainwater is re-used or recycled within the processes.

Special techniques have been developed for precious metal processes to detoxify nitrite by a reduction process and cyanide by hydrolysis in the waste water [ 161, Bobeth, A. 1999 ].

| Emission Source | Suspended solids | Metal compounds | Oil |
|---|---|---|---|
| Surface drainage | ••• | •• | ••• |
| Cooling water for direct cooling | ••• | ••• | • |
| Cooling water for indirect cooling | • | • | |
| Quenching water | ••• | •• | |
| Leaching (if not closed circuit) | ••• | ••• | • |
| Electrowinning (if not closed circuit) | | ••• | |
| Scrubbing systems | ••• | ••• | |
| NB: ••• More significant – • Less significant<br>*Source*: [ 527 ] | | | |

**Table 6.6: Source of potential emissions to water from precious metals production**

Emissions to water from seven processes are given in Table 6.7 and Table 6.8.

| Plant | Production (t/yr) | Effluent ($m^3$/hr) | Main components (mg/l) | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | Ag | Pb | Hg | Cu | Ni | COD |
| 1 | 2155 | 10 | 0.1 | 0.5 | 0.05 | 0.3 | 0.5 | 400 |
| 2 | 1200 | 2 | | <1 | <0.05 | <2 | <5 | |
| 3 | 2500 | 100 | 0.02 | <0.05 | <0.05 | <0.3 | <0.02 | 250 |
| 4 | 1110 | | | 3.9 kg/yr | 0.05 kg/yr | 194 kg/yr | 24 kg/yr | |
| 5 | 102 | | | 1260 kg/yr | | 2750 kg/yr | 1640 kg/yr | |
| *Source:* [ 527 ] | | | | | | | | |

**Table 6.7: Emissions to water from five large processes**

| Component emitted to water | Unit | Plant 1 | Plant 2 |
|---|---|---|---|
| Water consumption | $m^3$/yr | 111829 | 111829 |
| Water discharge (including rainwater, cooling water, process water) | $m^3$/yr | 61093 | 61093 |
| As | kg/yr | 1.73 | 9.5 |
| Pb | | 0.25 | 3.6 |
| Hg | | 0.04 | 0.01 |
| Zn | | 0.80 | 10.7 |
| Cd | | 0.002 | 0.1 |
| Cu | | 3.88 | 7.9 |
| Ni | | 7.03 | 6.1 |
| Cr | | 0.044 | 0.7 |
| Fe | | | 21.3 |
| Se | | | 31.7 |
| Ag | | | 9.5 |
| Se | | | 31.7 |
| Cyanide | | 126.22 | |
| COD kg/yr | | 37850 | 11500 |
| Chlorides (total as Cl) | | 408066 | |
| Nitrogen (total as N) | | 3240 | |
| Suspended solids kg/yr | | 4.313 | |
| *Source:* [ 525 ] | | | |

**Table 6.8: Emissions to water from two PM plants**

[ 525]

*From reference [ 525 ] it can not be concluded if these are the emission over a whole year, but probably they are.*

*This again is the wrong reference. The data for plant 7 and 8 are not from [282, KGHM} which is a polish plant. They are from two UK plants [525].*
*For the plant 1 some wrong data are inserted and some relvant pollutants are not used.*
*Chlorides have been deleted: 408066 kg/yr*
*Cyanides have been deleted: 126.22 kg/yr*
*Cr has been deleted: 0.044 kg/yr*
*Nitrogen has been deleted: 3240 kg/yr*
*And suspended solids are not 4313 kg/yr but 4.313 kg/yr according to [525].*

Other potential emissions to water may include ammonium, chloride and cyanide ions depending on the individual process stages. No data have been submitted to quantify these components.

### ~~6.2.4~~6.2.2.3 By-products, process residues and waste

The production of metals is related to the generation of several by-products, residues and wastes, which are also listed in the European Waste Catalogue (Council Decision 94/3/EEC).*This has been replaced by a new directive 75/442/EEC (see Section 5.2.4)* Most production residues are recycled within the process or sent to other specialists to recover any precious metals. Residues that contain other metals, e.g. Cu, are sold to other producers for recovery. Final residues from aqueous waste liquors generally comprise hydroxide filter cakes. Some typical examples are given in Table 6.9.

| Annual waste for disposal tonnes | Waste characterisation |
|---|---|
| 1000 | Iron hydroxide, 60 % water, (Cat 1 Industrial Waste) |
| 1000 | Effluent filter cake |
| 350 | Effluent filter cake |

**Table 6.9: Example of filter cake waste quantities**
[ 102, Hasenpusch, W. 1998 ]

## 6.3 Techniques to consider in the determination of BAT

The sections of this document entitled 'Techniques to consider in the determination of BAT' set out techniques considered generally to have potential for achieving a high level of environmental protection in the industries within the scope of the document. The background to the way the techniques are described is given in Section 2.1.2 and Table 2.2.

This section presents a number of techniques for the prevention or reduction of emissions and residues as well as techniques for reducing the overall energy consumption. They are all commercially available. Examples are given in order to demonstrate techniques which illustrate a high environmental performance. The techniques that are given as examples depend on information provided by the industry, European Member States and the valuation of the European IPPC Bureau. The general techniques described in Chapter 2, common processes, apply to a large extent, to the processes in this sector and influence the manner in which the main and associated processes are controlled and operated. Techniques used by other sectors are also applicable particularly those relating to the collection, re-use and scrubbing of organic solvents, nitrogen oxides and chlorine gas.

The use of hoods for tapping and casting is also a technique to consider. These fumes will consist mainly of oxides of the metals that are involved in the smelting process. The design of the hooding system should take account of access for charging and other furnace operations and the way the source of process gases change during the process cycle. For $SO_2$ or total carbon removal, the variation in raw gas concentration during batch processes may affect the performance of the abatement system.

The applied processes described above are used to process a wide range of raw materials of varying quantity and composition and are also representative of those used worldwide. The techniques have been developed by the companies in this sector to take account of this variation. The choice of pyrometallurgical or hydrometallurgical technique is driven by the raw materials used, their quantity, the impurities present, the product made and the cost of the recycling and purification operation. These factors are therefore site specific. The basic recovery processes outlined above therefore constitute techniques to consider for the recovery processes.

### 6.3.1 Raw material handling

The storage of raw materials depends on the nature of the materials used and the types of materials and the conditions needed are:

- dusty materials are stored in enclosed buildings or closed containers
- secondary raw materials that contain water soluble components are stored under cover
- massive, non soluble material (except batteries) may be stored in open stockpiles and large items individually in the open
- reactive and flammable materials should be stored separately ensuring an adequate segregation of materials capable of reacting together.

**Description**
The techniques to consider for the storage of raw materials are given in Table 6.10

| Material | Storage | Handling | Pretreatment | Comment |
|---|---|---|---|---|
| Coal or coke | Open with sealed floors and water collection, covered bays, silos | Covered conveyors if non-dusty<br>Pneumatic | | |
| Fuel and other oils | Tanks or drums in bunded areas | Secure pipeline or manual system | | |

| | | | | |
|---|---|---|---|---|
| Fluxes | Enclosed, Silo If dust-forming | Enclosed conveyors with dust collection<br>Pneumatic | Blending with concentrates or other material | |
| Concentrates | Enclosed. Drums, Bags<br>If dust-forming | Enclosed with dust collection<br>Closed conveyor or pneumatic | Blending using conveyors<br>Drying or sintering | |
| Circuit boards | Covered bays, boxes | Depends on the material | Grinding + density separation., incineration | Plastic content may provide heat input |
| Fine dust | Enclosed<br>If dust-forming | Enclosed with dust collection<br>Pneumatic | Blending, Agglomeration (pelletisation) | |
| Coarse dust (raw material or granulated slag) | Covered bays | Mechanical loader. | Roasting to remove VOCs | Oil collection |
| Film, catalysts sweeps | Drums, big bags, bales | Depends on the material | Incineration, roasting | |
| Plated material | Drums, boxes | Depends on the material | Stripping with CN or nitric acid | |
| Lump (raw material or slag) | Open | Depends on the material | | Oil collection |
| Whole items | Open or covered bays | Depends on the material | Milling grinding | Oil collection |
| Reactive materials | Isolated storage | Depends on the material | Crushing or whole feed | Acid collection |
| Acids:<br>Waste acid<br><br>Recovered acid | Acid resistant tanks.<br>Acid resistant tanks | | Sale or neutralisation<br>Sale | |
| Products -<br>Cathodes, billets and ingots<br>Rod and wire | Open concrete area or covered storage | | | |
| Process residues for recovery | Covered or enclosed depending on dust formation | Depends on conditions | | Appropriate drainage system |
| Wastes for disposal | Covered or enclosed bays, big bags or sealed drums depending on the material | Depends on conditions | | Appropriate drainage system |

**Table 6.10: Material handling and pretreatment**

**Achieved environmental benefits**
Prevention of emissions of dust.

**Cross-media effects**
No data has been reported.

**Operational data**
No data has been reported.

**Applicability**
These techniques are applicable to the storage of all material.

**Economics**
No specific data is available.

**Driving force for implementation**
Prevention of losses and reduction in environmental impact

**Example plants**

UK, DE, BE, PL.

**Reference literature**
[ 5, B R Lerwill et al. 1993 ], [ 103, Farrell, F. 1998 ], [ 290, EC 2006 ].

## 6.3.2 Metal production processes

**Description**
As reported above there are many potential processes and combinations of processes that are used for the recovery of precious metals. The exact combination depends on the raw materials and the matrix that contains the metals. Table 6.11 shows the generic process stages, the potential problems and the techniques to consider in the determination of BAT for these processes. The furnaces used are summarised in Table 6.12.

| Process | Potential problem | Techniques to consider | Comment |
|---|---|---|---|
| Incineration | Dust, VOC, PCDD/F, $SO_2$, $NO_X$ | Process control, afterburner and scrubber/fabric filter | Rotary kiln unless very small scale. |
| Crushing, blending or drying | Dust | Containment, gas collection and fabric filter | |
| Pelletisation | Dust | Containment, gas collection and fabric filter | |
| Smelting and selenium removal/ volatilisation | Dust, metals, VOC, $NO_X$ and $SO_2$ | Containment, gas collection and scrubber/fabric filter | Scrubber or wet ESP for selenium recovery. |
| Cupellation | Lead oxide | Containment, gas collection and fabric filter | Use of the copper route avoids lead emissions |
| Acid digestion | Acid gases<br>Acid spillage | Containment, gas collection and recovery/scrubbing system | See also Table 6.13 |
| Refining | Acid gases, $NH_3$<br>Acid spillage | Containment, gas collection and scrubber/fabric filter | See also Table 6.13 |
| Oxidation or reduction | Chemical components<br>Chemical spillage | Containment, gas collection and scrubbing/treatment | See also Table 6.13 |
| Melting, alloying and casting | Dust and metals | Containment, gas collection and fabric filter | |
| Solvent extraction | VOC | Containment, gas collection and recovery/absorption | See also Table 6.13 |
| Dissolution | HCl, $Cl_2$, $NO_X$ | Containment, gas collection and recovery/scrubbing system | See also Table 6.13 |
| Distillation | *?????Here is no information given but in the BAT section in table 6.17 there is? Why?* | Containment, gas collection and recovery/scrubbing system | See also Table 6.13 |

**Table 6.11: Techniques to consider for metal production stages and the potential problems**

*This table 6.11. is not very helpful. Ceramic filter which are considered to be BAT are not included. Low NOx burners, Oxy-fuel burners as well as SCR/SNCR are not included even if they are considered to be BAT. The whole table has to be revised and completed.*

| Furnace | Processes used | Advantages | Disadvantages |
|---|---|---|---|
| Blast furnace | Smelting | Established<br>*(all of the firnaces are established)* | Process control needs development. Tuyere injection of fine material is possible |
| Rotary furnace | Smelting | High smelting rate with oxygen<br>Rotation gives good mixing | Batch process |
| Electric furnace (resistance, induction, arc) | Smelting | Low gas volumes<br>Reducing conditions<br>Through electrode feeding | Energy cost |
| Ausmelt/ISA Smelt | Smelting | Range of material. Recovery with other metals, e.g. Cu | Minimum size |
| Reverberatory furnace | Smelting and cupellation | Established. Processes are combined | Batch process |
| Kaldo furnace (top blown rotary furnace) or tilting rotating oxy fuel (TROFF) furnace | Smelting or cupellation | Compact, easy to enclose<br>Combines processes | Can be expensive.<br>Batch process |
| Gas recirculating roaster | Selenium roasting, smelting | Improved heat transfer | |
| Bottom blown oxygen ~~cupel~~ cupelling furnace | Cupellation | Low fuel consumption. High recovery and process rate. Rising gases are washed by molten layer of litharge | Batch process |
| Cupelling furnace | Cupellation | | Relies heavily on fume collection |

**Table 6.12: Smelting and cupelling furnaces and their advantages and disadvantages**
[ 102, Hasenpusch, W. 1998 ]

Melting furnaces are also used in the industry. Electric (induction, arc, resistance) furnaces and gas/oil fired furnaces are used. Induction furnaces avoid the production of combustion gases and the associated increase in size of abatement plant.

**Achieved environmental benefits**
Easier, more efficient fume collection, prevention of emissions.
*Does this statement fits for all furnaces? If so all furnaces shpow this advantage and don't have to be mentioned in the BAT conclusion section.*

**Cross-media effects**
Energy use.

**Operational data**
No data has been reported.

**Applicability**
No data has been reported.

**Economics**
No data has been reported.

**Driving force for implementation**
Increased recovery of precious metals and reduction in environmental impact.

**Example plants**
UK, DE, BE, PL.

**Reference literature**

[ 5, B R Lerwill et al. 1993 ], [ 103, Farrell, F. 1998 ], [ 102, Hasenpusch, W. 1998 ].

### 6.3.2.1 Incineration of photographic and x-ray film

**Description**

The use of a rotary kiln with good process control, gas collection and gas treatment. Rotation and process control allows good mixing of material and air. (See Figure 6.4).

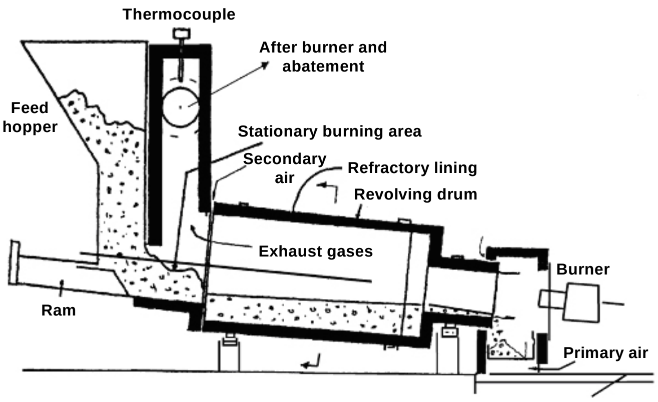


**Figure 6.4:** **Incinerator for photographic and X-ray film**
[ 102, Hasenpusch, W. 1998 ]

**Achieved environmental benefits**

Easier and more efficient afterburning and gas treatment compared to static or box incinerators using the calorific value of the film compared to similar systems.

*Missing example plants and data!!!*

**Cross-media effects**

No data has been reported.

**Operational data**

No data has been reported.

**Applicability**

This technique is applicable to the incineration of all photographic material.

**Economics.**

Capital cost estimated at EUR 650000 for a 500 kg/h plant (1988 data).

**Driving force for implementation**

Recovery of silver.

**Example plants**

UK.

**Reference literature**

[ 5, B R Lerwill et al. 1993 ], [ 103, Farrell, F. 1998 ], [ 102, Hasenpusch, W. 1998 ].

## 6.3.3 Fume/gas collection

The techniques discussed in Section 2.4.3 of this document are techniques to consider for the various process stages involved in the production of precious metals, etc. The use of secondary hoods for launders, moulds and charging doors is also a technique to be considered. The processes usually involve small-scale operation and so the techniques such as reactor sealing and containment can be relatively easy and cheap to incorporate.

### 6.3.3.1 Collection of fumes

*This example is used in other sections in this BREF but with different captions (see Section 2.4.5.1 4.3.6.3 and 5.3.8.2). Try to get precious metals specific examples for fume collection. And if available some info about the performace, i.e. % extraction efficiency.*

**Description**

The use of a co-incident charging and tapping zone in a rotary furnace allows good access to the furnace and good fume extraction. See Figure 6.5.

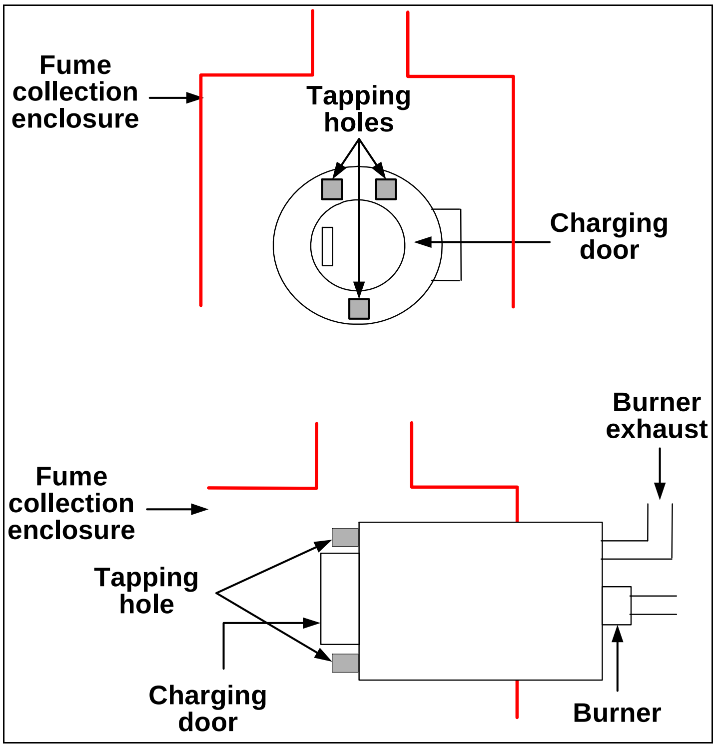


**Figure 6.5:** **Co-incident fume capture system**

*Is this an appropriate example for precious metals??*

Furnace lining wear may mean that door end tapping holes may not allow all of the metal to be tapped.

**Achieved environmental benefits**

Easier fume collection from a single point prior to treatment with reduced power consumption compared to similar systems.

**Cross-media effects**

No data has been reported.

**Operational data**

No data has been reported.

**Applicability**

This technique is applicable to all rotary furnaces.

**Economics**
This is a low cost of modification, viable in several installations.

**Driving force for implementation**
Capture of diffuse emissions.

**Example plants**
FR, UK, PL and DE.

**Reference literature**
[ 103, Farrell, F. 1998 ].

## 6.3.4 Fume/gas abatement

**Description**
~~There are several site-specific issues that will apply and some of these are discussed earlier in this chapter.~~ Essentially the process technologies discussed in this chapter, combined with suitable abatement will meet the demands of stringent environmental protection. Techniques to remove components from some of the off-gases are shown below in Table 6.13 [ 102, Hasenpusch, W. 1998 ].

| Reagent Used | Component in off-gas | Treatment Method |
|---|---|---|
| Solvents, VOCs | VOC, odour | Afterburner, containment, condensation, activated carbon, biofilter |
| Sulphuric acid (+ sulphur in fuel or raw material) | Sulphur dioxide | Wet or semi-dry scrubber system. |
| Aqua Regia | NOCl, $NO_X$ | Caustic scrubber system |
| Chlorine, HCl | $Cl_2$ | Caustic scrubber system |
| Nitric acid | $NO_X$ | Oxidise and absorb, recycle, scrubber system |
| Na or KCN | HCN | Oxidise with hydrogen peroxide<br>or hypochlorite(¹) |
| Ammonia | $NH_3$ | Recovery, scrubber system |
| Ammonium chloride | Aerosol | Recovery by sublimation, scrubber system |
| Hydrazine | $N_2H_4$ (possible carcinogen) | Scrubber or activated carbon |
| Sodium borohydride | Hydrogen (explosion hazard) | Avoid if possible in PGM processing (especially Os, Ru) |
| Formic acid | Formaldehyde | Caustic scrubber system |
| Sodium chlorate/HCl | $Cl_2$ oxides (explosion hazard) | Control of process end point |
| (¹)Hypochlorite is not permitted in some regions. | | |

**Table 6.13: Chemical treatment methods for some gaseous components**

*Missing example plants and Data!!!*
*This is by far too general to just mention all possible techniques.*
*What means chemical treatment? Afterburning is no chemical treatment, Condensation or activated carbon treatment not either. The first column has the heading reagent used. What means Reagent used? In most cases this is just the full name of the abbreviations used in the middle column.*

**Achieved environmental benefits**
Destruction or removal of gaseous components and prevention of emissions.

**Cross-media effects**
No data has been reported.

**Operational data**
No data has been reported.

**Applicability**
No data has been reported.

**Economics**
No data has been reported.

**Driving force for implementation**
Reduction in environmental impact and increased recovery of precious metals.

**Example plants**
UK, DE, BE, PL.
*If these treatment methods are applied we should get some good examples and measured data.*

**Reference literature**
[ 5, B R Lerwill et al. 1993 ], [ 103, Farrell, F. 1998 ].

### 6.3.4.1 Use of SCR and SNCR

**Description**
SCR or SNCR in precious metal processes is used in the manner shown in the process diagram of the incorporation of SCR in the ash recovery from precious metals [ 161, Bobeth, A. 1999 ]. See Figure 6.6.

*Why is SNCR included. Do we have examples? In the figure only SCR is included. Since there is only one example included in this section, on what is the assessment about the ammonia slips based????*

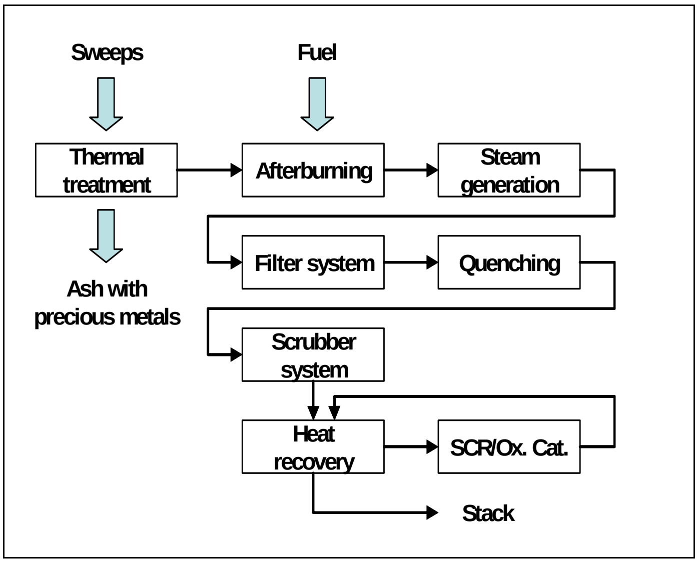


**Figure 6.6:** **Process diagram for the incorporation of SCR in the ash recovery from precious metals**

*Missing example plants and Data!!!*

**Achieved environmental benefits**
$NO_X$ removal.

**Cross-media effects**
Use of reagents and power ammonia slip.
*(This is unclear: what means power ammonia slip???)*
*Perhaps what is meant is: Use of reagents, additional fuel and possible ammonias slips (if SNCR is applied or for both?).*

**Operational data**
No data has been reported.

**Applicability**
No data has been reported.

**Economics**
Viable in one installation.

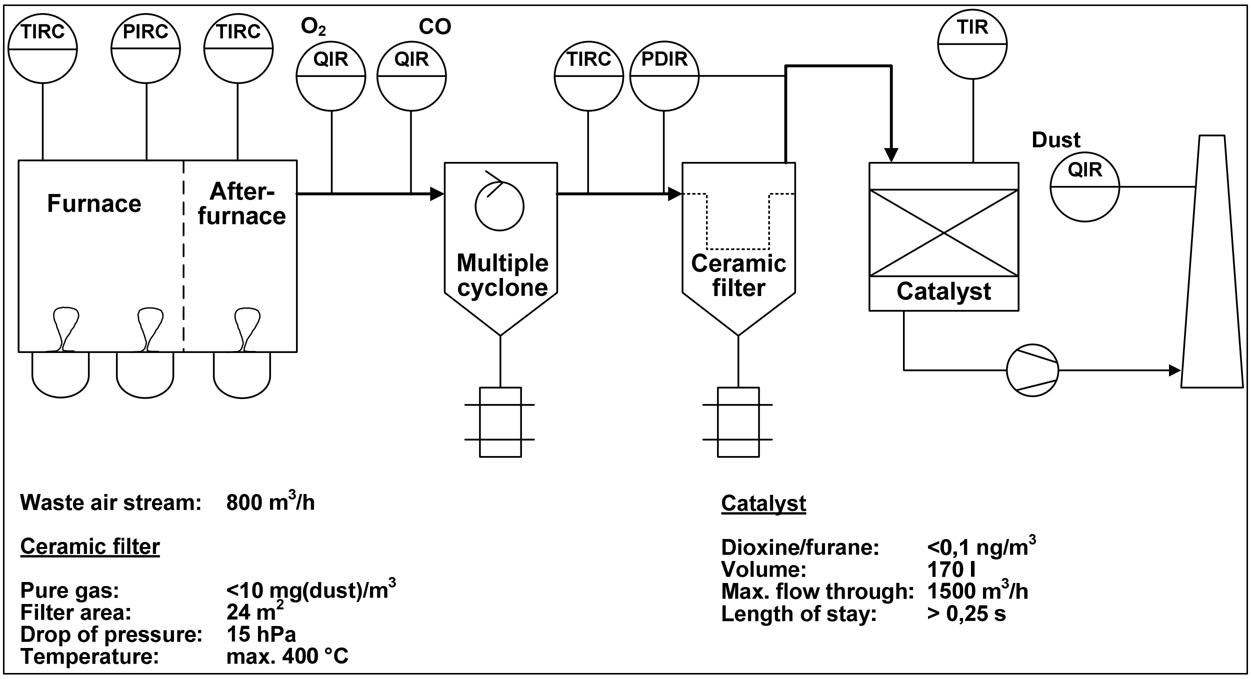
**Driving force for implementation**
Effective recovery of silver.

**Example plants**
Germany.

**Reference literature**
[ 161, Bobeth, A. 1999 ].

### 6.3.4.2 Catalytic destruction of PCDD/F

**Description**
A catalytic reactor is used to remove PCDD/F as shown by the process diagram of the furnace and abatement system in Figure 6.7.



Waste air stream: 800 $m^3/h$

Ceramic filter

Pure gas: <10 mg(dust)/$m^3$
Filter area: 24 $m^2$
Drop of pressure: 15 hPa
Temperature: max. 400 °C

Catalyst

Dioxine/furane: <0,1 ng/$m^3$
Volume: 170 l
Max. flow through: 1500 $m^3/h$
Length of stay: > 0,25 s

Figure 6.7: Process diagram of the furnace and abatement system
~~[ 234, UBA Copper, lead, zinc and aluminium 2007 ]~~
*Wrong reference. [234] is the German contribution to the revision of the NFM BREF but does not contain any information on this issue.*

*Which plant?*

### Achieved environmental benefits
Removal of PCDD/F.

### Cross-media effects
Increased use of energy.
*(This is unclear and needs further description)*

### Operational data
PCDD/F levels of <0.1 ng I-TEQ/$Nm^3$ are achieved.
*(In the existing BREF this is <0.01 ng I-TEQ/$Nm^3$. Where is the evidence for the changed figures?) Where are the data from?*

### Applicability
No data has been reported.

### Economics
Viable in one installation.
*What does this mean? This is by far too general to be useful for drawing a conclusion.*

### Driving force for implementation
Improved destruction of PCDD/F.

### Example plants
DE.

### Reference literature
[ 234, UBA Copper, lead, zinc and aluminium 2007 ].

### ~~6.3.5Process control~~

~~The principles of process control discussed in Section 2.8 are applicable to the production processes for precious metals. Some of the furnaces and processes are capable of improvement by the adoption of many of these techniques.~~

### ~~6.3.5.1~~6.3.4.3 Reduction of chlorine in the ~~Process control for the~~ Miller process~~furnace~~

**Description**
In the Miller process, gold is melted at about 1000 °C and chlorine gas is blown through the melt. Metallic impurities form chlorides and a slag or are fumed off. The initial uptake of chlorine is high and excess chlorine can be emitted easily. Manual control of chlorine addition is difficult. The formation of most of the metal chlorides is exothermic and the use of continuous temperature measurements can be used to control the rate of chlorine addition.

**Achieved environmental benefits**
Prevention of chlorine emissions is achieved with free chlorine release reported to be <1 ppm to air after a venturi scrubber and a wet ESP.
*We need specific examples and data for relevant pollutants in relevant process steps. What about the precipitation by venturi scrubber and wet ESP? 1 ppm is about 1,5 mg/m$^3$.*

**Cross-media effects**
No data has been reported.

**Operational data**
No data has been reported.

**Applicability**
This technique is applicable to all Miller processes.

**Economics**
Not assessed but the costs are low, so a viable operation is established.

**Driving force for implementation**
Prevention of chlorine emission.

**Example plants**
UK.

**Reference literature**
[ 5, B R Lerwill et al. 1993 ]

## ~~6.3.6~~6.3.5 Waste water

The hydrometallurgical processes are very important in some production processes. Because the hydrometallurgical processes involve leaching and electrolytic stages, gases evolved such as HCl, need to be recovered or treated. Adequate disposal of leached material and spent electrolyte also should be practised. The techniques discussed in Section 2.12.2 to prevent emissions to water for example by containing drainage systems are relevant as are techniques to recover VOCs and the use of benign solvents.

All waste water should be treated to remove dissolved metals and solids, cyanide wastes and liquors also need to be treated. Water supply and effluent lines can be separated. The techniques listed in Sections 2.12.2 and 6.2.2.2 are the techniques to consider. In a number of installations, cooling water and treated waste water including rainwater is re-used or recycled within the processes.

*All this is more or less a repetition of Section 6.2.2.2. What is needed are real examples of waste water treatment in preciuous metals production.*

### ~~6.3.7~~6.3.6 Other techniques

*Such a list of different techniques is hard to apply and to use in the BAT conclusion section. But overall it is impossible to fill the nine headings below because it would be unclear to which BAT the further information would belong.*

*The list includes:*

- *General examples for process optimisation, create a BAT section called "Process optimisation"*
- *General information about instruction, maintenance, staff training etc. This is for the generic chapter 2 and can be found under EMS already*
- *Specific BAT which should be part of the beforementioned, such as gas and water collection techniques, abatement systems for relevant pollutants, waste water treatment, relocate to where appropriate and try to get examples and data.*

*→ disaggregate and complete, delete unnecessary information.*

**Description**

There are many techniques that can be applied to prevent emissions or reduce the environmental impact but many of the process-specific details are commercially confidential. These are also often very site-specific but the general techniques are summarised below:

- The characterisation of raw materials before they are received so that unforeseen impurities and contamination can be identified and the handling, storage and processing difficulties can be taken into account and the material transferred to another processor if appropriate.
- Sampling and analysis of raw materials as soon as possible so that commercial aspects can be confirmed and the process options defined for a particular raw material.
- Raw material handling systems to minimise the leakage of liquids and the emission of dust. Robust packaging should be used during transport and for storage.
- Raw materials storage in enclosed buildings with the separate storage of reactive materials.
- Pretreatment stages for photographic film and paper using a rotary kiln and afterburner together with an ash quench system that is designed to a high standard. HCl may need to be scrubbed from the exhaust gas and dust removal used. In the case of raw material that contains minor quantities of paper, leaching processes based on sodium thiosulphate and enzymes.
- Pretreatment stages for catalysts and smaller quantities of material that contain pgms in box incinerators using an afterburner where necessary and fabric filters, scrubbers, etc. That are professionally designed and constructed to a high standard so that leakage is prevented. Heat recovery in the form of energy production or recuperation should be practised if possible.
- Pretreatment of small quantities of material in sealed box incinerators using professionally designed collection and abatement equipment including afterburners where necessary.
- Use of techniques such as calcining or leaching/dissolution where possible to recover catalyst support material. The material could be recovered as grinding material, aluminium salts, inert slag or catalyst support material.
- The use of proven precious metal recovery and refining processes in conjunction with proven, efficient abatement systems that are available to the operator, that achieve the environmental standards covered in Section 2.9 of this document. The use of copper rather than lead in the smelting circuit. *Can we get example plants and data for these BATs?*

- Solvent extraction systems using non-toxic solvents as far as possible. Use of containment and VOC recovery and abatement systems. *Can we get example plants and data for these BATs?*
- Furnace operation control to optimise operating conditions. Key parameters are temperature at various points in the furnace and gas handling system, oxygen and carbon monoxide concentrations and system pressure. These should be used to control the material feed rate as far as possible.
- Processes control of chemical and hydro metallurgical stages and abatement plant using relevant methods so that it is possible to maintain operating conditions at the optimum level and to provide alarms for conditions that are outside the acceptable operating range.
- The collection and re-use of acid gases such as HCL, $HNO_3$ and $Cl_2$. The treatment of CN in gas streams. *Can we get example plants and data for these BATs?*
- Professional design of dust, acid gas, CN, VOC and metal vapour collection and abatement systems. The operation of these systems to prevent and reduce emissions to the environment. *Can we get example plants and data for these BATs?*
- Use of contained plant drainage systems where possible. Effluents treated according to their content and analysed before discharge. Scrubbing liquids should also be treated and analysed before discharge. *Can we get example plants and data for these BATs?*
- Waste materials analysis before transfer to other sites so that the correct disposal or recovery route can be used.
- Plant operators should be trained and given instructions about the correct operating procedures and control parameters.
- Use of good maintenance practice for process plant, abatement systems and other associated processes. A system of inspection should be adopted for these systems.

**Achieved environmental benefits**
Prevention of emissions.

**Cross-media effects**
No data has been reported.

**Operational data**
No data has been reported.

**Applicability**
No data has been reported.

**Economics**
No data has been reported.

**Driving force for implementation**
Prevention of losses and reduction in environmental impact.

**Example plants**
UK, DE, BE, PL.

**Reference literature**
[ 5, B R Lerwill et al. 1993 ]; [ 103, Farrell, F. 1998 ].

### ~~6.3.8~~6.3.7 Energy use

The re-use of energy or the generation of electricity are techniques to consider provided site-specific conditions allow this to be achieved economically [ 296, Salo, S. et al. 2008 ] (see also Section 2.14).

*We need some examples where in precious metals production energy recovery is applied. The reference to Section 2.14 is  not helpful at all.*

## 6.4 Best Available Techniques

In understanding this section and its contents, the attention of the reader is drawn back to the Preface of this document and in particular the fifth section of the Preface: ‘How to understand and use this document’. The techniques and associated emission and/or consumption levels, or ranges of levels, presented in this chapter have been assessed through an iterative process involving the following steps:

- identification of the key environmental issues for the sector which for the production of precious metals are: VOCs, dust, fume, PCDD/F, odours, $NO_X$, other acid gases such as chlorine and $SO_2$, waste water and residues such as sludge, filter dust and slag;
- examination of the techniques most relevant to address these key issues;
- identification of the best environmental performance levels, on the basis of the available data in the European Union and worldwide;
- examination of the conditions under which these performance levels were achieved; such as costs, cross-media effects, and the main driving forces involved in implementation of the techniques;
- selection of the best available techniques (BAT) and the associated emission and/or consumption levels for this sector in a general sense, all according to Article 2(12) and Annex IV to the Directive.

Expert judgement by the European IPPC Bureau and the relevant Technical Working Group (TWG) has played a key role in each of these steps and in the way in which the information is presented here.

On the basis of this assessment, best available techniques, and as far as possible emission and consumption levels associated with their use, are presented in this section that are considered to be appropriate to the sector as a whole and in many cases reflect the current performance of some installations within the sector. Where emission and consumption levels 'associated with best available techniques' are presented, this is to be understood as meaning that those levels represent the environmental performance that could be anticipated as a result of the application, in this sector, of the techniques described, bearing in mind the balance of costs and advantages inherent within the definition of BAT. However, they are neither emission nor consumption limit values and should not be understood as such. In some cases, it may be technically possible to achieve better emission or consumption levels but due to the costs involved or cross-media considerations, they are not considered to be appropriate as BAT for the sector as a whole. However, such levels may be considered to be justified in more specific cases where there are special driving forces.

The emission and consumption levels associated with the use of BAT have to be seen together with any specified reference conditions (e.g. averaging periods).

The concept of ‘levels associated with BAT’ described above is to be distinguished from the term ‘achievable level’ used elsewhere in this document. Where a level is described as ‘achievable’ using a particular technique or combination of techniques, this should be understood to mean that the level may be expected to be achieved over a substantial period of time in a well maintained and operated installation or process using those techniques.

Where available, data concerning costs have been given together with the description of the techniques presented in the previous sections. These give a rough indication about the magnitude of the costs involved. However, the actual cost of applying a technique will depend strongly on the specific situation regarding, for example, taxes, fees, subsidies, and the technical characteristics of the installation concerned. It is not possible to evaluate such site-specific factors fully in this document. In the absence of data concerning costs, conclusions on economic viability of techniques are drawn from observations on existing installations.

The BAT (including the associated emission and consumption levels) given in this section are 'BAT in a general sense' (i.e. considered to be appropriate to the sector as a whole). It is intended that they are a reference point against which to judge the current performance of an existing installation or to judge a proposal for a new installation. In this way, they will assist in the determination of appropriate 'BAT-based' conditions for the installation or in the establishment of general binding rules under Article 9(8) of the IPPC Directive. It is foreseen that new installations can be designed to perform at or even better than the BAT levels presented in this section. It is also considered that existing installations could move towards the BAT levels presented in this section or do better, subject to the technical and economic applicability of the techniques in each case.

While the BAT reference documents do not set legally binding standards, they are meant to give information for the guidance of industry, Member States and the public on achievable emission and consumption levels when using specified techniques. The appropriate permit conditions for any specific case will need to be determined taking into account the objectives of the IPPC Directive and the local considerations.

**Recommendation to help users/readers of this document:**

It is strongly recommended that this section on BAT be read in conjunction with the sections of this document that describe the techniques to consider in the determination of BAT. The applicability of the techniques and measures are reported in these sections and should be taken into account at a local level. To help the reader, references to the appropriate sections are included in the description of BAT.

If not otherwise mentioned, BAT associated emission and consumption levels given in this section are expressed as follows:

- for pollutants emitted to air (except dioxins): expressed on a daily average basis with standard conditions of 273 K, 101.3 kPa, measured oxygen content and dry gas with the plant operating normally under steady-state conditions and no dilution of the gases;
- for dioxins: expressed as the average over the sampling period which should preferably be a minimum of 6 hours;
- for waste water: based on qualified random samples or 24 hour flow proportional composite samples.

As described in the Preface, this document does not propose emission limit values. The best available techniques and the ranges of emission or consumption levels associated with best available techniques (BAT-AEL ranges) are related to installations with different sizes, different kinds of operation and different raw materials. In this document, special local considerations cannot be taken fully into account. The determination of appropriate permit conditions will involve taking account of local, site-specific factors such as the technical characteristics of the installation concerned, its geographical location and the local environmental conditions. In the case of existing installations, the economic and technical viability of upgrading them also should be taken into account. Even the single objective of ensuring a high level of protection for the environment as a whole will often involve making trade-off judgements between different types of environmental impact, and these judgements will often be influenced by local considerations.

Although an attempt is made to address some of these issues, it is not possible for them to be considered fully in this document. The techniques and emission and consumption levels presented here will therefore not necessarily be appropriate for all installations. On the other hand, the obligation to ensure a high level of environmental protection including the minimisation of long-distance or transboundary pollution implies that permit conditions cannot be set on the basis of purely local considerations. It is therefore of utmost importance that the information contained in this document be fully taken into account.

Section 2.20 to this document reports BAT for the following common processes and the following sections should be referred to for those techniques that are BAT:

- environmental management systems (EMS) (Section 2.20.1)
- material handling and storage (Section 2.20.2)
- process control (Section 2.20.3)
- fume and gas collection (Section 2.20.4)
- the prevention and the destruction of PCDD/F (Section2.20.5)
- sulphur dioxide removal (Section 2.20.6)
- the removal of mercury (Section 2.20.7)
- effluent treatment and water re-use (Section 2.20.8)
- energy efficiency (Section 2.20.9)
- intermediate products, process residues and wastes (Section 2.20.10)
- emission monitoring (Section 2.20.11)
- prevention of the formation of $NO_X$ (Section 2.20.12)
- removal of dust and particles (Section 2.20.13)

BAT for the production of precious metals is the combination of the generally applicable techniques reported in Section 2.20 and the specific techniques indicated in this section.

## 6.4.1 Prevention and control of emissions to air

### 6.4.1.1 Pretreatment processes

**a) BAT is to prevent diffuse emissions and optimise the use of energy by using the pretreatment processes described in Sections 6.1 and 6.3** *(6.1 and 6.3 does not even contain a subheading pretreatment processes. A permit writer can not read the full sections 6.1 and 6.3 and pick whatever can be considered as relevant in this context.)* **to treat and sample the incoming materials. See Section 6.3.4.** *(The crossreference to Section 6.3.4 is misleading since this section is not limited to pretreatment processes at all.)* **The chemical treatment methods for some of the products of reactions are shown in Table 6.13.** *This is not correct. Table 6.15 in Section 6.3.4 does not contain chemical treatment methods. Table 6.15 contains abatment techniques for gaseous pollutants such as afterburner, containment, condensation, biofilter, activated carbon, scrubber etc.*

### 6.4.1.2 Pyrometallurgical stages

**a) BAT is to prevent the emissions of lead by using of the copper route for recovering and smelting precious metals if it is viable (see Section 6.3.2 and Section 2.8).** *Crossreference to 2.8 is not helpful: 2.8 consists of 36 subsections and comprises 32 pages. How should a reasonable conclusion be made? The same is valid for Section 6.3.2. This section comprises 12 process steps and contains no usful information to conclude on BAT.*

**b) BAT is to prevent and control emissions of dust, metals, chlorides, sulphur dioxide, acid gases, nitrogen oxides, total organic carbon and PCDD/F from materials pretreatment including incineration and hydrometallurgical processes, roasting, cupelling, thermal refining, and melting for precious metal recovery and optimise the use of energy by using a combination of the pyrometallurgical and abatement techniques given in Section 6.1, Table 6.14, Table 6.15 and Table 6.16 (see also Sections 2.9.2.4.1 and 2.9.2.4.2).**
*It is sufficient to have such a table in section 6.3.2. Here its not needed. Why is the reverberatory furnace not included? Why are hydrometallurgical processes included when they appear separately in Section 6.4.1.3 and furthermore they are not covered by the heading.*

| Technique | Raw Materials | Comments |
|---|---|---|
| Miller furnace | Gold alloy | Temperature control or chlorine metering. Effective collection systems |
| Cupelling furnaces. BBOC | Silver alloys (with Cu, Pb) | Oxygen lancing using reverberatory furnace or BBOC has lower energy use and higher recovery rate |
| Kaldo furnace (TBRC) and TROFF | Mixed concentrates, slimes and secondary materials | With copper/lead materials. Enclosed furnace |
| Blast furnace | Sweeps, Ashes and concentrate | Requires modern control, afterburner and efficient abatement. Acid gas removal may be needed |
| Gas recirculating roaster | Anode slimes | Selenium removal and recovery |
| Rotary furnace | Ashes and concentrate | Oxy fuel used. Efficient fume collection need throughout the process |
| Electric furnace | Ashes and concentrate | Sealed furnace. Through electrode feeding. Gas volumes can be lower |
| Ausmelt/ISA Smelt furnace | Mixed concentrates and secondary materials | With copper/lead materials |

**Table 6.14: BAT for furnaces used in the production of precious metals**

| Process stage | Component in off -gas | Techniques |
|---|---|---|
| Raw materials handling | Dust and metals | Correct storage<br>Dust collection and fabric filter with a bag burst detection system |
| Raw materials pretreatment | Dust and metals | Correct pretreatment<br>Gas collection and fabric filter |
| Sweeps and film incineration | Organic material(1) | Process operation, afterburning, correct gas cooling and fabric filter |
| Roasting and smelting | Dust and metals<br>Carbon monoxide and organic material (1)<br>Sulphur dioxide | Process operation, gas collection, cooling and fabric filter<br>Afterburner, carbon injection<br>Scrubbing |
| Selenium roasting | Dust and metals<br>Sulphur dioxide | Process operation, gas collection, cooling and dust removal<br>Scrubbing and wet ESP |
| Dissolution and chemical refining | Mist, metals and acid gases, $NO_x$ | Process operation and gas collection with oxidising scrubber, SCR, SNCR<br>(See Table 6.13) |
| Distillation | Chlorine, bromine and tetroxides | Enclosed area.<br>Absorber/condenser and scrubber |
| Solvent extraction | VOC and Odour | Containment, condenser<br>Carbon or bio filter |
| Electrowinning | Acid mists | Gas collection and scrubbing/demisting |
| Thermal refining (Miller process) | Dust and metals<br>Chlorine | Process operation.<br>Gas collection, scrubbing and wet ESP |
| Melting, alloying and casting~~.~~ | Dust and metals<br>Organic material(1) | Process operation. Gas collection cooling and fabric filter<br>Process operation, afterburning and correct gas cooling |
| Slag treatment [rr57]and cupelling | Dust and metals | Process operation<br>Gas collection, cooling and fabric filter |

| |
|---|
| ([1]) Organic material can include VOC reported as total carbon (excluding CO) and PCDD/F.<br>*PCDD/F is considered in table 6.2 to be significant. Thus it should appear in the table as in table 6.13.* |

**Table 6.15: BAT for abatement techniques in the production of precious metals**

*If you compare this table with table 6.13 in section 6.3.2 one can see that totally other pollutants are included and some of the process stage have another name what makes it extremely difficult to campare them. The techniques to consider and the BAT techniques are not fully consistant. Why? $NH_3$ from refining in table 6.13 is missing. For distillation chlorine, bromine, tetroxides are included here but not in table 6.13.*

**The emission levels given in Table 6.16 are the BAT-AELs.**

| Pollutant | Techniques | BAT-AELs | Comments |
|---|---|---|---|
| Dust | Fabric or ceramic filter | <1 to 5 mg/Nm$^3$ | A bag burst detection system should be used. (See Sections 2.9.2.2.4 and 2.20.13)<br>Includes the metal content |
| Cu<br>Pb<br>As<br>Cd | Fabric or ceramic filter | <0.3<br><0.2<br><0.01<br><0.001 | The concentration of metals is linked to the concentration of dust and content of the metals in the dust (see Section 6.2.2.1). |
| Chlorides, $SO_2$ and acid gases | Wet or semi-dry alkaline scrubber | $SO_2$ <100 mg/Nm$^3$<br>Chloride <5 mg/Nm$^3$<br>Fluoride <1 mg/Nm$^3$ | REF?? |
| $NO_X$ | Low-$NO_X$ burner or SCR or SNCR or<br>Oxy-fuel burner | <100 to 300 mg/Nm$^3$ | The higher values are associated with oxygen enrichment to reduce energy use. In these cases gas volume and mass emissions are reduced (See Sections 2.9.2.4.3, 2.20.12 and 6.2.2.1.6).*What about 6.3.4.1??? What is the sense of having such a technique included in section 6.3 without referring to it?* |
| Total organic carbon as C | Afterburner.<br>Optimised combustion | 1 to 10 mg/Nm$^3$ | Pretreatment of secondary material is needed to remove organic coatings (See Section 2.9.2.6). |
| PCDD/F | High efficiency dust removal system (i.e. fabric filter) or<br>Afterburner followed by quenchin or<br>Adsorption by activated carbon or<br>Use of an oxidation catalyst | <0.1 ng I-TEQ/Nm$^3$ | (See Sections 2.10.2.1, 2.20.5 and 6.3.4.2) |
| NB: Collected emissions only. BAT-AELs are given as daily averages based on steady-state operation or, in cases where continuous monitoring is not practicable as the average over the sampling period. For PCDD/F, the BAT-AEL is the average over the sampling period which should preferably be a minimum of six hours. $SO_2$ emissions depend on the fuel used. | | | |

**Table 6.16: BAT and BAT-AELs to prevent and control emissions to air from materials pretreatment including incineration and hydrometallurgical processes, roasting, cupelling, thermal refining, and melting for precious metal recovery**

*What about the other pollutants mentioned in table 6.17 and 6.13 such as chlorine, bromine?*
*Why are hydrometallurgical processes included when they appear separately in Section 6.4.1.3?*
*In the existing BREF the BAT-AEL for pyrometalugical and hydrometallurgical processes was clearly distinguished.*

**c) BAT is to prevent and control emissions of metals and sulphur dioxide from the smelter gases produced during precious metal production from raw materials that include sulphidic concentrates using one of the techniques reported in Section 2.11.3.1.**

### 6.4.1.3 Hydrometallurgical stages

**a) BAT is to prevent and control emissions of acid mists and VOC to air and optimise the use of energy by using the hydrometallurgical techniques given in Section 6.1, Table 6.15 and Table 6.16.** *The crossreference to Table 6.17 and 6.18 is misleading. 6.18 does not contain relevant information. Both tables are includede under the subheading "pyrometallurgical stages". This has to be rewritten entirely.*

**The emission levels given in Table 6.16 and Table 6.17 are the BAT-AELs.**

| Pollutant | Techniques | BAT-AELs | Comments |
|---|---|---|---|
| Sulphuric acid mists | Demister or wet scrubber | 10 – 35 mg/Nm³ as $H_2SO_4$ | A demister or water scrubber will allow the collected acid to be re-used (see Sections 2.11.3.1 and 5.3.5.9) |
| VOCs as C | Containment, condenser, carbon or biofilter | <5 mg/Nm³ | (See Section 2.9.2.6) |
| NB: Collected emissions only. BAT-AELs are given as daily averages based on steady-state operation or, in cases where continuous monitoring is not practicable as the average over the sampling period. | | | |

**Table 6.17: BAT and BAT-AELs to prevent and control emissions to air from hydrometallurgical and electrowinning processes in the precious metals sector**

## 6.4.2 Effluent treatment and water re-use

All waste water will be treated to remove solids, metals, oils/tars and absorbed components and will be neutralised. Waste water treatment for precious metals is given in the Section 6.3.6.

**a) BAT for waste water treatment is to use the techniques given in Section 2.20.8 and Section 6.3.6.**
*Crossreferring to Section 2.20.8 is misleading since it does not contain any information relevant for precious metals. Section 6.3.6 does not contain any information at all. Only general remrks can be found which are not helpful in deriving BAT conclusions.*

**The emission levels given in Table 6.18 are the BAT-AELs**.

| BAT-AELs (mg/l) | | | | |
|---|---|---|---|---|
| **Ag** | **Pb** | **Hg** | **Cu** | **Ni** |
| 0.02 | 0.05 | 0.01 | 0.3 | 0.03 |
| BAT-AELs are based on qualified random samples or twenty four hour flow proportional composite samples. | | | | |

**Table 6.18: BAT-AELs for emissions to water**

*If you compare these values with the values from table 6.9 in Section 6.2.2.2 it is unclear how the BAT-AEL have been drived. They are sometimes lower than the lowest value reported and generally exclude higher values.*

# 6.5 Emerging techniques

The 'J' process is not operated in Europe but can operate with a lower inventory of gold compared with other gold refining processes. It uses a regenerable iodine solution to dissolve impure gold (<99.5 %). The gold is reduced by potassium hydroxide, separated, washed and dried to a powder that contains 99.995 % gold. Liquor from the reduction stage is fed to an electrolytic cell where soluble impurities and any unreduced gold iodide are deposited on the cathode and removed for recovery in a precious metals circuit. The solution is then transferred to an electrolytic diaphragm cell fitted with inert electrodes. Iodine solution produced in the anode compartment and KOH solution produced in the cathode compartment are recycled [ 5, B R Lerwill et al. 1993 ].

A process has been designed to treat a pyrite concentrate that contains microscopic gold particles (<1 µm) to produce a gold dore, a lead/silver concentrate and a zinc concentrate [ 210, Greek State 1999 ]. The ore treatment and metallurgical flow sheets are shown below in Figure 6.8 and Figure 6.9.

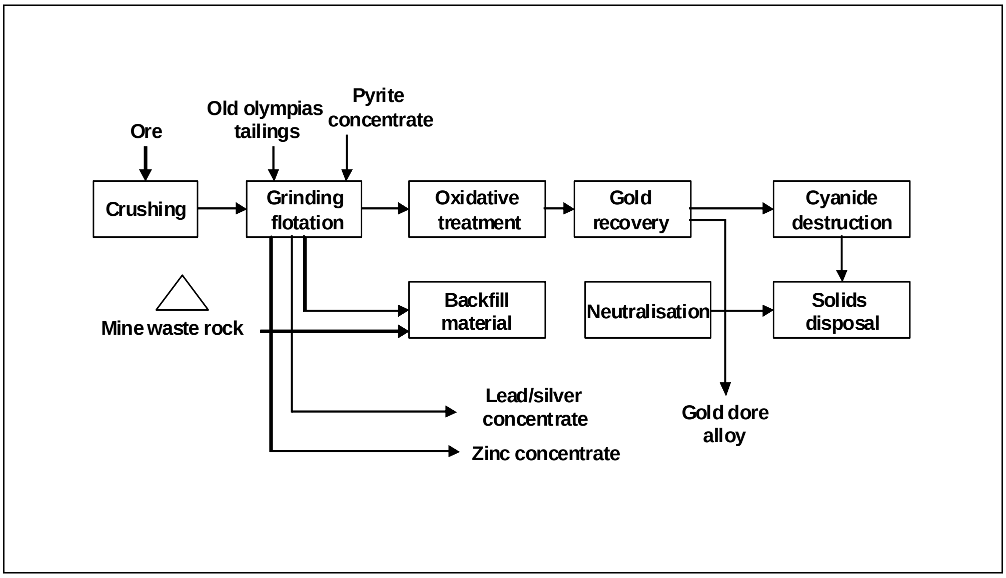


**Figure 6.8: Ore treatment flow sheet**

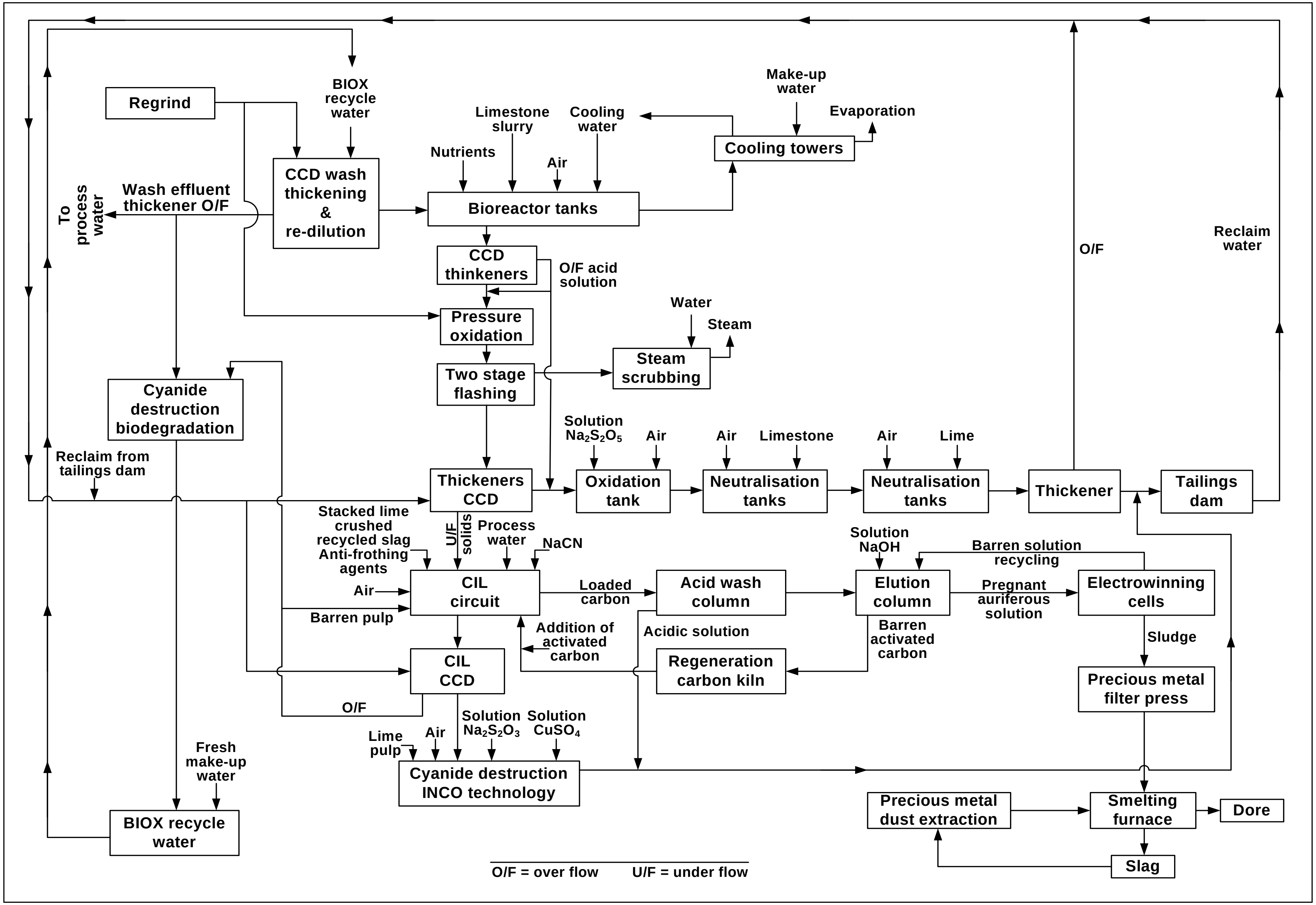


Figure 6.9: Metallurgical process flow sheet

# 7 PROCESSES TO PRODUCE MERCURY

## 7.1 Applied processes and techniques

The market for mercury has declined in recent years and this has had a significant affect on the sector. Primary production from cinnabar ore in Europe has now ceased but production from the mercury content of other non-ferrous processes such as copper, lead and zinc via the sulphuric acid plant scrubber systems continues to be a source of mercury. Secondary mercury production from the treatment of dental amalgam, batteries and lamps is now generally performed as a de-mercurising service to produce mercury free feedstock for precious metal recovery or disposal.

### 7.1.1 Primary production

#### 7.1.1.1 Production from Cinnabar

The production of mercury from Cinnabar ore in Europe has ceased.

#### 7.1.1.2 Production from the ores and concentrates of other metals

A *(there is no other significant source if production from cinnabar is ceased!)* significant source of primary mercury is the mercury recovered during the production of other non-ferrous metals. ~~It has been reported that the mercury content ranges from 0.02 to 0.8 kg per tonne of metal (Cu, Zn or Pb) [ 117, Krüger, J. 1999 ].~~ These processes remove mercury from the roaster or smelter gas streams prior to the production of sulphuric acid and are described in Section 2.9 and in the sections for the production of these metals *(they should be included either in 2.9 or in the specific metal sections)* [ 25, OSPARCOM 1996 ]. It should noted that any mercury that is not captured by the removal stage will be found in the sulphuric acid that is produced; most processes achieve <0.1 – 0.5 ppm of mercury in sulphuric acid. Mercury is normally recovered from the residues produced from the various scrubbing processes [ 117, Krüger, J. 1999 ].

*Question: In 5.2.4 is mentioned that:*
*Because of the restrictions in mercury use, mercury recovery from Hg-Se residues or from calomel from the mercury removal stage, is no longer an option. Both by-products need to be stabilised for final disposal. In exceptional cases when the Se to Hg ratio is high, recovery of selenium can be an option.*
*Does this mean there is no production of mercury from other metals either?*

### 7.1.2 Secondary production

Several companies operate mercury recovery systems using dental amalgam and silver oxide batteries as the raw material [ 15, HMIP (UK) 1994 ]. These are usually delivered in drums to a reception cupboard that has fume extraction. Batteries and pastes are loaded into suitable receptacles to fit the furnace retort. The temperature of the retort is raised to 700 °C by indirect heating and a vacuum of ~100 mm mercury is applied driving off the mercury from the complex substrate. Heating cycles last up to 18 hours. Gases pass through a steel condenser and a sealed cooling system is used. Mercury is condensed into sealed pots and transferred periodically to storage.

The vacuum can be produced by a variety of means for example a water ejector and a water ring pump can be used which allows wet feed material to be used. Vacuum pumps discharge to a scrubber system to remove mercury.

### 7.1.3 Process description of vacuum distillation for mercurial waste

*This is an example for 7.1.2. The new heading is not needed. Delete. If this example is completed by information according to the 9 headings of the techniques to consider section it could be relocated to 7.3.x. But for this data have to be provided about dust and Hg emissions concentrations and example plants should be reported.*

**Mercury distillation unit**

Mercury waste (>2000 ppm) can be treated in a distillation unit in order to recover metallic mercury. The waste material is fed into a dome under vacuum conditions and the dome is then filled with nitrogen. The waste is heated to a temperature of 600 °C, so that the mercury evaporates. The vapour is incinerated after the addition of oxygen at a temperature of 800 °C, to remove possible organic substances. The pure mercury vapour is then condensed at about 6 °C. An activated carbon filter impregnated with sulphur components is used to purify the air from the treatment process. The recovered material is 99.85 % pure Hg and is re-used in the chemical industry. (See Figure 7.1).

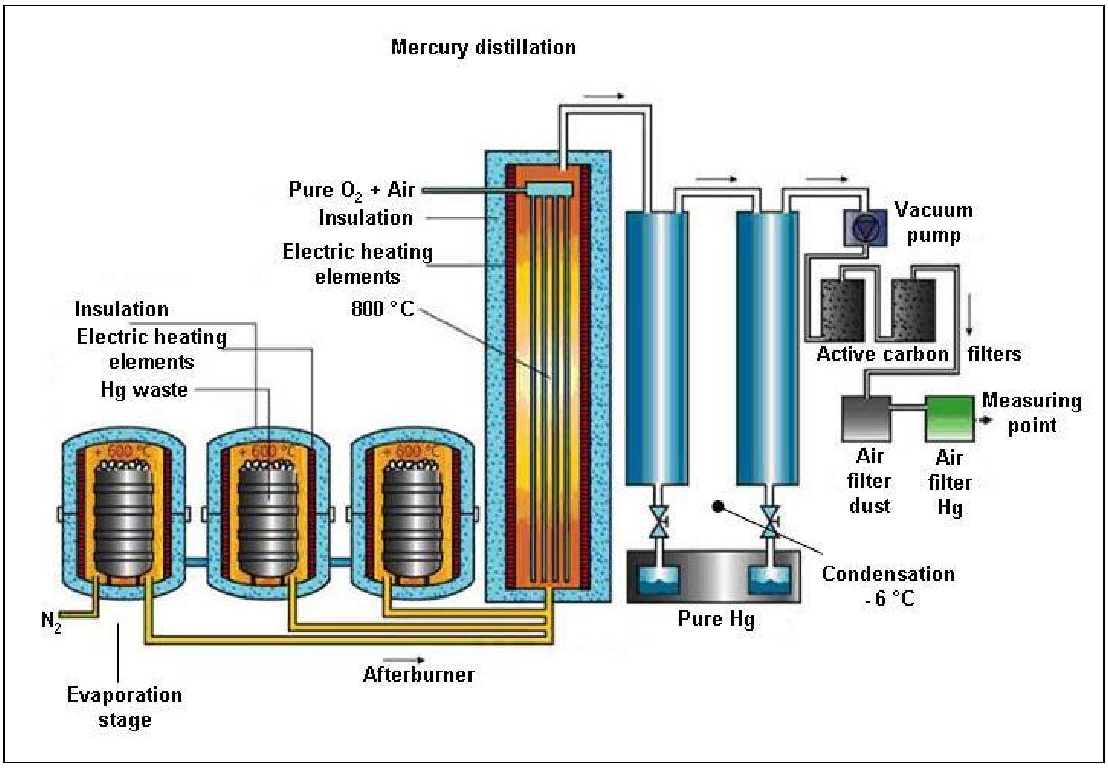


Figure 7.1: Mercury waste recovery process

## 7.2 Current emission and consumption levels

Emission and consumption data for other non-ferrous metal processes that also produce mercury are given in the relevant chapters on copper and zinc/lead. It has been reported that the mercury content ranges from 0.02 to 0.8 kg per tonne of metal (Cu, Zn or Pb) [ 117, Krüger, J. 1999 ]. ~~These processes generally produce mercury or calomel in the range 0.02 to 0.8 kg of mercury per tonne of metal produced depending on the mercury content of the concentrate [ 117, Krüger, J. 1999 ].~~ The key environmental issues for the production of mercury are: mercury vapour, dust, fume, odours, $SO_2$, other acid gases, waste water, residues such as sludge, filter dust and slag.

Regulation EC 1102/2008 classifies mercury and mercury compounds produced during the production of non-ferrous metals as waste effective 15 March 2011.

### 7.2.1 Process residues such as wastes and b~~B~~y-products~~, process residues and waste~~

The production of metals is related to the generation of several by-products, residues and wastes, which are also listed in the European Waste Catalogue (Council Decision 94/3/EEC). *This has been replaced by a new directive 75/442/EEC (see Section 5.2.4)*

Sludges from the waste water treatment process for both primary and secondary production contain mercury sulphide or calomel. For primary production, this material is pelletised and returned to the furnace to recover the mercury. For secondary purposes this is not always possible and small quantities are disposed of.

## 7.3 Techniques to consider in the determination of BAT

The sections of this document entitled 'Techniques to consider in the determination of BAT' set out techniques considered generally to have potential for achieving a high level of environmental protection in the industries within the scope of the document. The background to the way the techniques are described is given in Section 2.1.2 and Table 2.2.

This section presents a number of techniques for the prevention or reduction of emissions and residues as well as techniques for reducing the overall energy consumption. They are all commercially available. Examples are given in order to demonstrate techniques which illustrate a high environmental performance. The techniques that are given as examples depend on information provided by the industry, European Member States and the valuation of the European IPPC Bureau. The general techniques described in Chapter 2, common processes, apply to a large extent to the processes in this sector and influence the manner in which the main and associated processes are controlled and operated.

The processes described above are limited in range and represent the technology that is used worldwide. They therefore constitute the techniques to consider in the determination of BAT. However, there are several techniques used by the other non-ferrous metal processes to reduce the emissions of mercury and these techniques are also applicable to the production of mercury from primary and secondary raw materials. The techniques to consider that are described in Chapter 2 'common processes' also apply to the raw material handling, pretreatment, process control and abatement systems. The hierarchy of prevention, containment and collection/abatement should be followed as far as possible.

For the production of mercury from secondary raw materials, e.g. batteries, the small scale of the process allows equipment to be contained and the gases to be condensed and scrubbed.

### 7.3.1 Gas collection and abatement

Mercury is volatile at the temperatures encountered in most abatement processes and other techniques are therefore used to remove it [ 25, OSPARCOM 1996 ]. Techniques described in Section 2.9 *(Section 2.9 comprises much more than techniques to treat mercury. Nevertheless this crossreference is not helpful and not sufficient) In Section 2.9.2.8 nine processes are described where Hg occurs and how it can be reduced. I suggest to relocate this section here and improve the hole section according to the requirements of IED)* . are used as part of the gas-cleaning train of a sulphuric acid plant when there are trace concentrations of mercury in copper, zinc and lead smelter gases. The techniques are:

Boliden/Norzink process.
This based on a wet scrubber using the reaction between mercuric chloride and mercury vapour to form mercurous chloride (calomel), which precipitates from the liquor. Mercuric chloride can be regenerated from the calomel in a chlorination stage and mercury can be recovered by electrolysis. The process is reported to have the lowest capital and operating costs [ 136, Fugleberg, S. 1999 ]. Mercuric chloride is a very toxic compound of mercury and great care is taken when operating this process.

Sodium thiocyanate process.
A wet scrubbing process to precipitate mercury sulphide. Sodium thiocyanate is regenerated.

Outotec process.
Gases are washed with 90 % sulphuric acid in a packed tower to produce mercury sulphate, which is precipitated and removed for recovery. This process also removes selenium.

Systems based on the reaction between mercury and selenium are encountered but selenium is also toxic and great care is needed with the disposal of materials. The Outotec process removes both mercury and selenium using a sulphuric acid scrubber [ 45, Svens, K 1985 ]. Both metals can be recovered from the precipitate that is formed. The sodium thiosulphate scrubber is also very effective and uses a reactor/scrubber similar to the Boliden Norzink process.

The Boliden-Norzink process
~~This~~ is the most widely used technique for removing mercury from emissions to air. The production of calomel from mercuric chloride is straightforward but several processes stop at this stage and accumulate calomel. This is due to the falling price of mercury, which inhibits mercury recovery. The process is capable of achieving emissions in the range of 0.05 - 0.1 mg/Nm$^3$ mercury in air.

Activated carbon filter.
An adsorption filter using activated carbon is used to remove mercury vapour from the gas stream.

The activated carbon filter is used in a number of industries to reduce mercury emissions. The breakthrough of mercury from the filter is not easy to predict and consequently a double filter is used with the second filter dealing with the breakthrough. When the first filter is exhausted, it is charged with fresh carbon and the second filter becomes the lead unit. Carbon can be regenerated using the Herreshoff furnace and the mercury recovered. Activated carbon filters are capable of mercury concentrations of 0.002 - 0.007 mg/Nm$^3$ provided the double filter arrangement is used.

### 7.3.1.1 Boliden-Norzink process

**Description**
The gas is scrubbed in a packed bed tower with a solution of $HgCl_2$. This reacts with the metallic mercury in the gas and precipitates it as calomel, $Hg_2Cl_2$:

$$HgCl_2 + Hg \Rightarrow Hg_2Cl_2$$

The calomel is removed from the circulating scrubbing solution and partly regenerated by chlorine gas to $HgCl_2$, which is then recycled to the washing stage. The mercury product bleed is either used for mercury production or stored. In the Norzink process, part of the precipitate, the calomel, is electrolysed to give metallic mercury and chlorine gas which is reacted with the rest of the calomel to produce the reagent, $HgCl_2$, used in the scrubbing.

An alternative process uses sodium thiocyanate as the scrubbing medium and mercury is precipitated as the sulphide. This can be recovered in a primary mercury roaster.

**Achieved environmental benefits**
The removal of mercury from gases to 0.05 to 0.1 mg/Nm$^3$.
*(The achieved value in section 2.9.2.8 is 0.02 mg/Nm3.)*

**Cross-media effects**
Energy use for operating the scrubber.

**Operational data**
For a plant producing copper with a mercury input in the order of 400 ppm, sulphuric acid is produced with ~ 0.1 mg/l (ppm) of mercury in the acid. This corresponds to about 0.05 to 0.1 mg/Nm$^3$ in the feed gas to the acid plant.
*(The achieved value in section 2.9.2.8 is 0.02 mg/Nm3.)*
**Applicability**

This technique is applicable to most mercury removal systems depending on the reagent used.

**Economics**
Some cost data published indicate that the Boliden-Norzink process (and probably also the Bolchem process) had an investment cost of USD 200000 for about 200000 t/yr acid in 1972. The operating costs published were EUR 0.25 /tonne for the Boliden-Norzink process (1985).

**Driving force for implementation**
Prevention of mercury emissions and improved acid quality.

**Example plants**
Germany, Finland, Sweden

**Reference literature**
[ 136, Fugleberg, S. 1999 ].

### 7.3.2 Waste water

Effluents arise from scrubbing and vacuum systems and from spillage and surface run-off. Mercury is universally removed from aqueous effluents by precipitation as mercury sulphide. Sodium sulphide is used as the reagent and the pH of the effluent is controlled. Mercury sulphide is not soluble and is precipitated. Activated carbon is also used to remove final traces of mercury from effluents. Emissions to water of 0.05 mg/l are easily achievable provided that solids are removed efficiently. In some cases, sand filters are used for this purpose. Sludges and spent carbon from primary mercury production are returned to the furnaces [ 69, Mercury Expert Group et al. 1998 ].

Another main effluent stream arises from the removal of mercury from some roaster off-gases. The mercury removal step involves a gas-liquid contact tank with a solution of mercury chloride ($HgCl_2$). This mercury chloride reacts with metallic mercury from the gas to form a solid $Hg_2Cl_2$ precipitate (calomel). The precipitated slurry is removed and oxidised with $Cl_2$ to form a new $HgCl_2$ washing solution. Some of the slurry is dewatered by a filter press and sold as $Hg_2Cl_2$ for mercury recovery or disposed of as a special waste.

Effluents from the process are pretreated locally for mercury removal by reaction with zinc dust or by precipitation as HgS before processing in a final effluent treatment plant. Mercury sulphide can be recovered in the primary process.

~~http://www.facebook.com/photo.php?pid=3372871&id=704869607~~

# 7.4 Best Available Techniques

In understanding this section and its contents, the attention of the reader is drawn back to the Preface of this document and in particular the fifth section of the Preface: ‘How to understand and use this document’. The techniques and associated emission and/or consumption levels, or ranges of levels, presented in this chapter have been assessed through an iterative process involving the following steps:

- identification of the key environmental issues for the sector which for the production of mercury are: mercury vapour, dust, fume, odours, $SO_2$, other acid gases, waste water, and residues such as sludge, filter dust and slag;
- examination of the techniques most relevant to address these key issues;
- identification of the best environmental performance levels, on the basis of the available data in the European Union and worldwide;
- examination of the conditions under which these performance levels were achieved; such as costs, cross-media effects, and the main driving forces involved in implementation of the techniques;
- selection of the best available techniques (BAT) and the associated emission and/or consumption levels for this sector in a general sense, all according to Article 2(12) and Annex IV to the Directive.

Expert judgement by the European IPPC Bureau and the relevant Technical Working Group (TWG) has played a key role in each of these steps and in the way in which the information is presented here.

On the basis of this assessment, best available techniques, and as far as possible emission and consumption levels associated with their use, are presented in this section that are considered to be appropriate to the sector as a whole and in many cases reflect the current performance of some installations within the sector. Where emission and consumption levels 'associated with best available techniques' are presented, this is to be understood as meaning that those levels represent the environmental performance that could be anticipated as a result of the application, in this sector, of the techniques described, bearing in mind the balance of costs and advantages inherent within the definition of BAT. However, they are neither emission nor consumption limit values and should not be understood as such. In some cases, it may be technically possible to achieve better emission or consumption levels but due to the costs involved or cross-media considerations, they are not considered to be appropriate as BAT for the sector as a whole. However, such levels may be considered to be justified in more specific cases where there are special driving forces.

The emission and consumption levels associated with the use of BAT have to be seen together with any specified reference conditions (e.g. averaging periods).

The concept of ‘levels associated with BAT’ described above is to be distinguished from the term ‘achievable level’ used elsewhere in this document. Where a level is described as ‘achievable’ using a particular technique or combination of techniques, this should be understood to mean that the level may be expected to be achieved over a substantial period of time in a well maintained and operated installation or process using those techniques.

Where available, data concerning costs have been given together with the description of the techniques presented in the previous sections. These give a rough indication about the magnitude of the costs involved. However, the actual cost of applying a technique will depend strongly on the specific situation regarding, for example, taxes, fees, subsidies, and the technical characteristics of the installation concerned. It is not possible to evaluate such site-specific factors fully in this document. In the absence of data concerning costs, conclusions on economic viability of techniques are drawn from observations on existing installations.

The BAT (including the associated emission and consumption levels) given in this section are 'BAT in a general sense' (i.e. considered to be appropriate to the sector as a whole). It is intended that they are a reference point against which to judge the current performance of an existing installation or to judge a proposal for a new installation. In this way, they will assist in the determination of appropriate 'BAT-based' conditions for the installation or in the establishment of general binding rules under Article 9([8]) of the IPPC Directive. It is foreseen that new installations can be designed to perform at or even better than the BAT levels presented in this section. It is also considered that existing installations could move towards the BAT levels presented in this section or do better, subject to the technical and economic applicability of the techniques in each case.

While the BAT reference documents do not set legally binding standards, they are meant to give information for the guidance of industry, Member States and the public on achievable emission and consumption levels when using specified techniques. The appropriate permit conditions for any specific case will need to be determined taking into account the objectives of the IPPC Directive and the local considerations.

**Recommendation to help users/readers of this document:**

It is strongly recommended that this section on BAT be read in conjunction with the sections of this document that describe the techniques to consider in the determination of BAT. The applicability of the techniques and measures are reported in these sections and should be taken into account at a local level. To help the reader, references to the appropriate sections are included in the description of BAT.

If not otherwise mentioned, BAT associated emission and consumption levels given in this section are expressed as follows:

- for pollutants emitted to air (except dioxins): expressed on a daily average basis with standard conditions of 273 K, 101.3 kPa, measured oxygen content and dry gas with the plant operating normally under steady-state conditions and no dilution of the gases;
- for dioxins: expressed as the average over the sampling period which should preferably be a minimum of 6 hours;
- for waste water: based on qualified random samples or 24 hour flow proportional composite samples.

As described in the Preface, this document does not propose emission limit values. The best available techniques and the ranges of emission or consumption levels associated with best available techniques (BAT-AEL ranges) are related to installations with different sizes, different kinds of operation and different raw materials. In this document, special local considerations cannot be taken fully into account. The determination of appropriate permit conditions will involve taking account of local, site-specific factors such as the technical characteristics of the installation concerned, its geographical location and the local environmental conditions. In the case of existing installations, the economic and technical viability of upgrading them also should be taken into account. Even the single objective of ensuring a high level of protection for the environment as a whole will often involve making trade-off judgements between different types of environmental impact, and these judgements will often be influenced by local considerations.

Although an attempt is made to address some of these issues, it is not possible for them to be considered fully in this document. The techniques and emission and consumption levels presented here will therefore not necessarily be appropriate for all installations. On the other hand, the obligation to ensure a high level of environmental protection including the minimisation of long-distance or transboundary pollution implies that permit conditions cannot be set on the basis of purely local considerations. It is therefore of the utmost importance that the information contained in this document is fully taken into account.

Section 2.20 to this document reports BAT for the following common processes and the following sections should be referred to for those techniques that are BAT:

- environmental management systems (EMS) (Section 2.20.1)
- material handling and storage (Section 2.20.2)
- process control (Section 2.20.3)
- fume and gas collection (Section 2.20.4)
- the prevention and the destruction of PCDD/F (Section2.20.5)
- sulphur dioxide removal (Section 2.20.6)
- the removal of mercury (Section 2.20.7)
- effluent treatment and water re-use (Section 2.20.8)
- energy efficiency (Section 2.20.9)
- intermediate products, process residues and wastes (Section 2.20.10)
- emission monitoring (Section 2.20.11)
- prevention of the formation of $NO_X$ (Section 2.20.12)
- removal of dust and particles (Section 2.20.13)

BAT for the production of mercury is the combination of the generally applicable techniques reported in Section 2.20 and the specific techniques indicated in this section.

*I doubt that all of the aforementioned bullets are relevant for mercury production. Only relevant crossreferring to chapter 2 sections should be included.*

### ~~7.4.1.1~~7.4.1 Fume and gas collection and abatement systems

**a) BAT is to prevent and control emissions of mercury by using the techniques listed in Table 7.1 and Table 7.2 or a combination of them.**

| Process Stage | Abatement option | Component in the off-gas |
|---|---|---|
| Handling secondary material | Enclosed handling, scrubbing of ventilation gases | Dust, Hg vapour from handling free Hg and dried material |
| Product handling | Enclosed filling station, scrubbing of ventilation gases | Hg vapour. Depends on gas collection from furnace and launders |

**Table 7.1: BAT for the abatement techniques for components in the off-gas**

**The emission level given in Table 7.2 is the BAT-AEL.**

| Pollutant | Techniques | BAT-AEL | Comments |
|---|---|---|---|
| Mercury | Mercury scrubber (Boliden, thiosulphate, etc.) | <0.02 mg/Nm³ | See Section 2.20.7 for the full range of techniques |
| NB: Collected emissions only. BAT-AELs are given as daily averages based on steady-state operation or, in cases where continuous monitoring is not practicable as the average over the sampling period. | | | |

**Table 7.2: BAT and BAT-AELs to prevent and control emissions to air from secondary production and production from base metals associated with the use of BAT in the mercury sector**

### 7.4.2 Effluent treatment and water re-use

The emissions to water are based on a bleed from the scrubber and cooling systems.

**a) BAT is to precipitate mercury as mercury sulphide by neutralising the waste water, treating it with sodium sulphide and passing the water through a carbon filter before discharge (see Section 7.3.2).**

**The emission level of mercury to water of <50 µg/l as mercury is the BAT-AEL.** For waste water emissions, the BAT-AELs are based on qualified random samples or twenty four hour flow proportional composite samples.

### 7.4.3 By-products, process residues and waste

In any case, the provisions of regulation EC 1102/2008 on the banning of exports of metallic mercury and certain mercury compounds and mixtures and the safe storage of metallic mercury shall be complied with.

## 7.5 Emerging techniques

No techniques were reported.

# 8 REFRACTORY METALS

Refractory metals are high melting point metals that are characterised by other special physical and chemical properties, such as high density, inertness, corrosion and acid resistance, etc. Zirconium even has the ability to capture slow neutrons, which gives this metal an important role in nuclear power reactors. Refractory metals are produced both as metal ingot (buttons) by using electron beam furnaces and as metal powder that serves as raw material for powder metallurgical treatments like pressing and sintering.

## ~~8.1~~Applied processes and techniques

The following sections will define the applied processes and techniques for the production of the most common and most important refractory metals. The production of ferro-alloys, which normally contain the same metals are discussed in detail in the Chapter 9 of this document.

### 8.1.1 Chromium

Besides the use of chromium as an alloying element in the steel industry, chromium metal is also widely used in other industrial sectors. In the chemical industry, for instance, chromium is needed in large quantities to manufacture pigments that are used to produce paints and inks. Another considerable amount of chromium is consumed as an electroplated protective coating, because chromium is corrosion-resistant to a variety of corrosive materials at room temperature.

Chromium metal can either be made from chromite ore and concentrates by carbothermic and metallothermic reductions or by electrolysis from chromic acid. In order to get chromic acid, the chromite ore is roasted with sodium carbonate followed by a leaching process with sulphuric acid to produce sodium chromate that can further be transformed to chromic acid.

*This should be clearer described. Usually there are two major production processes for chromium: electrolytic and aluminothermic reduction (a special kind of metallothermic reduction). Check whether carbuthermic reduction is applied for chromium.*

#### 8.1.1.1 Production of chromium metal by metallothermic reduction

The thermic process uses carbon, silicon or aluminium as a reducing agent. The charge is automatically weighed and loaded into a bin at a computerised weighing station. The station utilises various abatement techniques to prevent airborne emissions. Once the charge is complete, the bin is taken to an enclosed room to mix the contents. To minimise dust in the workplace, a negative pressure is maintained by the ventilation fan within the blender room, which feeds through a filter unit to the atmosphere. The bin is finally located on an automatic feed platform at the firing station.

The firing pot is prepared by ramming refractory sand around a central former. Sand is fed from a storage hopper via a sand slinger and mixed with water. The pot is then vibrated in order to compact the sand. The feed hopper is fitted with an integral dust extraction and filter unit.

After ramming the firing pot, the inner surface is coated with a weak binder solution and dried under a gas-fired hood before being transferred to the firing station. Combustion fumes from the drying hood are fed via a stack to the atmosphere using natural convection.

The firing pot is located inside a firing chamber, which has a travelling fume hood, and an integral feed chute above it. The raw material mix is automatically fed at a controlled rate into the firing pot, where the exothermic reaction takes place. Fumes generated by the reaction are ducted to the main fabric filter plant. After the evolution of fume has subsided, a reduced volume of extraction is provided to the firing chamber.

When the metal has solidified following the reaction, the firing pot is removed and transferred by crane to a cooling conveyor. This *(What? The pot or the cooling conveyor?)* is partially enclosed by a hood and is ventilated by a number of extraction fans, which discharge to the atmosphere outside the building. Disposable fibreglass filter panels protect the fan inlets.

On removal from the cooling conveyor (by crane), the firing pot is placed on a stripping bogie for transferral to a stripping booth. Inside the closed booth, the pot casing is hoisted off the solidified metal/slag. Debris from the pot lining falls into a hopper and is transferred to a vibratory sieve. Cartridge filter extraction units control emissions during these operations.

The stripped metal/slag and firing pot casing are retrieved by means of the stripping bogie. The firing pot casing is removed and returned to the pot preparation station for re-use. The slag is separated from the chromium metal 'button' and sent to a dispatch storage area. The button is lifted by crane from the stripping bogie and transferred to a bosh tank where water is used to reduce the button temperature to below 100 ºC. Extraction of the steam generated by boshing is by means of a fan and ductwork which discharges to the atmosphere outside the building.

After cooling, the metal button is transferred to other departments on site for cleaning, breaking, crushing and grinding to achieve the desired product size. Packaging of the material is carried out in accordance with customer requirements and may utilise FIBCs, drums and plastic bags. A process flow sheet of the production of chromium by the metallothermic process is presented in Figure 8.1.

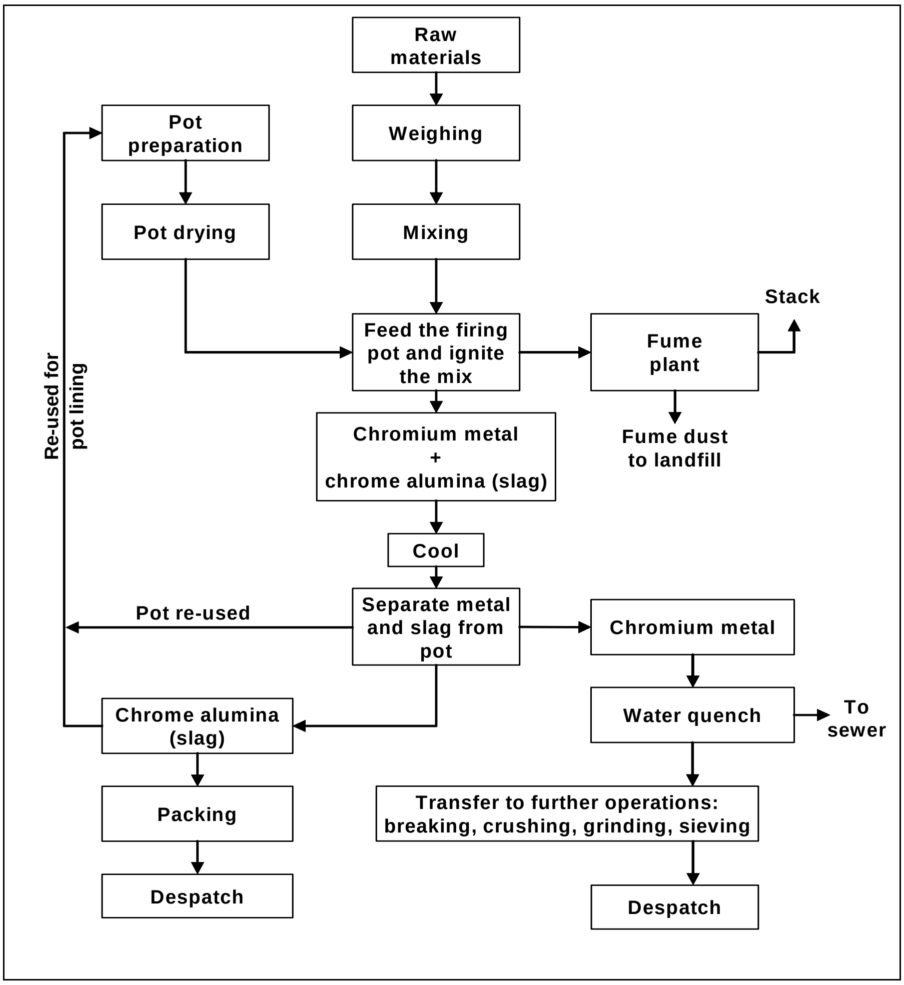


**Figure 8.1:** **Production of chromium metal by the metallothermic process**

The silicothermic reduction is not sufficiently exothermic to be self-sustaining and must therefore be performed in an electric arc furnace. If the carbothermic process is used, the chromium oxide will be reduced by carbon in an electric arc furnace. The chromium metal produced by this process contains high amounts of carbon.

### 8.1.1.2 Production of chromium metal by electrolysis

In the electrolytic process, high carbon ferrochrome is normally used as the feed material which is then converted into chromium alum by dissolution with sulphuric acid at temperatures at about 200 ºC. After several process steps using crystallisation, filtration and ageing, a second filtration and a clarifying operation produces alum which becomes the electrolyte for a diaphragm cell. The process is very sensitive, however, to a number of parameters, the most important being pH, catholyte temperatures, catholyte recirculation and density, current density and cathode preparation [ 7, St. Barbara Consultancy Services 1993 ]. Figure 8.2 presents a schematic process flow sheet of the production of chromium metal by electrolysis.

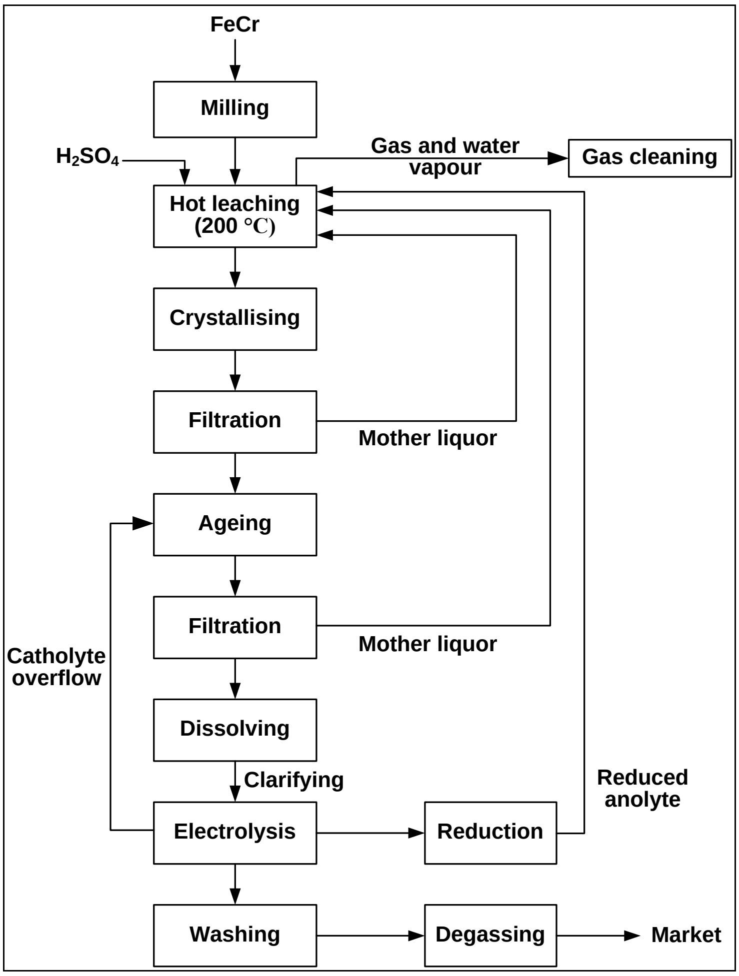


**Figure 8.2: Production of chromium metal by electrolysis**

The additional degassing stage is necessary because the carbon content of the electrolytic chromium is sometimes too high for further industrial applications. The cooled chromium metal is fragmented with a breaker prior to crushing and drumming. The generated slag can be re-used as refractory lining or sold as abrasive or refractory material. *Where and how slag is generated? During electrolysis?)*

### 8.1.2 Manganese

*As far as I know Manganese is not considered to be a refractory metal. See [513]*

Manganese metal is mainly used in the iron, steel and aluminium industry. In aluminium production for instance, manganese is used as an alloying element improving the product hardness. For the production of pure manganese metal, several processes are known [ 104, Ullmann's Encyclopedia 1996 ]:

- electrolysis of aqueous manganese salts
- electrothermal decomposition of manganese ores
- silicothermic reduction of manganese ores or slag
- aluminothermic reduction of manganese ores or slag
- distillation of ferro-manganese
- electrolysis of fused salts.

From the processes listed above, the first two are the most important ones. The other processes are not economically significant.

#### 8.1.2.1 Electrolysis of aqueous manganese salts

*(For me both 8.1.2.1 and 8.1.2.2 are Electrothermical processes)*

The production of manganese metal by the electrolysis of aqueous manganese salts requires at first a milling of the manganese ore. Milling increases the active surface and ensures sufficient reactivity in both the reduction and the subsequent leaching steps. After milling, the manganese ore is fed to a rotary kiln where the reduction and calcination takes place. This process is carried out at about 850 - 1000 ºC in a reducing atmosphere. As a reducing agent, several carbon sources can be used, e.g. anthracite, coal, charcoal and hydrocarbon oil or natural gas. The calcined ore should be cooled to below 100 ºC to avoid a further re-oxidation.

The subsequent leaching process is carried out with recycled electrolyte, mainly sulphuric acid. After leaching and filtration, the iron content is removed from the solution by oxidative precipitation and the nickel and cobalt are removed by sulphide precipitation. The purified electrolyte is then treated with $SO_2$ in order to ensure the plating of γ-Mn during electrolysis. Electrolysis is carried out in diaphragm cells [ 7, St. Barbara Consultancy Services 1993 ]. The cathode is normally made of stainless steel or titanium. For the anode, lead-calcium or lead-silver alloy can be used. After an appropriate reaction time, the cathodes are removed from the electrolysis bath. The manganese that is deposited on the cathode starter-sheet is stripped off mechanically and then washed and dried. The metal is crushed to produce metal flakes or powder or is granulated, depending on the end use.

#### 8.1.2.2 Electrothermal decomposition of manganese ores

The electrothermal process is the second most important process to produce manganese metal on an industrial scale. The electrothermal process takes place as a multistage process. In the first stage manganese ore is smelted with only a small amount of reducing agent in order to reduce mostly the iron oxide. This produces a low grade ferro-manganese and a slag that is rich in Mn oxide. The slag is then smelted in the second stage with silicon to produce silico-manganese. The molten silico-manganese can be treated with liquid slag from the first stage to obtain relatively pure manganese metal. For the last step, a ladle or shaking ladle can be used. The manganese metal produced by the electrothermal process contains up to 98 % of Mn.

### 8.1.3 Tungsten

Tungsten is the refractory metal with the highest melting point which is due to the extremely high bonding energy. This consequently leads to other extended properties, such as a very low vapour pressure, compressibility and thermal expansion.

Tungsten is used for a variety of different industrial applications. According to the amount of metal required, tungsten is mainly used to produce hard metal and metal carbide powder that can further be treated by powder-metallurgical methods to produce hard metal tools. Tungsten is also consumed in considerable amounts as an alloying element in the steel industry. Another major field is the use of tungsten as an alloying element with other non-ferrous metals and as tungsten compounds in the chemical industry.

The high melting point of tungsten precludes the use of smelting techniques. Beneficiated ores and concentrates are therefore processed by hydrometallurgy using acid or alkaline digestion to produce an intermediate, chemically-refined salt. This is then calcined to oxide and reduced to metal powder. Powder metallurgy techniques, in particular compacting and sintering are then employed, followed by a range of fabrication processes including extrusion, forging and rolling. Carburisation of metal powder to form tungsten carbide may be further cemented with cobalt to form hard metal [ 7, St. Barbara Consultancy Services 1993 ]. Due to the available raw materials, tungsten can either be made from primary or secondary materials. A typical tungsten flow sheet is presented in Figure 8.3.

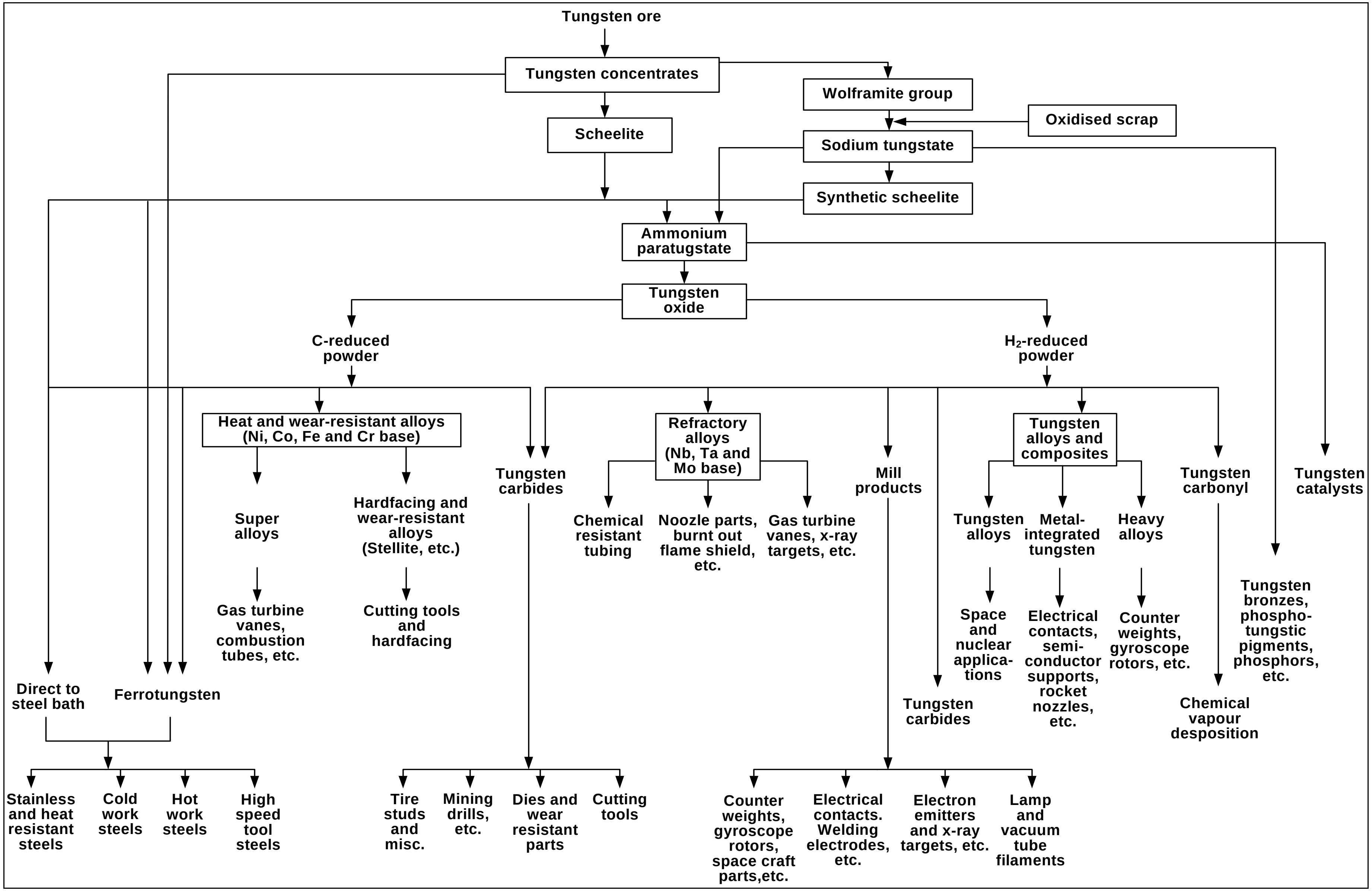


**Figure 8.3:** **Tungsten flow sheet**
[ 7, St. Barbara Consultancy Services 1993 ]

### 8.1.3.1 Production of tungsten metal powder from primary raw material

The first step for the production of tungsten, which is normally carried out directly at the mining site, is crushing and milling of the raw material in order to liberate the tungsten mineral from the gangue material. The next stage is the production of ammonium paratungstate (APT) by hydrometallurgical methods.

The Scheelite and Wolframite concentrates that are mostly used are dissolved by pressure leaching to produce a sodium-tungsten solution. The leaching process also dissolves other elements such as silicates, thiomolybdate as well as elements like As, Sb, Bi, Pb and Co that need to be removed from the solution by purification. Thiomolybdate can further be used for molybdenum production. The purified sodium tungstate solution is then converted into ammonium tungstate solution. The conversion of the sodium tungstate solution can be carried out either by a solvent extraction or an ion exchange process. In the subsequent crystallisation step, the water and ammonia are distilled. At the same time as the distillation takes place, the pH value decreases and the APT crystallises out of the solution. The solid APT is then calcined commonly in a rotary kiln in order to obtain tungsten oxides.

The two oxidic forms utilised for tungsten powder production are yellow and blue oxides ($WO_3$ and $W_4O_{11}$). Yellow oxide is produced by heating APT in air at temperatures above 250 °C. Blue oxide can be produced if the calcining step is carried out with the exclusion of air at temperatures from 400 to 800 ºC. The production of blue oxide is usually preferred, because a smaller amount of reducing agent is then required in the subsequent reduction stage and so the production costs are lower.

The reduction of tungsten oxides (blue or yellow tungsten oxide) to tungsten metal powder is normally carried out by hydrogen reduction. For the reduction, either a rotary furnace or a pusher furnace is used, in the latter case the powder passes through the furnace in boats. Modern automated band furnaces are also used for the production of tungsten powder. Hydrogen passes countercurrently to the oxides through the furnace, water vapour is formed in the reduction process in the furnace. The hydrogen is partly recirculated. Possible occurring dust is recovered by, e.g. a fabric filter, wet scrubber or similar equipment. The important process parameters are the furnace temperature, the amount of oxides charged to the furnace per unit time, the rate of hydrogen circulation and the depth and the porosity of the bed or boat. The process of producing tungsten metal powder is presented in Figure 8.4.

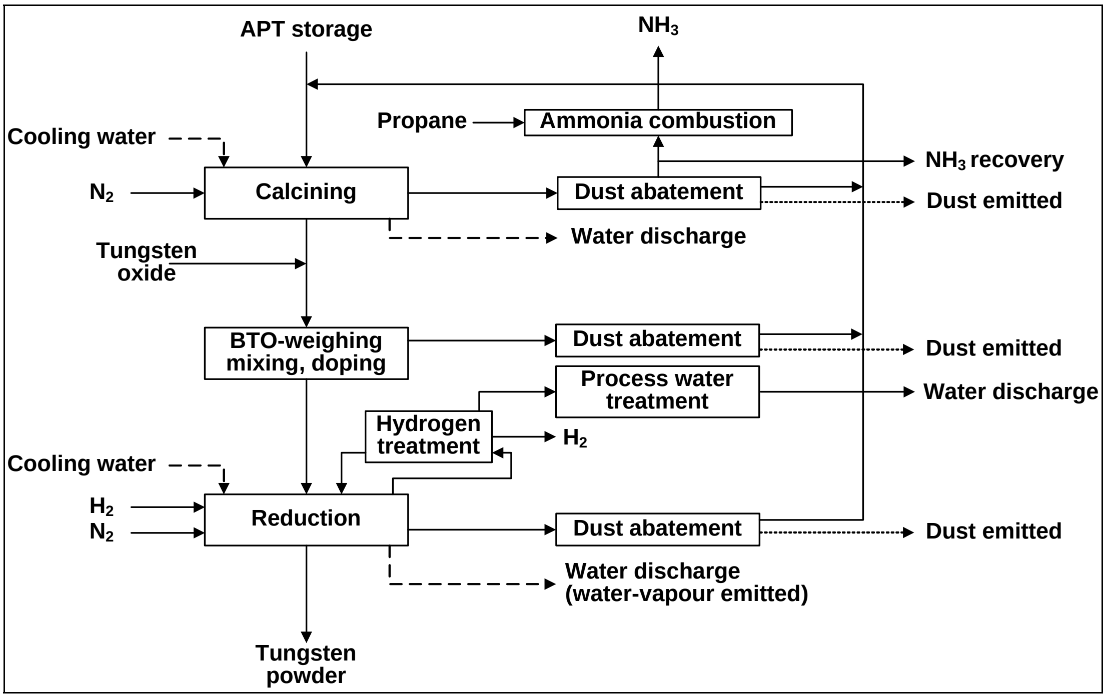


**Figure 8.4: Production of tungsten metal powder**
[ 179, ITIA 1999 ].

*What is BTO? Blue tungsten oxide?? Glossary !!!*

Most of the tungsten powder is converted to tungsten carbide. The tungsten powder is mixed with black carbon in the correct ratio to produce the monocarbide after the reaction. The following furnaces can be used for the carburisation.

- Pusher furnace:
  The mixture of tungsten and carbon is charged into graphite boats or crucibles and passes through the furnace continuously. Hydrogen is used as a protective atmosphere and passes through the furnace countercurrently and is flared off after exit using a propane flare as ignition control. The furnaces are electrically heated and operate in the temperature range of 1100 - 2000 ºC.
- Batch furnace:
  The mixture of tungsten and carbon is loaded into paper cylinders or other suitable-container and densified by tapping. The material is heated by induction in a water-cooled coil with hydrogen as protective atmosphere. Hydrogen is flared off when leaving the furnace. The process takes place at a temperature range of 1800 - 2000 ºC.

The process production of tungsten carbide by the carburisation of tungsten metal powder is shown in Figure 8.5.

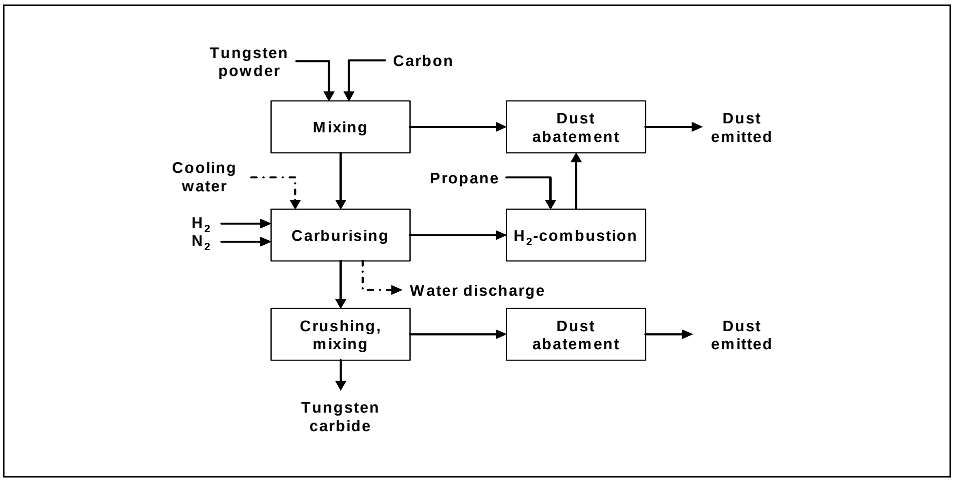


**Figure 8.5: Production of tungsten carbide**
[ 179, ITIA 1999 ]

### 8.1.3.2 Processing of tungsten secondary raw material

The increasing availability of tungsten scrap from various sources led to the development of different processes for processing tungsten secondary raw material (tungsten hard metal scrap). The three major processes for the recycling of tungsten scrap (tungsten carbide that contains some cobalt as a binder) are the Goldsteam process, the Zinc process and the Leach-Milling process [ 7, St. Barbara Consultancy Services 1993 ].

In the **Goldsteam process,** the fragmented carbide is carried in a stream of air at a high velocity and collides with a stationary target. The impact at below ambient temperatures creates adiabatic cooling and breaks the embrittled carbides. The products are air classified and the fines collected, the oversize material being recirculated. The process is limited in its application with hard metal as very high cobalt levels render the material ductile, although this may be mitigated by preheating and rapid quenching of the hard metal.

In the **Zinc process,** the scrap is contacted with molten zinc, which forms an amalgam with the cobalt and effectively breaks up the cemented carbide. After full penetration of the scrap, the zinc is removed by vacuum distillation, leaving the hard metal as a spongy material, which can be easily crushed. After crushing, milling and sieving the powder can be used as a raw material in the manufacture of graded, ready-to-press powder. The limitations of the process are on the size of the pieces to be treated again and the need for double zinc distillation. The zinc process is operated batch wise, with the scrap and zinc placed in a reactor or in graphite crucibles. After around 12 hours at 900 ºC the pressure is reduced and the zinc distilled, requiring typically a further 15 hours.

In the **Leach-Milling process,** the pieces of scrap are leached with batches of mineral acid in a lined mill. The cobalt dissolution reaction is slow and the recovered carbide has an undesirably high oxygen content. Further processing to recover the cobalt is necessary, and the process now finds little usage in modern plants.

Contaminated cemented carbide scrap, turnings, grindings and powder scrap are oxidised and chemically processed to APT in a way similar to that used for the processing of tungsten ores. If present, cobalt tantalum and niobium are recovered in separate processing lines.

## 8.1.4 Vanadium

Vanadium is consumed in general as an alloying component for the production of the iron-vanadium alloy called ferrovanadium. The development of vanadium technology started at the beginning of the 1950s effectively and was essentially related to ferrovanadium and to certain vanadium compounds. Vanadium became the vital constituent of the multi-component titanium alloys for aerospace applications. The major potential and applications of alloys can be found in nuclear reactors and superconductors. The use of vanadium in the chemical industry is based on the properties of vanadium, especially its changing of oxidation states in vanadium salts. Thus the most important behaviour of vanadium compounds in the chemical industry can be used in catalysts of key processes, such as the production of sulphuric acid, EPDM, adipic, maleinic or phthalic acid. Furthermore vanadium oxides, as the active component in deNOx catalysts, has been used for the reduction of nitrogen-oxides in the emission control of power plants (incineration facilities). New developments of vanadium salts are concentrated in the production of alternative yellow and orange pigments to replace ecologically critical chromium pigments.

### 8.1.4.1 Production of vanadium metal from primary and secondary raw materials

The majority of vanadium metal is produced from vanadium slag, which is obtained from a pre-reducing process of titanomagnetite ore in an electric arc furnace. The electric arc furnace produces pig iron that is oxidised further in an oxygen blown converter in order to transfer the vanadium into the slag. The slag that contains vanadium is then used as the world's major raw material source to produce vanadium oxide, which can further be transformed by reduction to vanadium metal, especially alloys that contain vanadium.

In the first step of the process, the vanadium slag is ground and liberated from the iron granulates. After grinding, commonly alkali metal salts are blended and fed to a multiple hearth furnace or rotary kiln where roasting, a disintegration of the slag under oxidising conditions, takes place at about 700 - 850 °C. Thus, both the oxidation of vanadium to $V(^{V})$ and the formation of a water-soluble salt, can be achieved. Afterwards, the roasted vanadium slag is leached to form a high concentrated liquid phase that contains vanadium. The separation and purification of the vanadium from the liquid phase can be usually done by precipitation of an ammonium vanadate by controlling the pH value and temperature. The achieved precipitate is filtered, dried and can be alternatively transformed in several process steps to high purity vanadium oxides, such as vanadium pentoxide, vanadium tetroxide or vanadium trioxide as a function of temperature and reduction/oxidation conditions.

In order to gain vanadium metal, the vanadium oxides can either be treated by carbothermic or metallothermic reduction. The carbothermic reduction forms vanadium metal with high oxygen and carbon contents, which is the reason for the rare use of this process. The more common method is the metallothermic process using calcium or aluminium as the reducing agent. By using calcium as a reducing agent, the reaction takes place in a closed pressure furnace that is lined with pure magnesium oxide. The aluminothermic process of exclusively vanadium pentoxide is a self-sustaining process without additional requirements of energy. The process is carried out in temperature resistant equipment where a mixture of high purity vanadium pentoxide is reduced by aluminium powder.

Melting in an electron beam furnace allows both the direct purification of the vanadium metal and the use of reduced vanadium oxides by the aluminothermic process.

Vanadium is present in a variety of natural materials such as crude oil that contains vanadium or bauxite that is used for alumina production. If these sources are used for energy generation or as raw material in technical processes, vanadium is sometimes transferred to the residues, e.g. boiler ashes or by-products, e.g. salts from the alumina production. During the last twenty years several different processing technologies have been developed in order to gain purified vanadium oxides from these secondary raw material sources. The recovery of vanadium from scrap is sometimes related to the recovery of other refractory metals, for instance by using spent catalysts either vanadium or molybdenum can be recovered.

Residues like oil that contains vanadium or spent catalysts can be digested with sulphuric acid and further transformed by an extraction step into an acid solution of vanadyl sulphate. In the subsequent process step the solution is treated by oxidation and precipitation, which produces a precipitate that is called red cake, a vanadium polyvanadate. The red cake can then be calcined to form vanadium pentoxide that contains an alkali.

Another method for processing residues that contains vanadium is a combination of a pyrometallurgical and hydrometallurgical method. The vanadium content of the residues is oxidised at elevated temperatures to produce a water-leachable alkali metal vanadate. After the leaching step, the vanadium is precipitated and calcined in order to generate vanadium pentoxide.

In the production of alumina, which is described in detail in Chapter 4 of this document, a salt is generated as a residue or a by-product. If alumina production is based on bauxite that contains high levels of vanadium, the salt can further be used to obtain vanadium pentoxide. In comparison to the other vanadium pentoxide production techniques using vanadium slag as the raw material, this process causes a waste water problem because the salt also contains arsenic that it transported into the leach liquor and further to the waste water.

The vanadium pentoxide produced either from primary or secondary raw material can be reduced by a variety of different metallurgical processes to produce metallic vanadium. The flow sheet in Figure 8.6 demonstrates the different production routes of vanadium pentoxide and the subsequent processes to produce vanadium metal.

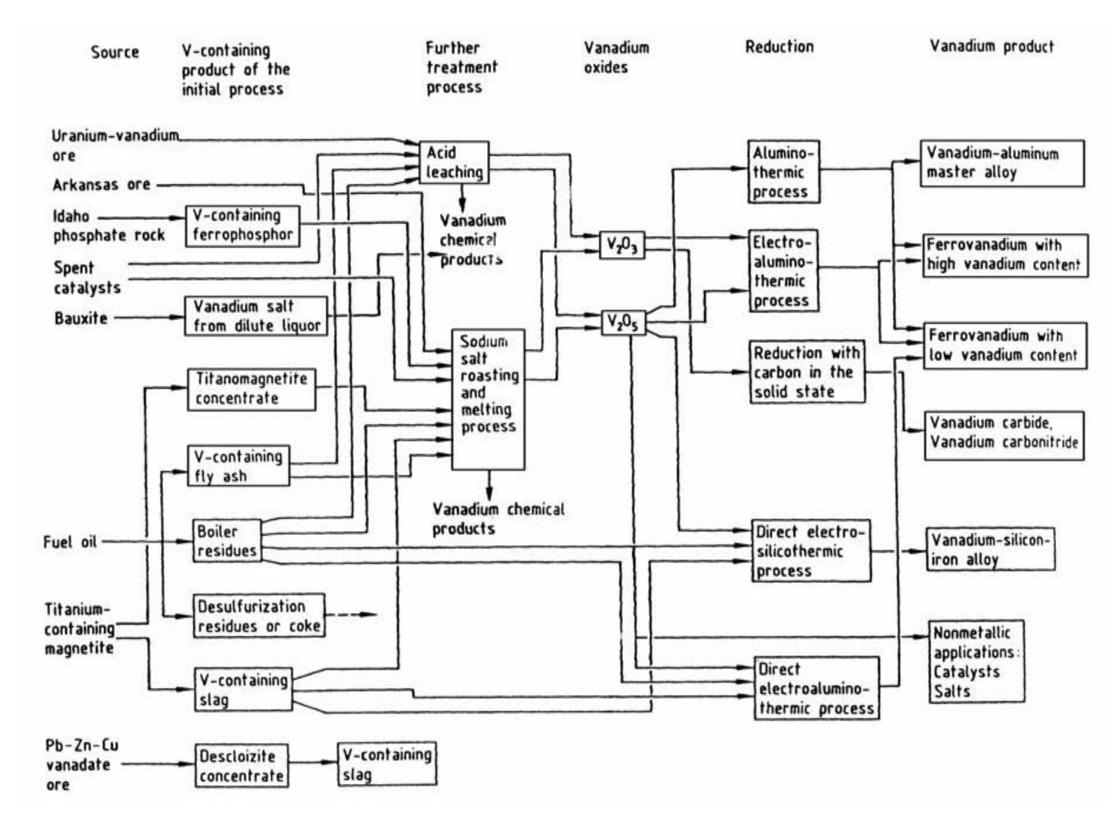


**Figure 8.6: Production of vanadium pentoxide and vanadium metal**
[ 7, St. Barbara Consultancy Services 1993 ]

### 8.1.5 Molybdenum

Molybdenum in its pure stage is a lustrous grey metal that can be used for a wide range of industrial applications. Molybdenum is used as an alloying element in steel production, as molybdenum compounds in the chemical and lubricant industries.

Molybdenum can be obtained from primary or secondary ores, e.g. molybdenum is also produced as a by-product of copper mining. The ore that contains molybdenum is first ground and floated in order to separate the molybdenite from the host rock. The molybdenite is then roasted to remove the sulphur and change the sulphide to oxide. Molybdenum trioxide ($MoO_3$) is used in the production of ferro-alloys and as the starting compound for all other products that contain molybdenum such as ammonium dimolybdate, sodium molybdate and molybdenum metal [ 104, Ullmann's Encyclopedia 1996 ]. ~~The conversion of concentrated molybdenite ore (molybdenum sulphide) into technical grade molybdenum trioxide for the metallurgical or chemical industry is performed by calcination and roasting.~~ The process of molybdenite roasting is described in detail under the production of ferro-alloys in Chapter 9.

#### 8.1.5.1 Production of molybdenum metal powder

Molybdenum metal powder can be produced in a two-stage process by reducing molybdenum trioxide ($MoO_3$) ~~with hydrogen~~. Compounds such as ammonium heptamolybdate and ammonium dimolybdate may also be used for powder production. In the first step of the process, $MoO_3$ is reduced at about 600 °C in an exothermic process to molybdenum dioxide ($MoO_2$). The second reduction stage, in which the metal powder is produced, takes place at ~1050 °C. The process can be carried out either in a pusher furnace, a walking beam furnace or a rotary kiln where the hydrogen is fed in a countercurrent flow. Pressing and sintering in order to get compact molybdenum metal can then be used to process the powder. Melting of molybdenum in a vacuum arc furnace or an electron beam furnace is another way to produce compact molybdenum metal.

#### 8.1.5.2 Processing of molybdenum secondary raw material

Molybdenum is used on a large scale as a catalyst in the petrochemical industry. Spent catalysts are therefore a valuable source of secondary raw material, which can be used for molybdenum recovery. The recovery of molybdenum and the recovery of the vanadium content can follow the following process steps [ 104, Ullmann's Encyclopedia 1996 ]:

- initial heating in air at 600 ºC to remove the residual sulphur, carbon and hydrocarbons and to oxidise the metals to soluble molybdate and vanadate;
- a leaching step resulting in preferential solubilisation of molybdate and vanadate, leaving the nickel-cobalt-alumina as a solid;
- separation of the molybdenum and vanadium;
- treatment of the Ni/Co alumina residue to recover the nickel and cobalt content.

### 8.1.6 Titanium

Titanium is consumed by the industry mostly as titanium dioxide ($TiO_2$) that is used as pigments in the paint, plastic and paper industries, and as titanium metal. Titanium metal even as a pure metal or alloy is used in applications where the relatively high cost of the metal is justified by its outstanding characteristics. Due to the high strength-to-weight ratio of its alloys and their corrosion resistance, titanium is important and widely used for high performance aircraft engines and airframes.

There are commonly two applied processes established for the production of titanium metal. The Kroll process, where titanium tetrachloride (TTC) is reduced with molten magnesium to produce pure titanium metal as well as titanium sponge. The Hunter process uses molten sodium for the reduction of TTC. The Hunter process has lost its importance and is now mostly replaced by the Kroll process.

Due to the reactivity of molten titanium, the production of titanium ingots is then carried out in special vacuum furnaces.

Titanium tetrachloride can be manufactured from ore that contains titanium oxide and from titanium rich slag that is generated by the metallurgical treatment of ilmenite ore. The chlorination is today exclusively carried out by a fluidised bed process. The choice of a fluidised bed reactor is due to its higher reaction and the improved heat transfer rate and therefore the higher achievable reaction temperatures. After chlorination, a subsequent separation and purification process is normally necessary in order to obtain a titanium tetrachloride of a purity of about 99.9 %.

#### 8.1.6.1 Production of titanium metal sponge

As already mentioned in Section 8.1.6, the production of titanium metal sponge is carried out by the Kroll process. In the Kroll process, pure titanium tetrachloride (TTC a colourless, fuming liquid) is reduced by reaction with molten magnesium under an inert gas atmosphere. The reaction takes place in a reaction vessel that is constructed of stainless or carbon steel, sometimes with a titanium coated interior. A typical reactor for the production of titanium sponge is shown in Figure 8.7.

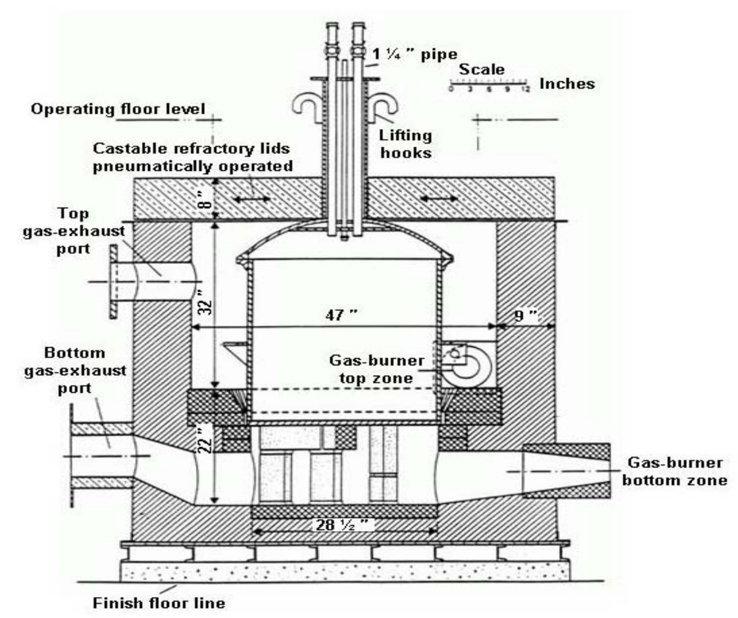


**Figure 8.7: Reaction vessel for titanium production using the Kroll process**
[ 7, St. Barbara Consultancy Services 1993 ]

The reactor is first charged with oxide-free magnesium and argon gas. When the magnesium is molten by using external heating, TTC is carefully charged to the reactor. Due to the exothermic nature of the reaction, the process can be operated and controlled by the rate of adding TTC to the reactor. The temperature range goes from 850 to 950 ºC, where the lower temperatures gives longer reaction times but purer titanium sponge. The process produces titanium metal sponge intimately mixed with magnesium chloride and other impurities such as unreacted magnesium, TTC and some subchlorides of titanium. These impurities can be removed by using the following techniques [ 7, St. Barbara Consultancy Services 1993 ]:

- acid leaching with dilutes nitric or hydrochloric acid;
- purging the reaction vessel and its contents with argon at 1000 ºC, thus volatilising and removing the impurities;
- vacuum distillation at a pressure of 0.2 mm mercury and a temperature of about 960 - 1020 ºC for 30 - 60 hours.

The titanium sponge can be melted in order to obtain titanium ingots by using the consumable electrode vacuum arc melting process.

### 8.1.6.2 Processing of titanium secondary raw material and titanium sponge

Growing titanium production has also increased the availability of titanium secondary raw materials. The melting operation to produce titanium ingots by re-using titanium secondary raw materials or melting titanium sponge is conducted in a vacuum in specially-designed furnaces. Batches of titanium scrap and titanium sponge are mixed and pressed in order to form blocks. The blocks are welded together to produce a consumable electrode. The electrode is then installed in the furnace chamber in a manner where a cooled copper crucible which collects the molten titanium encloses the bottom end of the electrode. An arc is struck between the lower end of the electrode and the bottom of the crucible and the electrode is moved downwards as it is consumed.

Untreated titanium scrap can also be used directly as an additive to steel, nickel, copper, aluminium or other metals, and for the production of ferro-titanium.

### 8.1.7 Tantalum

Tantalum metal plays an important role in the production of electronic components, chemical equipment and in aerospace technology, e.g. the manufacture of electronic capacitors or heat shields for rocket boosters. Tantalum is also used in the fabrication of corrosion-resistant process equipment like heat exchangers for acid liquids, columns, diaphragms, etc.

#### 8.1.7.1 Production of metallic tantalum from primary raw material

The production of metallic tantalum can be based on both minerals that contain tantalum or tantalum-rich slag that arises from the smelting of tin concentrates. The recovery of tantalum from tin slag has increased in recent years and accounts for about 30 % (worldwide) of the total tantalum production. The production of tantalum and niobium oxides from tin slag is presented in Figure 8.8.

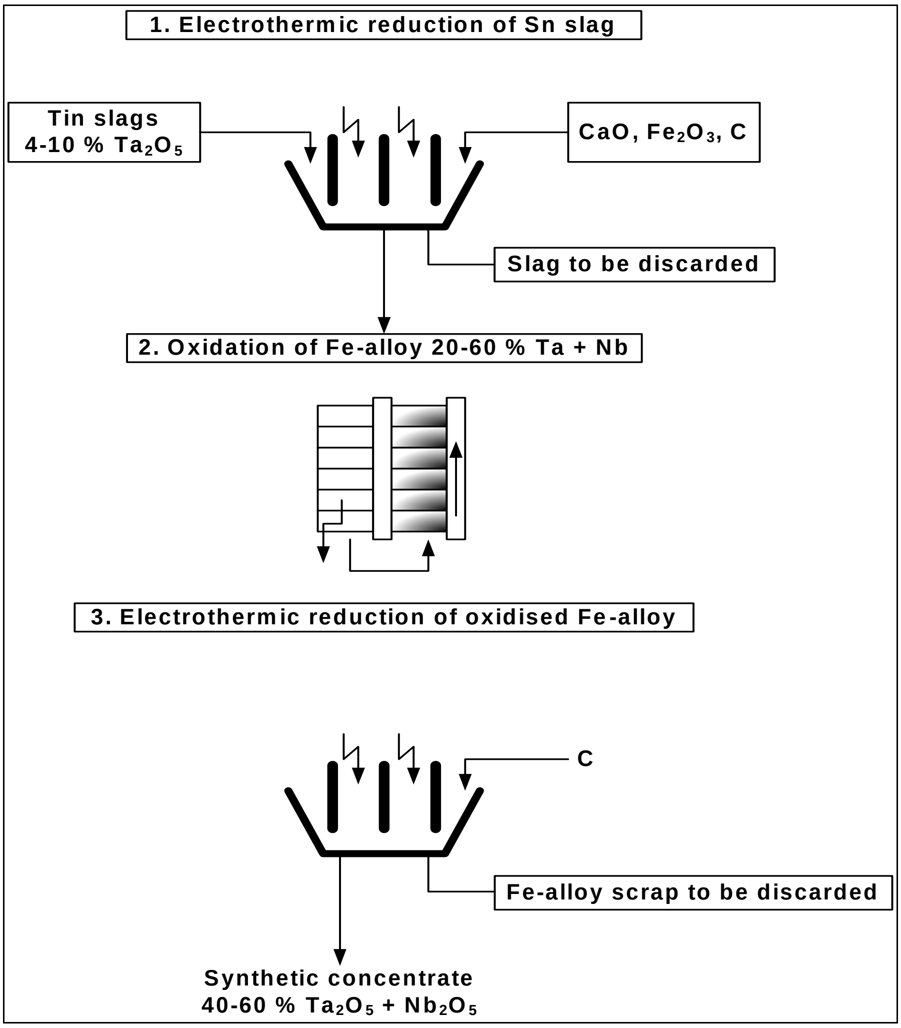


**Figure 8.8: The production of tantalum and niobium oxides from tin slag**

The mineral is first crushed and treated by flotation and subsequent leaching and concentrated by flotation or other benefaction processes. The concentrate is digested in hydrofluoric acid. Ta and Nb are subsequently extracted by organic solvents in order to obtain potassium heptafluorotantalate as an intermediate product. The potassium heptafluorotantalate is then reduced by sodium to tantalum powder. To produce a pure metal powder, two processes can be used. The first process is carried out by deoxidation of the tantalum powder with magnesium or a vacuum thermal treatment under protective gas. The second process takes place by melting the powder in an electron beam furnace (EBM). Due to the high melting point of tantalum, most of the impurities presented in the powder are volatilised and captured by the furnace off-gas. The purified powder can then further be used for the production of semi-finished products or the fabrication of tantalum capacitors. The tantalum process is summarised in Figure 8.9.

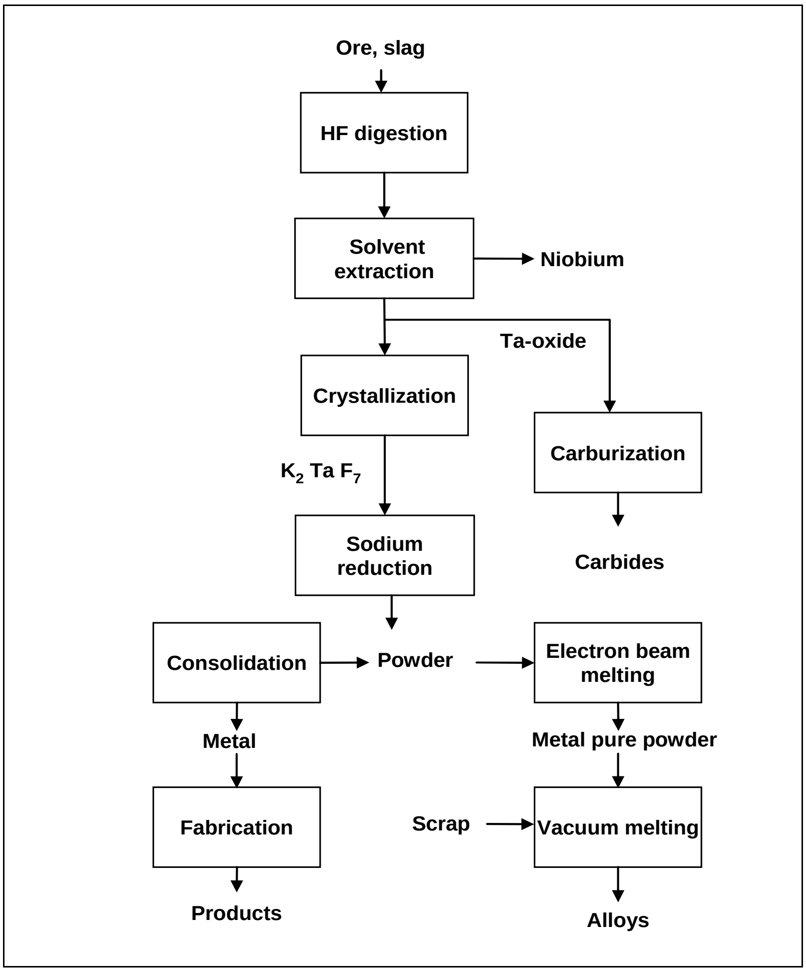


**Figure 8.9:** **Production of pure tantalum metal powder**

### 8.1.7.2 Processing of tantalum secondary raw material

The secondary raw materials used to produce tantalum are scrap consisting of unoxidised tantalum and oxidised tantalum related with other oxidised metals. The unoxidised tantalum scrap, e.g. sintered parts, can be remelted in an electron beam furnace or treated by dehydrogenation in an vacuum furnace in order to produce tantalum powder. The second type of scrap represents the oxidised tantalum, for instance oxidised tantalum anodes coated with manganese dioxide or with conductive silver [ 104, Ullmann's Encyclopedia 1996 ]. This scrap can be treated with nitric or hydrochloric acid and results in a residue that contains oxidised tantalum. Alternatively, the scrap that contains manganese dioxide can be melted directly by reducing the oxides in argon-hydrogen plasma to tantalum metal.

## 8.1.8 Niobium

Niobium is a refractory metal that is closely related to tantalum, and therefore offers nearly the same corrosion resistance as tantalum but a melting temperature which is close to the melting point of molybdenum. Niobium is used as tubing in nuclear reactors because of its resistance to neutron bombardment. Niobium is also used for rocket nozzles and jet engines because of the extended strength and oxidation resistance at the low weight of niobium.

### 8.1.8.1 Production of niobium from primary raw material

Niobium can be produced from pyrochlore ore, this also contains traces of polonium which is a volatile, radioactive metal. The smelting of pyrochlore requires enhanced safety and environmental procedures.

Niobium always occurs in the primary raw materials of tantalum and other elements such as columbite and tantalite. In order to separate the metals, niobium production should use the same separation process as tantalum. Niobium pentoxide is produced as an intermediate product in a series of different unit operations. Niobium pentoxide can be used in the chemical industry or further be reduced to niobium metal powder and niobium carbide. The processing of niobium and tantalum compounds is shown in Figure 8.10.

**Figure 8.10: Processing of niobium and tantalum compounds**

The production of niobium metal can be carried out by carbothermic or metallothermic reduction of niobium pentoxide, whereas the most important process is the reduction of niobium pentoxide with aluminium. The aluminothermic process today produces almost 90 % of niobium metal. The process is carried out under vacuum in an electric arc furnace and produces a low oxygen and carbon-free niobium metal.

For carbothermic reduction, niobium pentoxide is mixed with carbon, pelletised and reduced in a vacuum furnace. The process takes place at about 1950 ºC and produces a niobium metal with a high carbon and oxygen content that needs a further refining step.

The refining step is necessary in order to remove the impurities, which are carried into the process by the raw material or introduced during the process. The refining takes place at high temperatures using an electric arc or electron beam furnace. Due to the high melting point of niobium, most of the impurities are removed from the melt by vaporisation. To obtain a sufficiently refined result, the crude niobium needs a second refining cycle. The refining and electron beam melting process generates a highly purified niobium metal that can be used for high frequency superconductors.

### 8.1.9 Rhenium

Rhenium, the refractory metal with the second highest melting point (3180 °C) has only recently been exploited for a commercial use. The biggest consumption of rhenium is in the form of high temperature superalloys in which rhenium is an important constituent. Less than one quarter of the consumption is in platinum-rhenium catalysts used to produce lead-free petrol. Other uses include thermocouples and a variety of electrical applications.

Most rhenium is produced as a by-product from the molybdenite roasting process, where rhenium oxide is volatilised and exits with the roaster off-gas. In Poland, rhenium is recovered from complex copper ores, see Section 8.3.5. The rhenium can then be recovered from the off-gas stream by high efficiency scrubbers and electrostatic precipitators.

#### 8.1.9.1 Rhenium recovery by molybdenite roasting

The roasting process of molybdenite concentrates generates large amounts of dust and sulphur dioxide and also vaporised rhenium in the form of rhenium heptoxide ($Re_2O_7$). The rhenium heptoxide escapes with the roaster off-gas because of its high vapour pressure. Rhenium heptoxide and selenium oxide present in the off-gas can be removed from the waste gas stream be using a wet scrubbing operation. The recovery of rhenium from the flue-gases in the roasting of molybdenite is shown schematically in Figure 8.11.

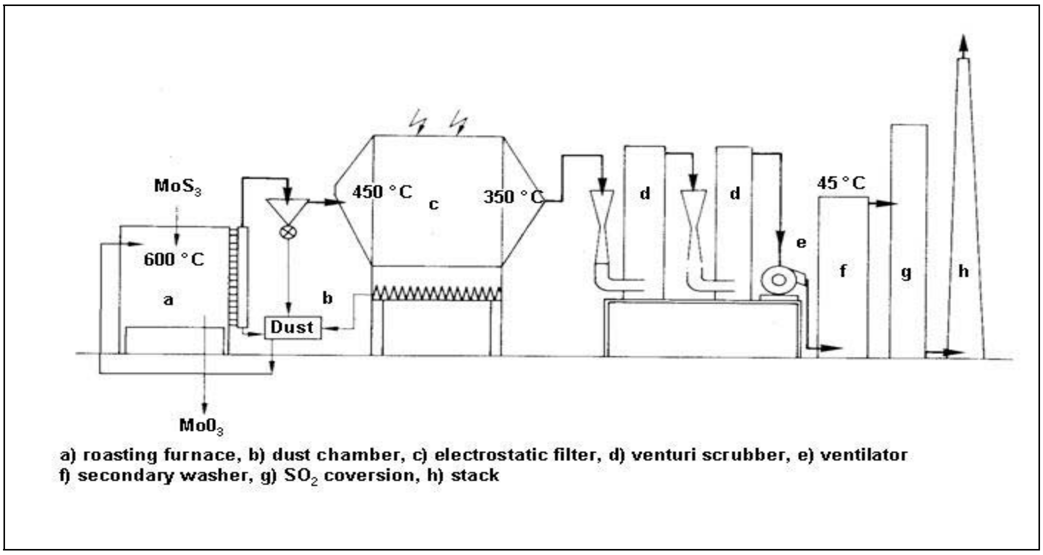


**Figure 8.11: The recovery of rhenium from the flue-gases in the roasting of molybdenite**
[ 104, Ullmann's Encyclopedia 1996 ]

Because of the ability of rhenium heptoxide to dissolve in water, it is transferred easily into the scrubbing liquor. The scrubbing water is recirculated to the scrubber in order to get a higher rhenium concentration. The concentrated scrubbing liquor that contains about 0.2 to 1.5 g/l of rhenium can then be treated by chemical precipitation or preferably by using ion exchangers or solvent extraction equipment in order to obtain rhenium metal.

The production of ammonium perrhenate from the weak acid produced in some copper production processes is described in Section 8.3.5.

### 8.1.9.2 Production of rhenium metal

After removal of the rhenium content from the roaster off-gas, it can be recovered from the scrubbing liquor by precipitation as the sulphide which is sparingly soluble, the use of ion exchangers or the use of solvent extraction. Further treatment with strong mineral acids leads to the intermediate product ammonium perrhenate. Ammonium perrhenate can then be reduced with hydrogen in order to obtain rhenium metal powder. The reduction process occurs as a two-stage process. In the first stage that takes place at about 300 - 350 ºC, rhenium dioxide will be produced. The second stage reduces the rhenium dioxide at 800 ºC to rhenium metal that can be obtained from the process as pure metal powder. The metal powder can then further be compressed and sintered in order to get pellets or large work pieces.

## 8.1.10 Zirconium and Hafnium

The sister metals zirconium and hafnium both have an important role in the nuclear industry because of their excellent metallurgical and corrosion-resistant properties in the extreme environment of the nuclear core while having exactly the opposite effect on thermal neutrons. Zirconium is also used in the chemical industry and zircon bricks are needed as furnace linings.

The production of zirconium and hafnium metal starts with mixing together zircon concentrates and carbon. The mixture can then be chlorinated in a fluidised bed reactor. The zirconium chloride can be removed from the reactor off-gas by condensation that is controlled by temperature. Dissolution in a low melting fused salt eutectic mixture followed by vaporisation of a zirconium/hafnium chloride. Separation of zirconium and hafnium is carried out by solvent extraction where zirconium or hafnium can selectively be extracted depending on the extractant that is used. Metal production uses the Kroll process, where the zirconium/hafnium tetrachloride is sublimed and reduced with magnesium and magnesium chloride. The product of this process step can then be treated by vacuum arc refining to produce the final metal.

## 8.2 Current emission and consumption levels

The manufacturing of refractory metals normally takes place at high temperatures. The environmental impact on air, water and land can be classified as follows:

- **Consumption of raw material and energy**

- **Emissions to air~~:~~**
    - dust and fume emissions from smelting, hard metal and carbide production
    - other emissions to air are ammonia ($NH_3$), acid fume (HCl), hydrogen fluoride (HF), VOCs and metals
    - emissions of noise and vibrations.

- ~~**Solid residues, wastes and by-products:**~~
    - ~~dust, fume and sludge~~
    - ~~slag.~~

- **Waste water emissions~~:~~**
    - overflow water from wet scrubbing systems
    - waste water from slag and metal granulation
    - blowdown from cooling water cycles.

- **Process residues such as wastes and by-products**
    - dust, fume and sludge
    - slag.

### 8.2.1 Consumption of raw material and energy

The available data of the consumption of raw material and energy for the production of refractory metals are presented in terms of specific input factors based on a tonne of produced product in Table 8.1.

| Input | Chromium | Tungsten |
|---|---|---|
| Ore and concentrates (kg/t) | Chrome oxide | NA |
| Energy consumption (kWh/t) | 139 | 1000 - 1500 (APT production)<br>3500 - 12000 (carbide production)<br>1500 - 2500 (zinc process) |
| Gas ($m^3/t$) | 6 | NA |
| Water ($m^3/t$) | 2(1) | NA |
| Aluminium powder (kg/t) | NA | NR |
| Calcium powder (kg/t) | NR | NR |
| Others (kg/t) | NA | NA |

(1)The presented figure on water consumption can only give an indication.
NA = data not available.
NR = not relevant in this production process.

**Table 8.1: Consumption data for the production of ~~refractory metals~~chromium and tungsten ~~as specific input factors~~**

Table 8.2 presents some information on process data for smelting refractory metals in an electron beam furnace. In electron beam furnaces electron guns produce high-energy electrons, which impact their energy to the furnace charge to affect its melting.

Electron beam furnaces are used to melt and/or refine refractory metals such as vanadium, niobium and tantalum, metals such as molybdenum and tungsten as well as reactive metals like zirconium and hafnium [ 104, Ullmann's Encyclopedia 1996 ].

| Metal | Crucible capacity (t) | Furnace power ($MW_e$) | Throughput (t/h) | Energy consumption (kWh/t) |
|---|---|---|---|---|
| Niobium | 0.5 - 2 | <1.2 | 0.02 - 0.4 | 6000 - 15000 |
| Tantalum | 0.5 - 2 | <1.2 | 0.02 - 0.4 | 6000 - 15000 |
| Molybdenum | | | 0.02 - 0.1 | <5000 |
| Tungsten | | | 0.02 - 0.1 | <5000 |
| Titanium | | | 0.2 - 1 | 1000 |

**Table 8.2: Process data for smelting refractory metals in an electron beam furnace** [ 104, Ullmann's Encyclopedia 1996 ]

*What is the relevance of these data. Are they uptodate or should they be revised or deleted? Titanium is not mentioned in the paragraph before but in the table, vanadium is mentioned but not in the table. Clarify.*

### 8.2.2 Emissions to air

According to the raw material that is needed and the unit operations used, e. g. crushing, drying, smelting, firing, metal and slag separation, calcining, hydrogen reduction, carburisation and product handling one of the most important sources of environmental impact are dust and fume emissions. The dust emissions either as stack or diffuse emissions are important because refractory metal compounds, such as those of tungsten, molybdenum, manganese and cobalt, may be part of the dust and are harmful. The metals tungsten and molybdenum are also toxic if ingested in dust form [ 248, M168 UBA Austria report, 2008 ].

Unloading and storage of raw materials can generate dust when the material is feed from packaging, such as drums, plastic bags or FIBCs into bins.

The dust and fumes that are generated by smelting or melting, for instance chromium or titanium metal, or from the production of hard metal powder, is collected by hoods and transferred to an abatement system and dedusted (e.g. by a fabric filter or a wet scrubber). Stack emissions are normally monitored continuously or periodically and reported by on-site staff or off-site consultants to the competent authorities.

Diffuse losses can also be measured as shown in Chapter 2, which gives an overview of common techniques used by producing non-ferrous metals. *(try to give more specific information about diffuse emissions from these processes)*

Metals are carried into the process as trace elements in the primary or secondary raw material. The metals with boiling points below the process temperature will escape as gases in the form of metal vapours, which partly condenses and oxidises to form part of the dust and fumes from the firing chamber. The metal vapour and off-gases generated by the melting or refining of refractory metals in an electron beam furnace are collected by a vacuum system and then condensed by intensive cooling.

Another environmental impact of the production of refractory metals such as tantalum, zirconium and hafnium are the radioactive levels of some raw materials. Also the toxicology of some refractory metals for instance chromium, manganese and vanadium should be taken into account. This is as well the case if cobalt takes part of the hard metal powder, where then the occurrence of "hard metal disease" has been found [ 7, St. Barbara Consultancy Services 1993 ].

### 8.2.3 Emissions to water

For the production of refractory metals, the emissions to water are very dependent on the process and the abatement system as well as the type of waste water treatment used. There are a variety of different water collection and waste water treatment systems. Some plants use a central waste water treatment plant in which water from different production processes as well as surface run-off water will be cleaned together. Other facilities are using a separate treatment system for rainwater and special treatment processes for the different process waste water streams. The main water pollutants are suspended solids and metal compounds. The waste water is treated in order to remove dissolved metals and solids and is recycled or re-used as much as possible in the process. The possible waste water streams are:

- surface treatment (pickling) ~~of metal~~
- surface run-off and drainage water
- waste water from wet scrubbers
- waste water from slag and metal granulation
- cooling water.

The contaminated water is normally led to a thickener or a settling pond to settle out the suspended solids. Precipitation steps are often used to remove metal compounds from the water. The particles mostly consist of very fine particles, it may therefore be necessary to add flocculent to assist the settling in thickeners. After the treatment in a thickener or a settling pond, the suspended solids are usually below 20 mg/litre, which allows re-use in scrubbers, as cooling water or as process water for other purposes.

For Mo and W the metals are removed and accumulated in the an_ion exchanger and precipitated through acidification as the oxidhydrate. *(the latter has to be explained)*

### 8.2.4 ~~By-products, p~~Process residues such as ~~and~~ waste and by-products

The production of refractory metals is related to the generation of a number of by-products, residues and wastes, which are also listed in the European Waste Catalogue in the directive 75/442/EEC~~(Council Decision 94/3/EEC~~). *This has been replaced by a new directive 75/442/EEC (see Section 5.2.4)* The most important process-specific residues are filter dusts, sludge from wet scrubbers, slag from the smelting process, used furnace linings and packaging material like drums or big bags. These residues are partly sold as by-products, recycled back to the process or in cases of wastes without recoverable metals, transported to a deposit or a disposal site. *(Very general. Try to get more information on this issue)*

### 8.2.5 Summary of emissions from the production of refractory metals

Taking into account the different processes used in the production of refractory metals, Table 8.3, Table 8.4, Table 8.5, Table 8.6, Table 8.7, Table 8.8 and Table 8.9 give an overview of the environmental input in terms of emission to air, water and land. The tables make a distinction between the use of primary and secondary raw material.

| Refractory metal | Emissions to air | | | Emissions to water | Generation, recycling and re-use of process residues | Remarks |
|---|---|---|---|---|---|---|
| **Chromium** | **Component** | **Source** | **(mg/Nm$^3$)** | | | |
| **Primary raw material** | Dust | From raw material storage handling and preparation cleaned by a fabric filter | 5 - 10 | Effluent from the water quench tank (bosh tank) | Dust collected in the abatement system.<br>The chrome alumina slag is sold as a raw material for use mainly in the -steel refractory industry or, as stated previously, re-used to line the firing pots.<br>Slag recovered from the boshing tanks, debris from the stripping booth and that from stripping used reaction pots is disposed of to a licensed landfill. | |
| | Dust | From the firing chamber cleaned by a fabric filter | <5 | | | |
| | Dust | Diffuse emissions from smelting and metal and slag separation | NA | | | |
| | Cr | The amount of chromium and its compounds as part of the total dust emissions is reported as be less than 2 | <2 | | | |
| **Secondary raw material** | | | | | | Chromium metal scrap is commonly used directly in steelworks or for the production of ferro-chrome |
| **Manganese** | **Component** | **Source** | **(mg/Nm$^3$)** | | | |
| **Primary raw material** | Dust | From raw material storage handling and preparation cleaned by a fabric filter | <10 | No data are available for the generation of waste water | Electrolyte purification waste<br>Waste electrolyte<br>No information is available for the generation of other residues | |
| | Mn | Manganese fumes manganese tetroxide and manganese organic compounds | NA | | | |
| **Secondary raw material** | | | | | | No data are available for the production of secondary manganese |

**Table 8.3: Emissions from the production of chromium and manganese metal**
[ 196, Finkeldei, L. 1999 ]

| Refractory Metal | Emission to air | | | Emission to water(1) | | Generation, recycling and re-use of process residues | Remarks |
|---|---|---|---|---|---|---|---|
| **Tungsten** | **Component** | **Source** | **(mg/Nm$^3$)** | **Component** | **(mg/l)** | | |
| **Primary raw material** | Dust | Raw material storage and handling (charging boats) | <5 | Mo | <0.1 | Dust that is collected in the abatement system is recycled to the production process<br>Residues from crystallisation and drying of apt. | Tungsten powder is toxic if inhaled and is also a valuable material<br>The only available measured dust emission concentrations that has been reported are exclusively in the range of 1 - 3 mg/Nm$^3$<br>This data are due for the production of tungsten metal powder and tungsten carbide<br>Ammonia is a very odour intensive substance, which may easily results in odour problems. |
| | Dust | Calcining | 1 - 6 | | | | |
| | Dust | Hydrogen reduction | <5 | W | 0.8 | | |
| | Dust | Powdering *(its unclear what is ment by powdering because this term is not used in the entire section 8 before.)* | <5 | | | | |
| | Dust | Product handling | <5 | Co | 0.5 | | |
| | Dust | Diffuse emissions from furnace loading and unloading.<br>Carryover of fine particles | NA | | | | |
| | $NH_3$ | Diffuse ammoniac decomposition fumes from calcination | <60. | F | 0.4 | | |
| | $H_2$ | Possible fire risk from hydrogen fumes | | | | | |
| **Secondary raw material** | Dust | Same as for primary production | <10 | Cooling water systems are designed as closed loops and are not in contact with the processed material<br>Waste water resulting from washing is treated in a special waste water treatment facility. | | Dust that is collected in the abatement system is recycled to the production process. | Cobalt is normally added to the hard metal powder. This can cause "hard metal disease" therefore the emission concentration of Co is less than 1 mg/Nm$^3$. |
| | Zn | Zinc fumes from the distillation process | NA | | | | |
| | Co | Cobalt fumes from the distillation process (Co is part of the hard metal scrap) | <1 | | | | |

(1) Cooling water systems are designed as closed loops and are not in contact with the processed material. Waste water resulting from scrubbing is checked for W and $NH_4$ contents and treated to reduce these *(How is it treated in order to reduce these?)*.This footnote was not in the existing BREF. It has been introduced by the former author. From where is this info? Should it be applied to other metals as well in this table? Why only tungsten?

**Table 8.4: Emissions from the production of tungsten metal and tungsten metal powder**

[ 196, Finkeldei, L. 1999 ]

*From which reference are the data for emissions to water from? For tungsten new data for emissions to air and water have been introduced whith adding the corresponding reference! This is also from [248] Most of the data used are ELVs.*

*The way the data for water emissions are inserted seems to indicate the sources ofgeneration which is not the case. This has to be changed.*

| Refractory Metal | Emissions to air | | | Emissions to water | | Generation, recycling and re-use of process residues | Remarks |
|---|---|---|---|---|---|---|---|
| **Vanadium** | **Component** | **Source** | **(mg/Nm$^3$)** | | | | |
| **Primary raw material** | Dust | From raw material preparation like grinding | <10 | No information are available for the generation of waste water | | Dust collected in the abatement system<br>Leach tailings<br>No information is available for the generation of other residues | Calcium powder that is used as a reducing agent should be stored very carefully because of the high risk of fire hazards |
| | Dust | From mixing with alkali metal salts for the roasting process | <3 | | | | |
| | Ca | Calcium fines may be emitted by using calcium powder as a reducing agent | NA | | | | |
| | Al | Aluminium fines may be emitted be using aluminium powder as a reducing agent | NA | | | | |
| **Secondary raw material** | Different emissions of process chemicals are possible, but dependent on the used raw material and the process used. Data are not available | | | No information are available for the generation of waste water | | Vanadium decomposition sludge no information are available for the generation of residues | |
| **Molybdenum** | **Component** | **Source** | **(mg/Nm$^3$)** | **Component** | **(mg/l)** | | |
| **Primary raw material** | Dust | ~~From raw material storage handling and preparation cleaned by a fabric filter~~ Whole plant, redution furnace | 0.03 | Mo | 0.4 | No information is available for the generation of residues | According to international classification, molybdenum trioxide ($MoO_3$) is classified as harmful (XN) |
| | Dust | Diffuse emissions from loading and unloading, carryover of fine particles | NA | W | 0.2 | | |
| | HF | Chemical surface treatment | <~~1~~0.59 | Co | <0.05 | | |
| | Mo | Whole plant, redution furnace~~Fumes~~ | 0.01 | F | 1 | | |

| | | | | | | |
|---|---|---|---|---|---|---|
| **Secondary raw material** | $H_2$ | Possible fire risk from hydrogen fumes | | ~~Possible fire risk from hydrogen fumes~~ | | |
| | Different emissions of process chemicals are possible, but dependent on the used raw material and the process. No data has been reported | | | No data are available for the generation of waste water | No information is available for the generation of residues | |

**Table 8.5: Emissions from the production of vanadium and molybdenum metal**

[ 196, Finkeldei, L. 1999 ] [248]

*Where are the new data for Molybdenite production from? For molybdenum new data for emission to air and water have been introduced whith adding the corresponding reference!New data are from ref. [248]. Wrong figure used for emissions into water for F. If the measured values for Dust and Mo of 0.03 and 0.01 are used the measured value for HF of <0.59 should also be used. There is no reason to deviate from the reference [248]. The dust emissions are not from raw material handling and preparationonly. All hot treatment process steps are extracted and dedusted. Dust and Mo emissions are measured.* $H_2$ *information should not be assigned to emissions to water.*

*The way the data for water emissions are inserted seems to indicate the sources ofgeneration which is not the case.*

| **Refractory Metal** | **Emissions to air** | | | **Emissions to water** | **Generation, recycling and re-use of process residues** | **Remarks** |
|---|---|---|---|---|---|---|
| **Titanium** | | | **(mg/Nm$^3$)** | | | |
| **Primary raw material** | Dust | | <10 | Liquid effluents are generated by using wet scrubbing systems. These effluents may contain hydrochloric acid, TTC and sodium hydroxide<br>Liquid effluents arise from the use of cooling water on a once-through basis or as blowdown from closed circuit cooling water systems serving reactor vessels and crucibles in melting furnaces<br>Scarp detergent wash-water<br>Acid leachate and rinse water<br>Sponge wash-water<br>Titanium chloride purification effluent | Dust collected in the abatement system<br>The dust contains titanium, titanium dioxide and sodium oxide<br>Some melting furnace crucibles are cooled with liquid sodium-potassium alloys (NaK) and small quantities of oxidised material of this source are generated in the form of sludge. The sludge is reacted with water and the resulting liquid is discharged to the effluent treatment plant | Particulate titanium consists of relatively coarse particles, which settle quickly and represent a fire hazard<br>Frequent cleaning ensures that accumulation do not occur and the dust can normally sold as a by-product<br>TTC (titanium-tetrachloride) |
| | Dust | Dust, titanium fines, salt and possibly small quantities of sodium are produced during the crushing of the melt removed from the reaction vessel. | | | | |
| | Dust | Diffuse emissions | NA | | | |
| | Acid fume | Hydrochloric, hydrofluoric and nitric fumes | NA | | | |
| | TiOCl | TTC vapour hydrolyses in contact with moist air producing a fog that contains titanium dioxide, titanium oxychloride (TiOCl) and hydrochloric acid | | | | |
| | TTC | The argon gas used to provide an inert atmosphere in the reactor vessel picks up traces of TTC and sodium | | | | |
| | $TiO_2$<br>NaO | Fumes from cleaning the reactor lids contain titanium dioxide and sodium oxide | | | | |
| | Cl | | <5 | | | |

| | | | | |
|---|---|---|---|---|
| **Secondary raw material** | Emissions that are comparable to the above-mentioned air emissions | Similar effluents as primary production | The same residues as primary production | |

**Table 8.6: Emissions from the production of titanium metal**
[ 196, Finkeldei, L. 1999 ]

| **Refractory Metal** | **Emissions to air** | | | **Emissions to water** | **Generation, recycling and re-use of process residues** | **Remarks** |
|---|---|---|---|---|---|---|
| **Tantalum** | | | (mg/Nm$^3$) | | | |
| **Primary raw material** | Dust | Raw material storage and handling (charging boats) | <10 | Cooling water systems for the electron beam furnace are designed as closed loops and are not in contact with the processed material<br>No information are available for the generation of other waste water sources | Dust that is collected in the abatement system is recycled to the production process<br>No data are available for the generation of other residues | Tantalum in non-toxic and bioinert. Allergic reactions are unknown [ 104, Ullmann's encyclopedia 1996 ]<br>Ammonia is a very odour intensive substance, which may easily results in odour problems<br>Some tantalum raw materials may have high levels of radioactivity<br>HF (hydrogen fluoride) is highly toxic and can easily be absorbed by skin contact. |
| | Dust | calcining | <5 | | | |
| | Dust | Hydrogen reduction | <5 | | | |
| | Dust | Carburisation | <5 | | | |
| | Dust | Powdering | <10 | | | |
| | Dust | Product handling (fine powder) | <10 | | | |
| | Dust | Diffuse emissions from furnace loading and unloading.<br>Carryover of fine particles | NA | | | |
| | NH$_3$ | Stack and/or diffuse ammoniac decomposition fumes from calcination | <60 | | | |
| | HF | Hydrogen fluoride | <1 | | | |
| | H$_2$ | Possible fire risk from hydrogen fumes | | | | |
| **Secondary raw material** | Dust | Same as for primary production | | Cooling water systems for the electron beam furnace are designed as closed loops and are not in | Dust that is collected in the abatement system is recycled to the | HF (hydrogen fluoride) is highly toxic and can easily be absorbed by a skin-contact |
| | H$_2$ | Possible fire risk from hydrogen fumes | | | | |

| | | | | | | |
|---|---|---|---|---|---|---|
| | $NH_3$ | Stack and/or diffuse ammoniac decomposition fumes from calcination | <60~~.~~ | contact with the processed material<br>Tantalum alloy leach and rinse<br>Tantalum sludge leach and rinse<br>Tantalum powder acid wash and rinse<br>Capacitor leach and rinse | production process<br>No data are available for the generation of other residues. | Storage and handling of HF should take this into account<br>Cobalt is normally added to the hard metal powder. This can cause "hard metal disease" therefore the emission concentration of Co is less than 1 mg/nm$_3$. |
| | HF | Hydrogen fluoride | <1 | | | |
| | Trace metals like Co, MnO, Ni and Ag can be presented in tantalum scrap and may be emitted | | Ni <1<br>Co <1 | | | |

**Table 8.7: Emissions from the production of tantalum metal**

[ 196, Finkeldei, L. 1999 ]

*The emissions for boat charging for Tantalum are 10 mg/Nm3. For Mo they were 5 mg/Nm3. What is the reference for these figures?*

| Refractory Metal | Emissions to air | | | Emissions to water | Generation, recycling and re-use of process residues | Remarks |
|---|---|---|---|---|---|---|
| **Niobium** | | | **(mg/Nm$^3$)** | | | |
| **Primary raw material** | Dust | From all sources cleaned by a fabric filter | <10 | No data are available for the generation of waste water | Dust collected in the abatement system<br>Slag from the reduction in the vacuum furnace<br>It is known that Pyrochlore, which is a significant raw material source may contain high radioactive levels and the thermal smelting process is thus potentially environmentally polluting with respect to disposal of slag<br>No information is available for the generation of other residues | Niobium and its compounds have very low toxicity<br>HF (hydrogen fluoride) is highly toxic and can easily be absorbed by a skin contact<br>Storage and handling of HF should take this into account levels. |
| | Dust | From handling fine powders | <5 | | | |
| | Dust | From the production of Niobium carbides | <5 | | | |
| | Dust | Diffuse emissions | NA | | | |
| | VOC | From solvent extraction | NA | | | |
| | HF | Hydrogen-fluoride emissions | <1 | | | |
| | HCl | | <5 | | | |
| | Al | Aluminium fines may be emitted by handling aluminium powder that is used as a reducing agent | | | | |
| | Other emissions are dependent on the used raw material and the process. Additional data are not available | | | | | |
| **Secondary raw material** | Dust | From all sources cleaned by a fabric filter | <10 | No data are available for the generation of waste | No data are available for the generation of residues | HF (hydrogen fluoride) is highly toxic and can easily be absorbed |

| | | | | | | |
|---|---|---|---|---|---|---|
| | HF | Hydrogen-fluoride emissions from digestion | <1 | water | | by a skin-contact<br>Storage and handling of HF should take this into account. |
| | Other emissions are dependent on the used raw material and the process. No data has been reported | | | | | |

**Table 8.8: Emissions from the production of niobium metal**
[ 196, Finkeldei, L. 1999 ]

| Refractory Metal | Emissions to air | | | Emissions to water | Generation, recycling and re-use of process residues | Remarks |
|---|---|---|---|---|---|---|
| **Rhenium** | | | **(mg/Nm$^3$)** | | | |
| **Primary raw material** | Dust | From all sources cleaned by a fabric filter | <10 | Production waste water<br>No information are available for the generation of waste water | Dust collected in the abatement system<br>Sludge as a residue from the removal of rhenium from scrubbing liquor<br>Refining residues<br>Sludge treatment solids<br>Rhenium raffinate | Rhenium and its compounds have very low toxicity levels |
| | Dust | From handling fine powders | <5 | | | |
| | Dust | Diffuse emissions | NA | | | |
| | Other emissions are dependent on the used raw material and the process. No data has been reported | | | | | |
| **Secondary raw material** | Emissions are dependent on the used raw material and the process. No data has been reported | | | No data are available for the generation of waste water | No data are available for the generation of residues | |
| **Zirconium and Hafnium** | | | **(mg/Nm$^3$)** | | | |
| **Primary raw material** | Dust | From all sources cleaned by a fabric filter | <10 | No data are available for the generation of waste water | Zr and Hf are also associated with radioactive metals (uranium, polonium and thorium) which can be present in residues | Zirconium processing has significant environmental risk associated with its residual radioactivity from radioactive metals (uranium, polonium |
| | Dust | Diffuse emissions | NA | | | |
| | F | Fluoride emissions | NA | | | |
| | Radioactivity from zircon | | NA | | | |

| | | | | |
|---|---|---|---|---|
| | The chlorination process for parting zircon concentrate and volatilisation of zirconium tetrachloride requires strict containment procedures.<br>Other emissions are dependent on the used raw material and the process. Additional data are not available | | Acid leachate from zirconium metal and alloy production<br>Leaching rinse water from zirconium metal and alloy production<br>Waste acid | and thorium) being presented in the heavy sand that is used as raw material, radiation levels are not published |
| **Secondary raw material** | Emissions are dependent on the used raw material and the process. No data has been reported | No data are available for the generation of waste water | No data are available for the generation of residues | |

**Table 8.9: Emissions from the production of rhenium, zirconium and hafnium metal**
[ 196, Finkeldei, L. 1999 ]

## 8.3 Techniques to consider in the determination of BAT

The sections of this document entitled 'Techniques to consider in the determination of BAT' set out techniques considered generally to have potential for achieving a high level of environmental protection in the industries within the scope of the document. The background to the way the techniques are described is given in Section 2.1.2 and Table 2.2.
*(What is the significance of this paragraph?)*

This section presents a number of techniques for the prevention or reduction of emissions and residues as well as techniques for reducing the overall energy consumption. They are all commercially available. Examples are given in order to demonstrate techniques which illustrate a high environmental performance. The techniques that are given as examples depend on information provided by the industry, European Member States and the valuation of the European IPPC Bureau. The general techniques described in Chapter 2 as 'common processes' apply to a large extent to the processes in this sector and influence the manner in which the main and associated processes are controlled and operated.

Due to the fact that only a very few companies in Europe produce refractory metals and many of the processes are commercially confidential with the exception of chromium metal only outline descriptions which focus strongly on environmental issues can be presented.

### 8.3.1 Process of aluminothermic production of chromium metal

*This section is combining all process steps in one. If feasible the section should be disaggregated into relvant parts and further information and examples plants should be provided. Can such information also be provided for other than aluminothermic production??*

**Description**
The following description gives details of a new plant installed in the UK, for the production of aluminothermic chromium metal. The plant was built to replace an existing chromium metal production plant, which had been in operation for more than 40 years. The plant was commissioned in 1997 [ 159, Coulton, G. 1999 ].

***1. Raw materials storage*****:** raw materials such as chromic oxide and aluminium powder as well as various oxidising and conditioning agents are stored at one end of the building in separate areas to prevent cross-contamination. The oxidising agents are stored in a secure compound to avoid the risk of fire.

***2. Weighing operation*****:** the chromic oxide FIBCs are attached to discharge stations situated above weighing hoppers mounted on load cells at floor level. Screw feeders transfer the raw materials into the weighing hoppers. The discharge stations are connected to cartridge filters situated outside the building. The aluminium powder discharge stations are not connected to cartridge filter units. They have antistatic vent socks fitted because of the explosion risks associated with this material.

The minor additions are added from a mezzanine floor via sack/drum tip stations. Each individual station has its own integral dust extraction unit. Vacuum lifting equipment allows the operator to empty the containers at a comfortable working height. All material caught by the dust extraction is shaken from the filter media periodically and is collected in an integral storage hopper below.

The weighing bin for each batch sits on an electrically driven bogie, which travels on a rail track situated in a pit beneath each discharge point. The various raw materials are automatically dispensed into the weighing bin. This process and the positioning of the bin on the track are computer controlled.

***3. Mixing operation*:** the weighing bin is transferred to a separate enclosed room where the contents are mixed in a rotating blender. Ventilation of this room is provided by an axial flow fan, which discharges to atmosphere. Disposable fibreglass filter panels protect the fan inlet.

***4. Firing pot preparation*:** the firing pot base is prepared with granular refractory on a stand placed at a comfortable~~-~~working height. The pot is secured on to the base and transferred to a vibratory turntable~~-~~situated in an adjacent pit. Refractory material is screw fed from a storage hopper around a central former placed in the firing pot, which is rotated slowly. The lining is compacted by the vibratory turntable.

The refractory storage hopper is fitted with an integral dust extraction and filter unit.

The rammed lining is sprayed with a binder solution and dried in one of several gas-firing units. Emissions are ducted out of the building at roof level by natural convection.

***5. Firing operation*:** The firing pot is located inside one of several firing chambers situated below ground level. Travelling fume extraction hoods are moved forward to cover the firing pot and to connect with the main extraction ducting.

The weighing bins are located on an automatic vibratory feeder platform. The feed rate of material into the firing pots is computer controlled. Once the mixture is ignited and the reaction is underway, the fume generated is ducted to the main fabric filter plant. The filter plant is located outside the main building in an extension adjacent to the firing chambers.

After the reaction fumes have subsided, a reduced extraction volume is provided to each chamber that contains a cooling pot. Powered dampers isolate the ducting to a firing chamber when it is empty.

***6. Firing pot cooling*:** when the metal has solidified, the firing pot is removed and transferred by crane to a long, slowly moving, cooling conveyor. The latter is partially enclosed by a hood and is ventilated by a number of extraction fans which discharge to atmosphere outside the building. The fan inlets are protected by disposable fibreglass filter panels.

***7. Button stripping operation*:** the cooled firing pot is transferred by a jib crane onto a bogie for transporting into a stripping booth. Inside the closed booth, the pot casing is automatically lifted off the base. The bogie is then rotated and a scraper bar removes the refractory lining. A cartridge filter plant provides dust extraction from the stripping booth.

The debris from the pot lining falls into a collection hopper and is transferred to a vibrator sieve. The sieved refractory material is collected in pans and is recycled. A filter unit provides dust extraction from the sieve and sieve discharge.

***8. Quenching operation*:** the chromium button and slag are removed from the stripping booth on the bogie. The slag is separated from the metal button, cooled and sent to a despatch area. The chromium button is transferred to a quenching tank for final water-cooling. Steam generated in this quenching operation is extracted by fans and ducted to atmosphere outside the building.

The cooled ~~Chromium~~ chromium button is transferred to other departments for cleaning; breaking; crushing and grinding, prior to packing and final despatch.

**Achieved environmental benefits**
[ 159, Coulton, G. 1999 ]
***1) The main filter plant*:** firing can only take place in one chamber at a time due to a system of interlocks on the travelling hoods and firing feed conveyor.

During the firing process when large amounts of fumes are generated for a relatively short period of time, the extraction volume is at its maximum. During this period, a lower ventilation volume is available at the other remaining chambers, one or more of which may contain a pot which is cooling but emitting little fume.

When no firing is taking place, the fume plant is automatically shut down to the lower extraction rate in order to minimise the energy consumption of the filter unit.

The filter plant comprises four compartments, with 132 filter bags per compartment. The cleaning cycle is fully automated with each chamber cleaned 'off-line' in turn by means of a reverse air pulse system.

A monitoring and recording system is installed on the fume plant to continuously monitor dust emissions. This comprises of a probe mounted in the exhaust stack and a combined control unit/microprocessor based data logger. Emissions from the stack are continually monitored and any deviation above a pre-set level will signal an alarm. The fume plant operates with a total dust emission levels below 5 mg/Nm$^3$.

***2) Emissions to air:*** Total dust emissions are below 5 mg/Nm$^3$ where the part of chromium and its compounds are less then 1 - 2 mg/Nm$^3$.

***3) Emissions to water (sewer):*** The only liquid emission is from the water quenching tanks.

***4) Emissions to land:*** Waste fume dusts from the process are taken to a licensed disposal site. The quantity of fume dust generated will depend upon the quantity of chromium metal being produced.

**Cross-media effects**
The nature of the operation is such that most of the emissions are to air rather than to either of the other two environmental media.

For most applications, the metals industry has generally used a fabric filter plant to control airborne emissions. A fabric filter plant (i.e. a dry system) was chosen for this application, as it would provide good filtration with the lowest environmental impact.

Wet scrubbing systems were considered, but rejected. A wet type of abatement such as a Venturi scrubber would result in a sludge waste, which would be more difficult and costly to dispose of, and would contain a significant proportion of water. The plume from the main stack would also be wet and not so well dispersed. *(This information refers to a certain plant where wet scrubbing was rejected. Can this be generalised?)*

**Operational data**
The plant uses the following utilities:

| | |
|---|---|
| Electricity | 139 kWh/tonne of Cr metal |
| Gas | -6m$^3$/tonne (calorific value of gas is 39.2 MJ/Nm$^3$) |
| Water | ~2 m$^3$/tome |

**Applicability**
The techniques presented above are applicable as a whole to a new plant, but it can partly also be applied to existing plants.

**Economics**
The total cost of the project was in the order of about EUR 4.35 million included in which were the following:

| | |
|---|---|
| weighing station | EUR 0.72 million |
| firing chambers/feeders | EUR 0.29 million |

| | |
|---|---|
| • cooling conveyor/stripping booth | EUR 0.36 million |
| • pot preparation | EUR 0.24 million |
| • main fume plant | EUR 0.65 million |
| • building and civil work | EUR 1.88 million. |

[ 159, Coulton, G. 1999 ]

**Driving force for implementation**
Emission reduction and product quality

**Example plants**
UK.

**Reference literature**
[ 159, Coulton, G. 1999 ].

### 8.3.2 Material handling and storage

The raw materials used for the production of refractory metals are basically metal oxides, reducing agents such as aluminium or calcium powder, hydrogen, and additives. The main environmental impact by storage and handling of these materials are diffuse dust emissions and sometimes, depending on the produced metal and the used process, contamination of surface waters and soil caused by wash out from rainwater.

There are several techniques that are based on the recovery of refractory metals from scrap. In these cases the scrap quality should be monitored in order to avoid radioactive or other contaminants in the metals to be processed. High levels of radioactivity may also be present during the processing of some raw materials such as zircon and pyrochlore.

Raw materials are preferably stored in a closed containment on hard surfaces indoor to prevent soil contamination. The storage area can also be divided in different storage bays. Dry fine-grained materials should be stored in closed silos, bins and hoppers to prevent diffuse emissions to the environment as well as to the workspace.

Closed conveyors and transfer systems are used for the handling of dusty fine materials like metal powders, where extraction and filtration equipment is used for dusting delivery points. The dust-laden air from the silos, closed conveyors and charging systems are cleaned by using fabric filters, which may be monitored by measuring the pressure drop to control the cleaning mechanism. The collected dust is normally fed back to the storage area because raw materials for producing refractory metals (hard metals) are valuable minerals.

Metal scrap, turnings and swarf for the production of secondary titanium metal sometimes have to be liberated from oil and cutting liquids, which may take place by drying in a rotary kiln. Ducting carries the oil-bearing gases away from the dryer and through a cyclone to remove dust and carryover. The gases then pass through an afterburner, which is heated by a gas-fired burner. Combustion gases/fumes are either recirculated through the dryer or are ducted to a second cyclone. After passing through the cyclone, sorbent (sodium bicarbonate) is introduced to neutralise the gas stream. Finally the gas passes through a ceramic filter unit before being discharged to the atmosphere via a stack. A detailed example of this technology is presented in Chapter 9 ferro-alloys. *(The measures described in the previous paragraph belongs to material pretreatment and not to storage and handling. Relocate to an appropriate section)*

Hydrofluoric acid is used in several processes to produce refractory metals such as Ta and Nb. The handling of HF requires precautionary measures with respect to health and safety at work, since HF is recognised as aggressive and very toxic. An essential requirement for health and safety of workers for example is the permanent availability of a calcium digluconate solution as a first aid in cases of skin contact.

**Achieved environmental benefits**
Prevention and capture of dust.
*Real measured data are needed where off-gas treatment and measurements take place.*

**Cross-media effects**
No data has been reported.

**Operational data**
Given in the descriptions of the process above.

**Applicability**
These techniques are applicable to most installations.

**Economics**
No data has been reported.

**Driving force for implementation**
Environmental impact and energy costs due to lost material.

**Example plants**
UK, ES, DE
*Find real cexample plants.*

**Reference literature**
[ 290, EC 2006 ].
*This reference is referring to the emissions from storage BREF. This is not a correct reference for the introduced new and in red indicated information. Where are the example plants in the UK, ES, DE and were can the corresponding information be found??*

### 8.3.3 Smelting, firing, hydrogen reduction and carburisation processes

**Description**
During the production of refractory metals, hard metal powder and metal carbides, one of the most important stages is the reduction of metal oxides. Depending on the reducing agent, different types of smelting techniques are techniques to consider in determining BAT. Table 8.10 gives an overview of these furnaces.

**Achieved environmental benefits**
The environmental benefits are the prevention of diffuse emissions of metals, dust and other compounds.

**Cross-media effects**
None are reported.

**Operational data**
See Table 8.10.

**Applicability**
The processes and the techniques are suitable for use with new and existing installations.

**Economics**
None was provided but the processes are operating economically.

**Driving force for implementation**
The reduction of emissions and saving raw materials.

**Example plants**

Plants in DE, AT, FR, BE, PL and NL.

**Reference literature**

[ 196, Finkeldei, L. 1999 ], [ 233, Farrell Nordic Mission 2008 ] [510].

*[196] is a reference to a personal communication which took place 1999. The outcome is the text in this section. Furthermore the reference Winter, 1998, UBA AT, Emissionserklaerung Treibacher Chemische Werke was cited in the existing BREF.*

| Firing, smelting or reduction system | Metal produced | Gas collection and abatement | Advantages | Disadvantages |
|---|---|---|---|---|
| Electric arc furnace | Mo<br>(under vacuum) | | Remelting of secondary metals | |
| Firing pot (crucible) | Cr | Movable closed hood connected with a fabric filter | | |
| Pusher furnace | Ta, W powder<br>Ta, W carbides<br>$MoO_3$ reduction with hydrogen | Fabric filter<br>Wet scrubber | Production of refractory metal powder<br>Production of refractory metal carbides by carburisation<br>Quasi continuous production | The raw material should be charged in small containers called boats |
| Band furnace | Ta, W powder<br>Ta, W carbides | Fabric filter<br>Wet scrubber | No loading and unloading of the boats<br>Continuous production<br>Fully automated | |
| Rotary furnace | W powder | Fabric filter<br>Wet scrubber | Production of tungsten metal powder | |
| Batch furnace | Ta and W carbides | Fabric filter<br>Wet scrubber | Production of refractory metal carbides by carburisation | The raw material should be charged under sealed conditions |
| Electron beam furnace | Melting of Nb, Ta, Mo, W and Ti. | Vacuum extraction, condenser and scrubbing system | High power density<br>Very high temperature<br>Water cooled inert crucible<br>Controlled atmosphere<br>Low off-gas volume | High specific energy consumption<br>Low melting rate |
| | Refining of V, Nb, Ta, Hf and Zr | Vacuum extraction, condenser and scrubbing system | Removing of C, O, N, H and divers other impurities | |

**Table 8.10: Summary of advantages and disadvantages of the used smelting systems used in the production of refractory metals**
[ 196, Finkeldei, L. 1999 ]

## 8.3.4 Production of tungsten metal powder and tungsten carbide

The techniques for the production of tungsten metal powder and tungsten carbides is reported here and the same techniques can also be used to produce tantalum metal or other refractory metal powder. *(The heading is inappropriate. The information that other metals can be produced by the same techniques might be included in the improved heading which indicates the environmental relevance of this section)*

**Description**

The installation produces tungsten metal powder. Ammonium paratungstate (APT) is used as raw material and calcined to yellow and blue oxide ($WO_3$ or $W_{20}O_{58}$). Subsequently the yellow and blue oxide is reduced to tungsten metal powder by using hydrogen as a reducing agent. The reduction takes place in a modern automated band furnace, which is equipped with a closed system where excess hydrogen is directly recycled. A condenser is used for removing water and dust carryover. The dust (hard metal powder) is recycled. The tungsten metal powder can further be transformed by carburisation into tungsten carbide. The techniques is shown in Figure 8.12.

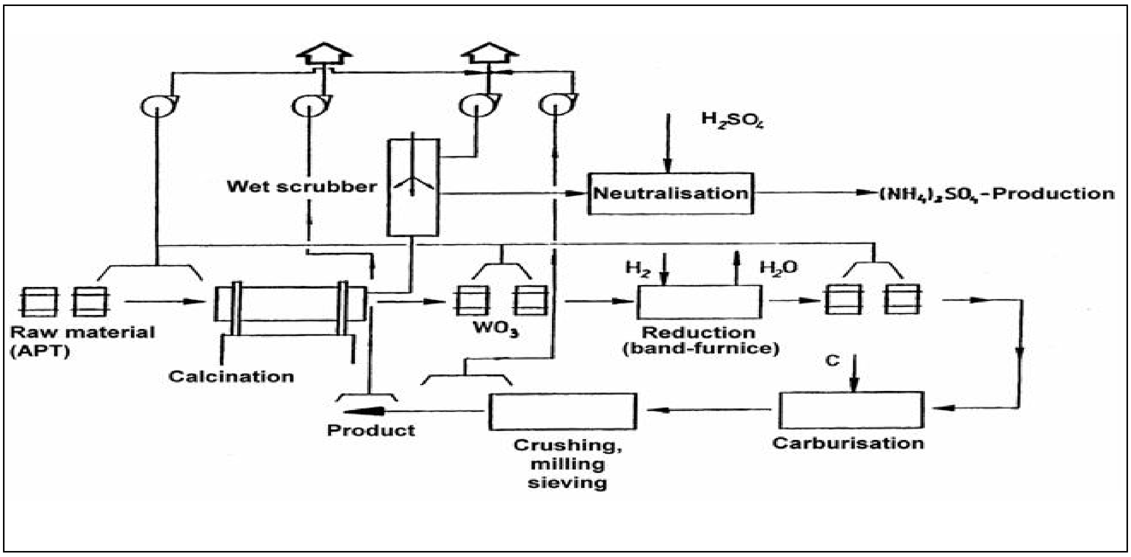


**Figure 8.12: Production of tungsten powder and tungsten carbide**

**Achieved environmental benefits**

Two fabric filters clean the suction air that is collected by appropriate hoods and the process equipment see Table 8.11. The dust that is collected by the filter consists of nearly 100 % of tungsten powder and is recycled to the production process.*(In the figure a wet dedusting system is shown. Here under achieved*

| Process step | Dust after abatement (mg/Nm³) |
|---|---|
| Raw material handling | <1.0 |
| Calcining (rotary furnace) | <4 |
| Conveyor r~~R~~eduction furnace ~~(band fu~~rnace) | <1.0 |
| Powdering | <4 |
| Product handling | <4 |

**Table 8.11: Dust emissions after abatement**

[ 178, UBA (A) 1998 ] ~~[510]~~

*Clarify with Austria who provided the information [510] if table 8.11 is still needed.. Table 8.12 and 8.13 gives the updated data for the same installation.*

| Process step | Off-gas flow Nm$^3$/h | Dust (mg/Nm$^3$) | Tungsten (mg/Nm$^3$) |
|---|---|---|---|
| Conveyor reduction furnace and mixer | 1488 | 0.66 | 0.52 |
| Rotary furnace (Continuous reduction furnace) | 744<br>744 | 0.77<br>0.84 | 0.61<br>0.67 |
| Tungsten mixer | 60 | 0,81 | 0.64 |
| NB.: Measured data, no side information about measurement conditions | | | |

[510]

**Table 8.12: Off-gas flows and captured emissions after abatement**

| Process step | Off-gas flow Nm$^3$/h | CO (mg/Nm$^3$) | NO$_X$ (mg/Nm$^3$) | SO$_2$ (mg/Nm$^3$) |
|---|---|---|---|---|
| Two Pusher-type furnaces | 2500 each | < 80 | < 150 | < 300 |
| NB.: The values are ELVs | | | | |

[510]

**Table 8.13: Off-gas flow and emissions from atwo pusher-type furnaces**

**Cross-media effects**
A small amount of washing liquid from the wet scrubber should be neutralised and treated. There are no other important cross-media effects. *This only applies if wet scrubbers are used.*

**Operational data**
No data has been reported.

**Applicability**
This technique is applicable to all new and existing hard metal powder and carbide productions.

**Economics**
No data has been reported.

**Driving force for implementation**
Clean technology. *(This is not the driving force.)*

**Example plants**
AT

**Reference literature**
[ 178, UBA (A) 1998 ] [510]

.

### 8.3.5 Recovery of rhenium from weak acid

**Description**

[ 280, Polish Report 2008 ]
Polish copper deposits contain rhenium. The concentration is 1 - 2 ppm in the ore and 5 - 15 ppm in the concentrate. The metal is mainly present in the form of rhenium sulphide ($Re_2S_7$). The compound is volatile and is easily oxidised in a flash smelting furnace operated to produce blister copper. Rhenium oxide is removed from the gases by the first scrubber of the sulphuric acid plant gas treatment system and weak sulphuric acid (2 - 8 % of $H_2SO_4$) is produced. This acid contains 20 to 50 mg/l of rhenium as rhenic (VII) acid. This is used for the production of ammonium perrhenate - APR (ammonium rhenate(VII).

The weak acid is filtered and also contains molybdenum (5 – 8 mg/l), arsenic (480 – 800 mg/l), copper (3 – 8 mg/l), selenium (6 – 8 mg/l) and hydrochloric/hydrofluoric acids. The filtered acid is then treated in an ion exchange process processing up to 30 $m^3$/h of the acid and rhenium is removed. A weak acid ion exchange resin, especially designed and produced for Re recovery is used.

Four columns are used in series and the flow is stopped when breakthrough is detected from the first column. The outlet from the last column during the sorption cycle contains <1 mg/l of rhenium. The bed of the first column is washed with demineralised water, and rhenium is eluted with 6 % ammonium hydroxide solution and washed again to prepare the column for the next cycle as the last in line. The eluate contains 10 - 20 g/l Re and is concentrated in glass vacuum evaporators.

The concentrated solution is pumped into a crystalliser where crystals of APR are formed and then filtrated and sent to the recrystallisation stage. Crude crystals are dissolved in hot water filtered and cooled. Crystals produced in this step are the final product. Mother liquor from recrystallisation is sent back to the evaporation stage.

Mother liquor from the first crystallisation stage is returned to the ion exchange stage.

The process produces APR to the following specification:

Re 69.4 %, Fe <0.0005 %, Ni <0.0005 %, Cu <0.0005 %, Ca <0.005 %, Mg <0.0005 %, Mo <0.0005 %, Na <0.0005 %, Pb <0.0005 %, K <0.001 %, Si <0.001 %, Cl <0.005 %, Al, Tl, Se, S, Ni, Zn, Sb, P <0.005 %.

**Achieved environmental benefits**
Environmental benefits are mainly related to improvement of natural resources utilisation and the elimination of rhenium in the final effluent.

**Cross-media effects**
Use of energy and materials.

**Operational data**
*Emissions*
The process recovers rhenium from the effluent, which was normally directed to the effluent treatment plant. The volume of the effluent is increased by 30 – 40 $m^3$/day due to the resin bed washing waters.

Solid waste is not produced, effluent treatment plant filter cake contains some metals (Pb, Cu) but is returned to the smelter. So far the life-time of the implemented resin is not known. The used bed will eventually be incinerated.

No significant air emission occurs, because the evaporators are fully equipped with vapour condensers.

*Consumption data*

Production of 1 kg of APR uses:

- 8 – 10 $m^3$ of water, including 0.15 $m^3$ of drinking water and 0.14 $m^3$ of deionised water
- 80 – 90 kWh of electricity
- 0.22 – 0.28 GJ of heat energy
- 50 – 60 kg of $NH_3$aq (25 %)
- 10 – 12 kg of sulphuric acid
- 6 – 7 kg of nitric acid
- 3 – 4 kg of $H_2O_2$aq (30 %).

**Applicability**
The ion exchange technology may have some limits in its application with more concentrated washing solutions. The data show that it can be operated when the concentration of Re in a solution is extremely low. The resin selectivity makes possible and effective the recovery of rhenium even from contaminated solutions.

**Economics**
The process is operating profitably.

**Driving force for implementation**
Improvement in mineral resources utilisation and economic profitability.

**Example plants**
The installation is operated by Polish company KGHM Ecoren S.A. (www.ecoren.pl), a part of KGHM Polska Miedź S.A.

**Reference literature**
[ 280, Polish Report 2008 ].

### 8.3.6 Gas collection and abatement

The techniques for fume collection and abatement discussed in Section 2.4.4 are techniques to consider for the production of refractory metals. Fabric filter and wet scrubbers are normally used for dedusting the process off-gases.

A number of different fabric filter designs exist using different kinds of filter materials, which in principle all achieve very low emission values of dust below 5 mg/Nm$^3$. The use of modern filtration techniques, like membrane filter (surface filtration) results additionally in an increasing bag life, high temperature limit (up to 260 ºC) and relatively low maintenance costs combined with very low dust emissions. Due to the low off-gas volume in the hard metal powder and metal carbide production, emission concentrations of dust in the range of less than 1 mg/Nm$^3$ are possible with modern filter materials. Low dust emissions are both environmental and economically interesting, because hard metal powder and carbides are valuable products. Nevertheless, low dust emissions of hard metals, especially by recycling tungsten scrap that contains cobalt, are important in order to protect the working area and to minimise the risk of health damage.

~~In the metallurgical industry, baghouse filters are often pressure filters with fans on the dirty gas side. Recent developments led to a closed suction filter with fans on the clean gas side. This combines the advantages of gentle bag cleaning meaning a longer bag life with low operating and maintenance costs and a defined gas volume [ 141, Elkem Asa 1998 ].~~

Hooding systems are used to collect process off-gases, especially fume from metal smelting and dust where hard metal powder and metal carbides are produced. Hooding systems are therefore techniques to consider also with the aim to minimise diffuse emissions. The design of the hooding system should take account of access for charging and other furnace operations and the way the source of process gases change during the process cycle.

### 8.3.7 Process control

The principles of process control discussed in Sections 2.5 and 2.20.3 are applicable to the production of refractory metals. *(2.20.3 is a BAT conclusion section. We are still in the Technique to consider section. Furthermore the cross reference to section 2.5 is not helpful at all. )*

### 8.3.8 Waste water

Existing treatment systems in Section 8.1 are reported to be to a high standard. All waste water should be treated to remove dissolved metals and solids. For Mo and W the metal removal and accumulation in the anion exchanger and precipitation through acidification as the oxidhydrate is the technique to consider for dissolved metals.

In a number of installations cooling water and treated waste water including rainwater is re-used or recycled within the processes.

Water treatment is needed in the processes with wet scrubbers and granulation processes, because suspended solids should be removed before the water is recirculated. To reach acceptable values of harmful components, it may in some cases, be necessary to polish the bleed that should be taken from the scrubbing water cycle. This may take place by using sand filters, carbon filters or by adding suitable ~~-~~chemicals to precipitate harmful compounds.
*Please provide complete examples for waste water treatment including all applied different steps and sufficient data.*

### 8.3.9 By-products, process residues and waste

The processes and recycling routes that were discussed earlier in Section 8.1 and 8.2 for the different refractory metals are techniques to consider in the determination of BAT. The most important factor to reduce the environmental impact of discharging residues as waste are process-integrated measures that result in the generation of fewer residues. If the amount of process residues is minimised by using primary measures, the extended amount should be recycled or re-used as much as possible. The specific feed materials will influence the final process choice. The techniques discussed in Chapter 2 should also be considered in conjunction with these processes.

## 8.4 Best Available Techniques

In understanding this section and its contents, the attention of the reader is drawn back to the Preface of this document and in particular the fifth section of the Preface: ‘How to understand and use this document’. The techniques and associated emission and/or consumption levels, or ranges of levels, presented in this chapter have been assessed through an iterative process involving the following steps:

- identification of the key environmental issues for the sector which for the production of refractory metals, hard metal powder and metal carbides are: dust and fume, solid hard metal and metal compounds, waste water, residues such as filter dust, sludge and slag. Process chemicals, such as hydrogen fluoride (HF) that are used for processing tantalum and niobium, are highly toxic and need to be taken into account by handling and storage of these materials;
- examination of the techniques most relevant to address these key issues;
- identification of the best environmental performance levels, on the basis of the available data in the European Union and worldwide;
- examination of the conditions under which these performance levels were achieved; such as costs, cross-media effects, and the main driving forces involved in implementation of the techniques;
- selection of the best available techniques (BAT) and the associated emission and/or consumption levels for this sector in a general sense, all according to Article 2(12) and Annex IV to the Directive.

Expert judgement by the European IPPC Bureau and the relevant Technical Working Group (TWG) has played a key role in each of these steps and in the way in which the information is presented here.

On the basis of this assessment, best available techniques, and as far as possible emission and consumption levels associated with their use, are presented in this section that are considered to be appropriate to the sector as a whole and in many cases reflect the current performance of some installations within the sector. Where emission and consumption levels 'associated with best available techniques' are presented, this is to be understood as meaning that those levels represent the environmental performance that could be anticipated as a result of the application, in this sector, of the techniques described, bearing in mind the balance of costs and advantages inherent within the definition of BAT. However, they are neither emission nor consumption limit values and should not be understood as such. In some cases, it may be technically possible to achieve better emission or consumption levels but due to the costs involved or cross-media considerations, they are not considered to be appropriate as BAT for the sector as a whole. However, such levels may be considered to be justified in more specific cases where there are special driving forces.

The emission and consumption levels associated with the use of BAT have to be seen together with any specified reference conditions (e.g. averaging periods).

The concept of ‘levels associated with BAT’ described above is to be distinguished from the term ‘achievable level’ used elsewhere in this document. Where a level is described as ‘achievable’ using a particular technique or combination of techniques, this should be understood to mean that the level may be expected to be achieved over a substantial period of time in a well maintained and operated installation or process using those techniques.

Where available, data concerning costs have been given together with the description of the techniques presented in the previous sections. These give a rough indication about the magnitude of the costs involved. However, the actual cost of applying a technique will depend strongly on the specific situation regarding, for example, taxes, fees, subsidies, and the technical characteristics of the installation concerned. It is not possible to evaluate such site-specific factors fully in this document. In the absence of data concerning costs, conclusions on economic viability of techniques are drawn from observations on existing installations.

The BAT (including the associated emission and consumption levels) given in this section are 'BAT in a general sense' (i.e. considered to be appropriate to the sector as a whole). It is intended that they are a reference point against which to judge the current performance of an existing installation or to judge a proposal for a new installation. In this way, they will assist in the determination of appropriate 'BAT-based' conditions for the installation or in the establishment of general binding rules under Article 9(8) of the IPPC Directive. It is foreseen that new installations can be designed to perform at or even better than the BAT levels presented in this section. It is also considered that existing installations could move towards the BAT levels presented in this section or do better, subject to the technical and economic applicability of the techniques in each case.

While the BAT reference documents do not set legally binding standards, they are meant to give information for the guidance of industry, Member States and the public on achievable emission and consumption levels when using specified techniques. The appropriate permit conditions for any specific case will need to be determined taking into account the objectives of the IPPC Directive and the local considerations.

**Recommendation to help users/readers of this document:**

It is strongly recommended that this section on BAT be read in conjunction with the sections of this document that describe the techniques to consider in the determination of BAT. The applicability of the techniques and measures are reported in these sections and should be taken into account at a local level. To help the reader, references to the appropriate sections are included in the description of BAT.

If not otherwise mentioned, BAT associated emission and consumption levels given in this section are expressed as follows:

- for pollutants emitted to air (except dioxins): expressed on a daily average basis with standard conditions of 273 K, 101.3 kPa, measured oxygen content and dry gas with the plant operating normally under steady-state conditions and no dilution of the gases;
- for dioxins: expressed as the average over the sampling period which should preferably be a minimum of 6 hours;
- for waste water: based on qualified random samples or 24 hour flow proportional composite samples.

As described in the Preface, this document does not propose emission limit values. The best available techniques and the ranges of emission or consumption levels associated with best available techniques (BAT-AEL ranges) are related to installations with different sizes, different kinds of operation and different raw materials. In this document, special local considerations cannot be taken fully into account. The determination of appropriate permit conditions will involve taking account of local, site-specific factors such as the technical characteristics of the installation concerned, its geographical location and the local environmental conditions. In the case of existing installations, the economic and technical viability of upgrading them also should be taken into account. Even the single objective of ensuring a high level of protection for the environment as a whole will often involve making trade-off judgements between different types of environmental impact, and these judgements will often be influenced by local considerations.

Although an attempt is made to address some of these issues, it is not possible for them to be considered fully in this document. The techniques and emission and consumption levels presented here will therefore not necessarily be appropriate for all installations. On the other hand, the obligation to ensure a high level of environmental protection including the minimisation of long-distance or transboundary pollution implies that permit conditions cannot be set on the basis of purely local considerations. It is therefore of utmost importance that the information contained in this document be fully taken into account.

Section 2.20 to this document reports BAT for the following common processes and the following sections should be referred to for those techniques that are BAT:

- environmental management systems (EMS) (Section 2.20.1)
- material handling and storage (Section 2.20.2)
- process control (Section 2.20.3)
- fume and gas collection (Section 2.20.4)
- the prevention and the destruction of PCDD/F (Section2.20.5)
- sulphur dioxide removal (Section 2.20.6)
- the removal of mercury (Section 2.20.7)
- effluent treatment and water re-use (Section 2.20.8)
- energy efficiency (Section 2.20.9)
- intermediate products, process residues and wastes (Section 2.20.10)
- emission monitoring (Section 2.20.11)
- prevention of the formation of $NO_X$ (Section 2.20.12)
- removal of dust and particles (Section 2.20.13)

BAT for the production of refractory metals is the combination of the generally applicable techniques reported in Section 2.20 and the specific techniques indicated in this section.

## 8.4.1 Prevention and control of emissions to air

### 8.4.1.1 Material handling and storage

**a) BAT is to prevent diffuse emissions by using the following techniques for materials in this sector.**

- Characterisation of raw materials before they are received so that handling, storage and processing difficulties can be taken into account. *(this is general and be relocated to chapter 2)*
- Off-loading of pure titanium tetrachloride (TTC) from rail or road tankers with argon and stored under a blanket of argon. The storage tanks need to be vented to an argon gas-holder via a cold trap to recover any TTC in the vent system. *(I can not find a corresponding Technique to consider in the determination of BAT in the whole document. Where is this information coming from?)*
- Treatment of acid fumes vented from storage tanks prior to being discharged to atmosphere. *(I can not find a corresponding Technique to consider in the determination of BAT in the whole document. Where is this information coming from?)*
- Sampling and analysis of raw materials so that the process options can be defined for a particular raw material and radioactive raw materials can be identified. *(this is general and be relocated to chapter 2)*
- Precautionary handling of HF.

### 8.4.1.2 Smelting, firing, hydrogen reduction and carburisation process

*(Why is only hydrogen reduction included? The are other reduction agents such as carbon, calcium, aluminium, magnesium, magnesium chloride)*

The production of different refractory metals and the environmental impact of the processes are widely influenced by the smelting, reduction and carburisation system that are used.

*This sentence is redundant.*

**a) BAT is to prevent diffuse emissions and optimise the use of energy for refractory metal production by using the techniques given in Table 8.14 and Table 8.15 or a combination of them (see also Section 8.1).**

*What about the prevention of non-diffuse emissions? Should the requirements in table 8.13 be applied for all processes?*

| Furnace type | Produced metal | Gas collection and abatement technique | Remarks |
|---|---|---|---|
| Reaction chamber (firing pot) | Cr produced by metallothermic reduction | Movable closed hood connected to a fabric filter | Recovery of heat energy will not be practised because the metallothermic reduction takes place as a batch process, which needs only a short reaction time |
| Pusher furnace | Ta, W powder<br>Ta, W carbides<br>$MoO_3$ reduction with hydrogen | fabric filter<br>wet scrubber | The reduction furnace of metal oxides is equipped with a closed system where excess hydrogen is directly recycled. A condenser is used for removing water and dust carryover. The dust (metal- or carbide powder) is re-used. Each furnace needs a nitrogen purge. The stoker arm should be sealed to the tube entrance. Boats are emptied over a screen into drums. |
| Band furnace<br>Conveyor furnace | Ta, W powder<br>Ta, W carbides | fabric filter<br>wet scrubber | The reduction furnace of metal oxides is equipped with a closed system where excess hydrogen is being directly recycled. A condenser is used for removing water and dust carryover. The dust (hard metal powder) is re-used.<br>Each furnace needs a nitrogen purge |
| Rotary furnace | W powder | fabric filter<br>wet scrubber | The kiln is sealed to prevent egress of fume and dust |
| Batch furnace | Ta and W carbides- | fabric filter<br>wet scrubber | The extraction system should be able to handle variable off-gas volumes |
| Electric vacuum furnace | Secondary refractory metals from scrap, e.g. titanium | fabric filter<br>wet scrubber | Melting of the metals<br>Energy recovery may only be possible from the cooling water cycle |
| Electron beam furnace | Nb, Ta, Mo, W and Ti. | vacuum extraction condenser and scrubbing system | Melting or refining of the metals<br>High energy consumption<br>energy recovery may only be possible from the cooling water cycle<br>Zr and Hf are also associated with radioactive metals (uranium, polonium and thorium) which can be present in residues |
| | V, Nb, Ta, Zr and Hf | vacuum extraction condenser and scrubbing system | |

**Table 8.14: BAT furnaces for the production of refractory metals**

*In this case the remarks to the furnace type are useful. They can be used to rephrase the BAT conclusions.*

**The emission levels given in Table 8.15 are the BAT-AELs.**

| Pollutant | Techniques | BAT-AELs ($mg/Nm^3$) | Comments |
|---|---|---|---|
| Dust | Fabric or ceramic filter | <1 – 5 | A bag burst detection system should be used. *(redundant)* (See Sections 2.9.2.2.4 and 2.20.13) |
| Metals | Fabric or ceramic filter | Cr and its compounds <1<br>Mo 0.01 – 0.1<br>Ni and Co <1 | High performance fabric filters (e.g. membrane fabric filters) can achieve low levels of metals. The concentration of metals is linked to the concentration of dust and the proportion of the metals as part of the dust (see Section 8.2.5). |
| $NH_3$ | Wet scrubbing and subsequent neutralisation with $H_2SO_4$ | <60 $mg/Nm^3$ | For the production of Tantalum. In the production of tungsten metal powder and metal carbide, $NH_3$ can also be recovered for the APT production (see Section 8.2.5) |
| HF | Wet scrubbing system | <1 $mg/Nm^3$ | (See Section 8.2.5). |
| NB: Collected emissions only. BAT-AELs are given as daily averages based on steady-state operation or, in cases where continuous monitoring is not practicable as the average over the sampling period. | | | |

**Table 8.15: BAT and BAT-AELs to prevent and control emissions to air from refractory metal production processes**

*What about the prevention of non-diffuse emissions? Should the requirements in table 8.13 be applied for all processes? It is unclear for which processes these BAT-AEL should be applied. I assume for the ones mentioned in the heading of the section: Smelting, firing, hydrogen reduction and carburisation process*

### 8.4.2 Effluent treatment and water re-use

**a) BAT is to use the techniques for waste water treatment given in Sections 2.20.8 and 8.2.5.** *But there is almost no information in 8.2.5!*

**The emission levels given in Table 8.16 are the BAT-AELs.**

| Component | BAT-AELs (mg/l) |
|---|---|
| $Cr^{total}$ | 0.1 to 0.2 |
| $Cr^{VI}$ | 0.01 to 0.05 |
| Hg | 0.01 to 0.05 |
| Mo | <0.1 to 0.4 |
| W | 0.2 to 0.8 |
| Co | <0.05 to 0.5 |
| NB: BAT-AELs are based on qualified random samples or twenty four hour flow proportional composite samples. | |

**Table 8.16: BAT-AELs for emissions to water**

*Where is the reference for these values????Its [242, Table 9] . But only for Mo, W, Co. Where are the data for Cr, Hg taken from? Shall these values be applied for all waste waters from all processes?*

### 8.4.3 By-products, process residues and waste

Specific techniques for the refractory metals sector are given here.

**a) BAT is to recycle and re-use slag, filter dust and sludge using the techniques reported in Table 8.17 (see also Section 2.20.10). If recycling or re-use is not economically possible, secure disposal should be used.**

| Refractory metal | Residue | Techniques |
|---|---|---|
| Chromium | Dust<br>Slag | Dust might partly be re-used.<br>Slag can be re-used for a variety of purposes.<br>Chrome-alumina slag can be sold as raw material to the steel and refractory industry |
| Manganese | Dust | Dust is partly recycled back to the process |
| Tungsten | Dust | Additive in the iron and steel industry |
| Vanadium | Dust | Dust is recycled back to the process |
| Molybdenum | Dust | Additive in the iron and steel industry |
| Titanium | Dust | Dust is recycled back to the process.<br>Some melting furnace crucibles are cooled with liquid sodium-potassium alloys (NAK) and small quantities of oxidised material of this source are generated in the form of sludge. The sludge is reacted with water and the resulting liquid is discharged to the effluent treatment plant |
| Tantalum | Dust | Dust is recycled back to the process |
| Niobium | Dust | Dust is recycled back to the process.<br>Slag from the reduction in the vacuum furnace.<br>It is known that pyrochlore, which is a significant raw material source, may contain high radioactive levels and the thermal smelting process is thus potentially environmentally polluting with respect to disposal of slag |
| Rhenium | Dust | Dust is recycled back to the process.<br>Sludges as a residue from the recovery process of rhenium from scrubbing liquor that was generated by a molybdenum roasting process. The sludge should be treated. |
| Zirconium | Dust<br>Slag | Zr is also associated with radioactive metals (uranium, polonium and thorium) which can be present in residues. |
| Hafnium | Dust<br>Slag | Hf is also associated with radioactive metals (uranium, polonium and thorium) which can be present in residues. |

**Table 8.17: BAT for the prevention of waste generation by recycling or re-use of by-products, process residues and wastes from the production of refractory metals**

## 8.5 Emerging Techniques

Due to strategic and environmental considerations, the recycling of hard metal scrap becomes more and more important, therefore a lot of research have been done in recent years in this field. Selective electrolytic dissolution has been researched for the recycling of hard metal scrap but not detailed information is available to describe the current stage of the developments.

Further information on the development of new processes and furnace improvements are very difficult to get, because process developments and improvements are sometimes carried out directly by the hard metal producing companies, which will then be covered by commercial confidentiality.

# 9 FERRO-ALLOYS

Ferro-alloys are mainly used as master alloys in the iron, foundry and steel industry, because it is the most economic way to introduce an alloying element in the steel melt. Besides this, special ferro-alloys are also needed for the production of aluminium alloys and as starting material in specific chemical reactions.

As an additive in the steel production, ferro-alloys improve the properties, especially the tensile strength, wear and corrosion resistance. The effect of the improved properties of steel by using ferro-alloys as an alloying element depend more or less on the following influences [ 104, Ullmann's Encyclopedia 1996 ]:

- a change in the chemical composition of the steel
- the removal or the tying up of harmful impurities such as oxygen, nitrogen, sulphur or hydrogen
- a change in the nature of the solidification, for example, upon inoculation.

Depending on the raw material that is used (primary or secondary raw material), the production of ferro-alloys can be carried out as a primary or secondary process. The principal chemistry of both processes can be shown as follows.

Primary processes:

Oxidic metal ore + iron ore/scrap + reducing agent → ferro-alloy + reducing agent oxide + slag

Secondary processes:

*Check whether in Ferro Alloy production usually a difference is made between primary and secondary production.*

Metal scrap + iron scrap → ferro-alloy

Primary ferro-alloys are principally produced either by the carbothermic or metallothermic reduction of oxidic ores or concentrates. The most important process is the carbothermic reduction in which carbon in the form of coke (metallurgical coke), coal or charcoal is normally used as a reducing agent. When a blast furnace is used, coke is also needed as an energy source [ 255, VDI (D) 2576 2008 ].

The metallothermic reduction is mainly carried out with either silicon or aluminium as the reducing agent. The following chemical equations show the basic principles of the carbothermic and metallothermic production routes.

Carbothermic reduction: metal oxide + carbon → metal + carbon monoxide

Silicothermic reduction: metal oxide + silicon ↔ metal + silicon oxide

Aluminothermic reduction: metal oxide + aluminium → metal + aluminium oxide

## 9.1 Applied processes and techniques

Depending on the production rate, ferro-alloys can be divided into two main categories: bulk alloys and special alloys. Bulk ferro-alloys (ferro-chrome, ferro-silicon, ferro-manganese, silico-manganese and ferro-nickel) account for about 90 % of the total production of ferro-alloys in the European Union.

Compared to bulk ferro-alloys, the production rate of special ferro-alloys is rather small. Special ferro-alloys (ferro-vanadium, ferro-molybdenum, ferro-tungsten, ferro-titanium, ferro-boron, and ferro-niobium) are mostly used in the iron, steel and cast-iron industries. Besides this, some special ferro-alloys are increasingly also used in other industry sectors, e.g. aluminium and chemical industries.

### 9.1.1 Ferro-chrome

Ferro-chrome, along with nickel (ferro-nickel) is the major alloying element in the production of stainless steel. Stainless steel is used in a variety of areas from cutlery to aircraft engine turbine blades.

The chromium content of ferro-chrome normally varies from 45 to 75 % together with various amounts of iron, carbon and other alloying elements. The use of ferro-chrome depends widely on the carbon content. Ferro-chrome can therefore be classified as follows.

- high-carbon ferro-chrome (HC FeCr) with 2 - 12 % C (*ferro-chrome carburé*)
- medium-carbon ferro-chrome (MC FeCr) with 0.5 - 4 % C (*ferro-chrome affiné*)
- low-carbon ferro-chrome (LC FeCr) with 0.01 - 0.5 % C (*ferro-chrome suraffiné*).

#### 9.1.1.1 Raw materials

The main raw material to produce ferro-chrome is chromite ore, which is a mineral that contains iron and chromium oxides. The ratio between Cr and Fe in the chromite ore determines the chromium content of the alloy produced, e.g. a high Cr to Fe ratio is advantageous for the production of a ferro-alloy with high chromium content. Chromite ore and concentrates are used in the form of hard lump and friable lump types, as well as chromite fines.

Depending on the different production routes and the desired carbon content of the ferro-chrome, carbon or silicon is used as a reducing agent [ 255, VDI (D) 2576 2008 ]. For the production of HC FeCr, carbon is added to the process as a reducing agent in the form of metallurgical coke, coal or charcoal. Metallurgical coke is the most common reducing agent. It is important that a coke with a low phosphorus and sulphur content is used because 60 - 90 % of the phosphorus and 15 - 35 % of the sulphur is transferred into the metal. For the production of LC FeCr ferro-silico-chromium and ferro-silicon are used in a silicothermic reduction as reducing agents and raw material.

In order to achieve the right metal analysis, a good metal recovery and a satisfactory furnace operation, auxiliary materials such as quartzite, bauxite, corundum, lime and olivine can be added to the burden as fluxing agents.

#### 9.1.1.2 Pretreatment techniques

Chromite is used as a raw material for the production of ferro-chrome in the form of lumpy ore, fines and concentrates. It should be noted that about 70 - 80 % of the world's chromite sources are available as fines (<10 mm). To convert ore fines and concentrates to furnaceable material, they first need to be agglomerated by briquetting, pelletising/sintering or sintering.

Agglomeration is necessary to achieve good recoveries and also to give a permeable burden, which allows the gas from the reaction zone to escape [ 255, VDI (D) 2576 2008 ].

Green pellets are made by rolling fine-grained moist ore with the addition of a binder and fine-grained coke breeze into balls in a rotary drum or on a disc. These are later sintered in a steel belt furnace to hard, porous pellets with constant physical and chemical properties. The coke breeze in the pellets with an addition of furnace gas is used as fuel for the sintering.

Where thermal treatment (sintering) is involved, process off-gases must be cleaned in cascade scrubbers or fabric filters. For all the agglomeration processes, collected raw material dusts from these processes or from other raw material handling processes, can be recycled.

### 9.1.1.3 Production of ferro-chrome and silico-chromium

#### 9.1.1.3.1 High-carbon ferro-chrome

High-carbon ferro-chrome (HC FeCr) is produced almost exclusively by the direct carbothermic reduction of chromite ore in three-phase submerged electric arc furnaces (EAF) with continuous operation. The burden can be preheated in a shaft furnace or rotary kiln by using the CO gas from the smelting process. Pre-reduction in a rotary kiln is also possible. In both cases the specific consumption of electrical energy will be reduced. Closed, semi-closed or open submerged electric arc furnaces including three-phase AC (alternating current) operation and single phase direct current plasma furnaces are used. The DC arc furnace includes a single hollow graphite electrode. *(Isn't this contradictory to the first sentence? Check whether closed furnaces are really applied!)*

The submerged arc furnaces use Søderberg electrodes where the electrode may be formed by hot paste, briquettes, blocks or paste cylinders. The electrode paste is charged on top of the electrode in accordance with its consumption. The material is subject to increased heat as it moves downwards in the electrode column. It melts at about 80 ºC and bakes at 500 ºC. To control the smelting process, the furnace operation can be based on resistance or current control, so that the electrodes are lifted and lowered when necessary to keep resistance or current constant. A system of electrode sealing is needed to prevent air leakage into the furnace. As an alternative, another practice is commonly used where the electrode moves only during slipping and otherwise stands in place.

During the smelting process, the metal oxides are reduced by the coke, with metal carbides as the final product. The reduction produces large volumes of CO gas from the reaction zone under the electrode tips. In an open furnace, the CO gas is burned at the surface of the furnace. By using a closed, sealed furnace the volume of the off-gas can be reduced by a factor of 50 - 75 and by the factor of 10 - 20 in the case of a semi-closed furnace. The investment cost for the off-gas-cleaning systems for closed furnaces are much lower than for open furnaces. The cleaned CO gas can be used as fuel for raw material preheating, coke drying and similar processes, substituting oil or other fossil fuels. The heating value of the CO rich gas is wasted. In contrast the heating value of the off-gas ~~Energy can be recovered~~ from semi-closed furnaces can be recovered in the form of steam or hot water. *See also Section 9.3.11.4. There the same information is used to describe the wrong purpose. Check [516]. The off-gas flows for open furnaces are 15000 – 55000 Nm3 per tonne FeCr. For semi-closed furnaces the off-gas flow is 10000 – 15000 Nm3 per tonne FeCr. For closed furnaces after cooling and scrubbing the corresponding gas volume is 650 – 850 Nm3 off-gas. Check the aforementioned factors. At least for semiclosed furnaces they seem to be percentages not factors!*

Ferro-chrome and the slag are tapped off at regular intervals from tap-holes near the bottom of the furnace. Slag and metal are tapped through the same tap-hole by using cascade tapping into the same metal vessel. The lower density slag will float to the top and eventually overflow through the ladle spout to the slag-pot or via a secondary launder to a slag pit, granulating basin or other slag vessel. Bed casting and layer casting are the most frequently used methods of casting ferro-chrome because of the simplicity and the low costs of these methods. The cooled castings are crushed and screened on the product handling line to produce the commercial lot specified by the customers. If it is possible the molten ferro-chrome can also be transferred directly to an adjacent stainless steel making plant[rr58]. ~~Less frequently, metal is tapped directly to the casting area. After the slag is skimmed off, the molten metal is cast or transferred to an adjacent steel plant.~~

The slag can either be granulated with a high pressure water jet or cast outdoors in layers, cooled, crushed and screened. Slag that contains metal is also crushed and the metal content recovered by means of slag-metal separation [ 255, VDI (D) 2576 2008 ]. Recovered slag-free lump metal can be sold, while slag contaminated metal and fines can be sold or recycled to the smelting process. Slag can also be treated by heavy media separation, magnetic separation or jigging. Both the granulated and the lump slag are re-used as building and road construction material. (See Section 2.20.10).

An example of a high-carbon ferro-chrome production process using a closed submerged electric arc furnace is shown in Figure 9.1.

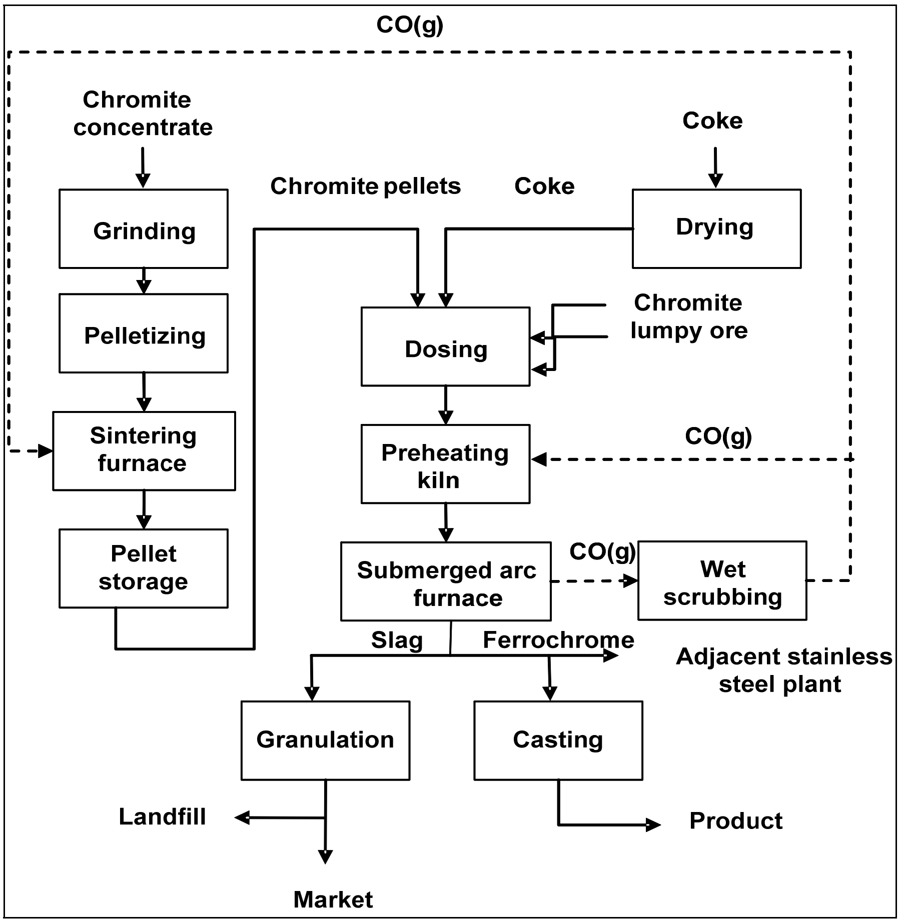


**Figure 9.1:** **High-carbon ferro-chrome production by using a closed submerged electric arc furnace**

### 9.1.1.3.2 Medium-carbon ferro-chrome

Medium-carbon ferro-chrome (MC FeCr) can be produced by the silicothermic reduction of chromite ore and concentrates or by the decarburisation of HC FeCr in an oxygen-blown converter. The oxygen can be introduced in the molten metal from the top of the melt by using water-cooled lances or by injection from the bottom of the converter. The bottom-blowing process has the advantage that a high decarburisation rate can be achieved together with a high chromium recovery ~~[ 255, VDI (D) 2576 2008 ]. ~~.The high bath temperature in a bottom-blown converter affects the high decarburisation and chromium recovery rate.

The silicothermic route is more economical and therefore more important for producing MC FeCr. The reason may be the small amount of MC FeCr that is needed compared with the high demand of HC FeCr together with the fact that low-carbon ferro-chrome can be produced by the same process as well.

#### 9.1.1.3.3 Low-carbon ferro-chrome

In order to get the desired low carbon content in the low-carbon ferro-chrome, a carbothermic process cannot be used. The most commonly used processes are therefore metallothermic reductions known as the Duplex, Perrin or Simplex processes.

The only process used in the European Community to produce LC FeCr is the Duplex process. In this process, LC FeCr is produced by the silicothermic reduction of[rr59] a lime-chromite slag. The slag smelting process takes place in a tiltable ~~-~~AC arc furnace with Søderberg electrodes. The furnace is operated at about 1750 ºC. The liquid melt is tapped in regular intervals into a first reaction ladle. When SiCr, ore and lime are added to the ladle, the reacting mixture is converted into LC FeCr and an intermediate slag. During this process the ladle is covered by a smoke hood. About 70 % of the intermediate slag is transferred to a second reaction ladle, which is also covered by a fume collection hood. Adding Si, FeSi, sand and boric acid to the mixture produces a final slag and a metal. The metal is recycled back to the first ladle. A fabric filter cleans the off-gas of the furnace from both reaction ladles. The dust from the baghouse is recycled into the smelting furnace. The Perrin process is similar but uses two arc furnaces.

LC FeCr can also be produced by the Simplex process. In the Simplex process HC FeCr is crushed in a ball mill in order to get a ferro-alloy powder. After briquetting, the HC FeCr powder together with $Cr_2O_3$, $Fe_2O_3$ the mixture can be de-carburised by annealing at about 1350 ºC in a vacuum furnace.

#### 9.1.1.3.4 Silico-chromium

Silico-chromium is also used as an alloying element in the steel industry. It can be produced in the same kind of three-phase submerged electric arc furnaces as used for HC FeCr production. The reduction of $SiO_2$ to Si is combined with the generation of huge amounts of CO gas. The high generation rate of CO makes it important to use a porous burden (e.g. gas coke), a semi-closed or closed furnace with an appropriate energy recovery system.

### 9.1.2 Ferro-silicon and silicon alloys

Ferro-silicon, silicon metal and silico-calcium (CaSi) are used as additives in different industrial products. As an alloying element, ferro-silicon increases the strength of steel and is therefore used in steel that is needed to produce wire cords for tyres or ball bearings. High purity FeSi is used to produce high permeability steel for electric transformers. Silicon metal is important as an alloying element in aluminium and for the production of chemicals and electronic products. The major user for silico-calcium is also the steel industry. The above-mentioned metals can be classified by their silicon content as follows:

- ferro-silicon: silicon content of less than 96 %
- Si-metal: silicon content of above 96 %
- silico-calcium: silicon content of about 60 - 65 % and calcium content of 30 - 35 %.

### 9.1.2.1 Raw materials

The raw materials that are commonly used for the production of ferro-silicon, silicon metal and silico-calcium are listed in Table 9.1.

| Raw material | Ferro-silicon | Si-metal | Silico-calcium |
|---|---|---|---|
| Quartz | ■ | ■ | ■ |
| Coke | ■ | | ■ |
| Petrol coke | | ■ | |
| Coal | ■ | ■ | ■ |
| Charcoal | ■ | ■ | |
| Woodchips | ■ | ■ | |
| Limestone | | ■ | ■ |
| Iron-ore/steel scrap | ■ | | |
| Amorphous carbon | | ■ | |
| Graphite electrodes | | If a combined graphite/ Søderberg electrode is used | |
| Søderberg electrode paste | ■ | | ■ |

**Table 9.1: Raw materials for the production of ferro-silicon, silicon metal and silico-calcium**

In order to achieve good process results, the selection of the raw material is due to strict quality requirements. The thermal strength of the quartzite for example is of special importance, because it is connected to the gas permeability of the charge where too much fine-sized material may prevent gas flow. The carbon quality is important for the environmental performance of the process, because the coal and coke contains sulphur and trace elements which can be emitted into the environment [ 226, Nordic Report 2008 ]. If carbon contains mercury or other vaporous elements, they will evaporate in the process and will be emitted as part of the off-gas into the environment.

### 9.1.2.2 Production of ferro-silicon, silicon metal and silico-calcium

Raw material is normally supplied to the plant by truck and train. Several ferro-silicon and silicon plants are located near the sea or a river where boats are mainly used for the transportation of raw materials and products. The loading and unloading of raw material is done with the use of crane grips, front-end loaders or dump trucks.

The different raw materials that are used for the Si, FeSi and SiCa production are preferably stored on hard surfaces in order to prevent contamination. The reducing agents are normally stored indoors, to avoid the material from humidity caused by rain. Some of the reducing agents can have self-igniting characteristics. In these cases, appropriate methods have to be implemented to avoid self-combustion in, e.g. charcoal or coal with a high content of volatile matter and woodchips.

Ferro-silicon, silicon metal and silicon-calcium are commonly produced in low-shaft three phase submerged electric arc furnaces [ 255, VDI (D) 2576 2008 ]. The electric furnace can be of the open or semi-closed type. The furnace normally rotates in order to connect the reaction areas around each electrode tip to break down crust in between the electrodes. The rotation gives rise to some difficulties in obtaining good capture efficiency of the diffuse emissions at the tap-hole as the location of the tap-hole will rotate with the furnace. The raw material is fed from storage bins above the furnace, through feeding tubes. In small furnaces, the raw material can also be fed by using stocking cars.

The smelting of silicon metal and silicon alloys normally takes place in open or semi-closed furnaces. The open furnaces are commonly built up with moveable curtains or gates around the furnace hood to secure access for maintenance and possible manual feeding. The furnace/smoke hood is the upper part of the furnace. The hood has several tasks, first of all, it collects the process off-gas and shields the equipment from the process heat. Secondly the hood is where the electrodes are placed and raw materials are charged. Hoods often include a cooling arrangement. For the FeSi and CaSi production Søderberg technology is used. For silicon production the electrode is often prebaked and screwed on top of the previous electrode according to the electrode consumption. In recent years, an electrode has been developed utilising a combination of the Søderberg technology and a graphite core with a stable -iron electrode casing. This combined electrode allows the implementation of the Søderberg technology in the production of silicon metal. The aim is to reduce the iron impurities caused by the electrode casing and reducing the high costs of prebaked graphite electrodes [ 233, Farrell Nordic Mission 2008 ], [ 226, Nordic Report 2008 ]. The semi-closed furnace has been introduced to control the suction of air into the furnace top and thereby reducing the total gas stream from the furnace. This increases the gas temperature and requires an improved temperature control on the off-gas side, but at the same time allows for an even higher energy recovery. The process off-gas that contains silica fumes is cleaned in a baghouse using fabric filters.

The liquid metal is tapped continuously or at regular intervals. The metal is cast from the ladle after the tapping is finished. Transportable -tapping vessels can be brought to the tapping position by suitable -vehicles or by overhead cranes. The metal can also be directly tapped to the casting area without using transport vessels. The silicon alloy is then cast into moulds and crushed by using jaw, rotary or roll crushers or granulated in water.
*As proposed by Germany in a mail from 27 October figure 2 from the VDI 2576 Metallurgical silicon/ferrosilicon process including offgas cleaning and heat recovery should be included here.*

It should be noted that the production of silicon metal and ferro-silicon is an almost slag-free process as nearly all the impurities present in the raw material are transferred to the products, metal or micro-silica. To obtain a higher purity metal, a further refining step is needed. The refining takes place by oxidising the impurities in a ladle. Injection of oxygen gas or air is done through immersed lances, porous plugs in the ladle bottom or injectors. Correcting slag can also be added to improve the refining process. The refining stage is covered with a fume collection system, e.g. a fume collection hood that is connected with a baghouse.

### 9.1.3 Ferro-manganese and manganese alloys

Ferro-manganese is another bulk ferro-alloy of great importance mainly in the steel and stainless steel industry. Initially employed as a deoxidising and desulphurising agent, today ferro-manganese is mostly used to improve the hardness and wear resistance of steel. Ferro-manganese and other important manganese alloys can basically be classified as:

| | |
|---|---|
| • high-carbon ferro-manganese | (HC FeMn) with max 7.5 % C |
| • medium-carbon ferro-manganese | (MC FeMn) with max 2.5 % C |
| • low-carbon ferro-manganese | (LC FeMn) with max 0.75 % C |
| • silico-manganese | (SiMn) with max 2.0 % C |

*Why isn't this called ferro-silico manganese? What about FeMnSi with 15 to 35% C content? See [255] Ask Mr. Radermacher!*

•

| | |
|---|---|
| • low-carbon silico-manganese | (LC SiMn) with max 0.10 % C. |

[226]

### 9.1.3.1 Raw materials

The production of ferro-manganese and silico-manganese is based on a blend of ores that contain manganese as primary raw material. In order to obtain good process efficiency the manganese ore and concentrates (with a low iron content) should be of a lump type or as sintered material. Other raw materials that are required for the smelting process are iron ore and fluxing agents such as limestone and dolomite. Coke is used as a reducing agent and in the case of HC FeMn production in a blast furnace, also as an energy source[rr60]. For the production of silico-manganese, rich ferro-manganese slag, ferro-silicon scrap, silicon skulls and quartz are needed.

### 9.1.3.2 Pretreatment techniques

To use fine ores in the production of ferro-manganese an agglomeration, pelletising and sintering step is used. Besides ore fines, the burden for sinter incorporates fuels (coke fines, coal fines, gas for ignition) and fluxes like limestone and dolomite as well as recycled fines and dust. Sintering is used in order to get a more suitable ~~-~~size and to reduce the natural ore to an intermediate metallurgical grade raw material ~~[ 255, VDI (D) 2576 2008 ]~~. The main advantages of the agglomeration and sinter process are [ 104, Ullmann's Encyclopedia 1996 ]:

- fine ore, which has a limited application and value in conventional smelting, is agglomerated and converted to a superior product;
- reduced gas volumes, and hence fewer furnace eruptions result when smelting sinter;
- furnace availability and operating loads are increased;
- better porosity of the burden with easier penetration and elimination of the gas generated by the reduction reactions.

### 9.1.3.3 Production of ferro-manganese and silico-manganese

#### 9.1.3.3.1 High-carbon ferro-manganese

High-carbon ferro-manganese (HC FeMn) is produced by the carbothermic reduction of lumpy or sintered manganese ore in a three-phase submerged electric arc furnace ~~[ 255, VDI (D) 2576 2008 ]~~.

The commonly used electric arc furnaces are of the closed, semi-closed and open type, which has no or only limited consequences on the furnace itself but affects the gas composition, flowrate, recovery and dedusting system. The diameter of the furnace varies from 2 to 20 m. Smaller furnaces have the advantage to be more flexible, because they can switch more easily between different products.

The raw material is fed to the smelting process by gravity from storage bins above the furnace. The feeding tubes are placed around the electrodes in order to ensure an even distribution of raw material to the furnace.

The electric arc furnace for the production of HC FeMn should be adapted compared to the furnaces that are normally used to produce ferro-alloys. According to the high vapour pressure of ferro-manganese, the smelting process needs a careful temperature control because the charge should not be overheated. The vapour pressure together with a relatively low resistivity of the ferro-manganese burden results in a low current density of the electrodes. As a consequence, the furnace should be operated at low voltage which requires a larger diameter of the electrodes for the high current that is needed for the process. A typical closed electric arc furnace for the production of ferro-manganese operating Søderberg electrodes is shown in Figure 9.2.

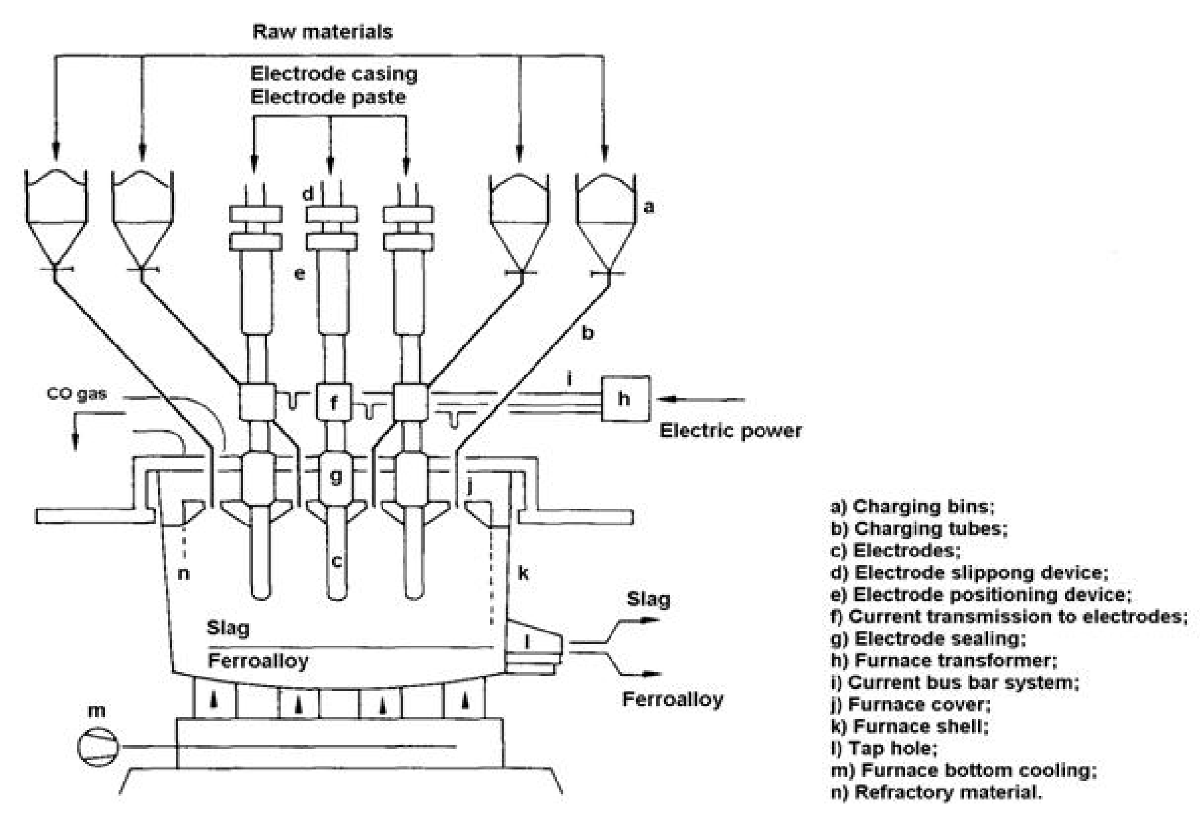


**Figure 9.2: Closed electric arc ferro-manganese furnace operating with Søderberg electrodes** [ 104, Ullmann's Encyclopedia 1996 ]

Electric arc furnaces for the production of ferro-manganese are operated only with self-baking Søderberg electrodes. Because of the large diameter, the use of pre-baked electrodes is uneconomic compared with the Søderberg electrodes. (See Figure 9.2).

The Søderberg electrodes consist of a mild steel or stainless steel casing which is stiffened with internal fines and are filled with a carbonaceous paste, consisting of a solid aggregate, usually calcined anthracite, and a binder of coal tar pitch. The tar becomes plastic when hot and fills the entire volume of the casing. On further heating of the electrode by the current and furnace heat, the paste is baked and becomes solid [ 104, Ullmann's Encyclopedia 1996 ].

The molten metal and the slag can be tapped off continuously or in regular intervals. The metal is cast into moulds lined with crushed ferro-manganese. A casting machine can also be used for casting the liquid metal. The solidified metal in then crushed and screened for the specific needs of the customers. Slag is normally obtained as rich slag (with about 30 % Mn) and is used further for the production of silico-manganese.

There are some facilities where the CO-rich off-gas is used to produce electricity. The CO-rich gas can also be utilised for other industrial uses, for instance as a raw material for chemical synthesis[rr61].

#### 9.1.3.3.2 Medium-carbon ferro-manganese

For the production of medium carbon ferro-manganese (MC FeMn) two different routes can be used:

- the silicothermic reduction of manganese ore

- the de-carburisation of HC FeMn in the oxygen blown converter.

The most important process in the EU is the decarburisation of HC FeMn and is also known as the refining process of HC FeMn.

For the decarburisation of HC FeMn, oxygen is blown into the molten metal, which is tapped off from the furnace into a ladle. The oxygen blown into the melt oxidises part of the manganese and increases the bath temperature from about 1350 to 1550 ºC. With increasing temperatures the carbon present in the HC FeMn also tends to be oxidised which again raises the temperature from 1550 up to 1750 ºC. The oxidisation of carbon consequently reduces the carbon content of the ferro-manganese. For the production of MC FeMn, the decarburisation process ends when a corresponding carbon content of about 1.3 % is reached. The high temperature also leads to the vaporisation of ferro-manganese that leaves the process as fumes. The fumes can be collected by using hoods *(and further abatement by FF?)* and sent back to the HC FeMn smelter or sold.

In contrast to the refining process that uses HC FeMn as a raw material, the silicothermic production needs manganese ore and lime or a high-grade slag and silico-manganese. The reduction itself is performed in a three-phase electric arc furnace, with electrodes made of graphite. At the end of the cycle, the molten alloy and the slag are cast and separated. The slag is recycled after cooling and crushing as a raw material to the silico-manganese production plant *(What is meant by silico-manganese production plant?).* The fumes of the furnaces will be dedusted in a fabric filter. With the silicothermic reduction, the production of MC FeMn that contains $\leq$1 % C is possible.

The main advantages of the refining process are the lower operating and capital investment costs. The advantage of the silicothermic process is to produce low-carbon ferro-manganese in the same process[rr62].

#### 9.1.3.3.3 Low-carbon ferro-manganese

Low-carbon ferro-manganese (LC FeMn), which usually contains less than 0.75 % C is traditionally produced by a silicothermic process route. ~~Recent process developments has made de-carburisation of HC FeMn an economical and environmental favourable processing route for LC FeMn. A carbon content of less than 0.5 % can be reached, but usually 0.75 % is produced [ 226, Nordic Report 2008 ].~~

A rich slag is suitable ~~-~~as a raw material because of the low level of impurities. Also the presence of already reduced manganese oxides in the rich slag is favourable for the process. The production of LC FeMn takes place in an electric arc furnace very similar to that used for MC FeMn, produced by a silicothermic process. The slag obtained is used for silico-manganese production as a raw material or sold for other applications in the metallurgical industry.

Recent process developments has made de-carburisation of HC FeMn an economical and environmental favourable processing route for LC FeMn. A carbon content of less than 0.5 % can be reached, but usually 0.75 % is produced [ 226, Nordic Report 2008 ].

*(decide whether the term 'high-grade slag'or 'rich slag' is synonymous and which should be used. Be consistent) Ask northern countries if the new changes are correct.*

#### 9.1.3.3.4 Silico-manganese

Silico-manganese is required as an alloying element in the steel industry as well as a raw material to produce MC and LC FeMn. The production of silico-manganese is based on manganese ore or sinter and quartz as raw material. Instead of manganese ore, a rich ferro-manganese slag like that produced as rich slag in HC, MC and LC FeMn production may be used as a manganese source[rr63]. Silico-manganese is only produced in submerged electric arc furnaces, which can be closed, semi-closed or open types. The furnaces are the same or very similar to those used for HC ferro-manganese production and often a furnace is operated with alternate campaigns of each alloy. According to the composition of the feed mix, silico-manganese with a silicon content from 15 to 35 % can be produced. For proper furnace operation and effective silicon reduction, it is necessary to penetrate the electrodes deeper into the burden in order to reach the high temperature needed for the process [517].

## 9.1.4 Ferro-nickel

### 9.1.4.1 Raw materials

Ferro-nickel (FeNi) as well as ferro-chrome is the major alloying agent in the production of stainless steel. Laterite ore is the main raw material. Laterite ore is characterised by a relatively low nickel content (1.2 - 3 %) and a high moisture content (up to 45 %) together with chemically bound water in the form of hydroxide [ 104, Ullmann's Encyclopedia 1996 ]. Typical European ores contain 1 to 3 % Ni and a moisture content of 5 to 10 %.

Besides laterite ore, coke or coal is the second raw material that is needed in the ferro-nickel production. Coke or coal is used as a reducing agent because the ferro-nickel production takes place by a carbothermic process. FeNi can also be produced from secondary raw materials, such as spent catalysts and sludge from the galvanising industry.

### 9.1.4.2 Production of ferro-nickel from primary raw material

The production of ferro-nickel from primary raw material is carried out exclusively by the rotary kiln electric furnace process. As mentioned before, the raw material can carry a significant amount of water, therefore when there is a high moisture content, the first step of the process is a drying operation. Drying normally takes place in a directly-fired rotary dryer where the moisture content can be reduced from about 45 to 15 %. Further drying below 15 % should be avoided in order to keep the dust generation in the subsequent calcining and smelting process as low as possible.

The next process step is homogenisation where the different ores are mixed with coal and pelletised dust, which is recycled from the main process. The feed is then fed to a rotary kiln. The rotary kiln is used to dehydrate the ore by calcination and to pre-reduce the nickel and iron oxide. The process takes place at about 800 - 1000 °C. The calcining and pre-reducing process results in a furnace feed which contains the nickel as a metal and the iron content in the form of iron (II) oxides.

The hot pre-reduced calcine can be introduced directly to the smelting furnace or by insulated containers. The containers may be used for two reasons; first to conserve the heat and second to add coke or coal required for complete reduction before they are discharged into the electric furnace, where or[rr64] melting and final reduction occurs [ 110, Anthony, T. 1997 ].

Ferro-nickel smelting takes place in electric arc furnaces(which type? Submerged?). In the electric furnace, the reductive smelting operation occurs by the combined action of carbon electrodes and added solid carbonaceous reducing agent. The choice of the most suitable operation mode (open bath or closed bath[rr65]) depends mainly on the oxides content of the slag (primarily FeO, $SiO_2$, MgO, CaO) as well as the mass relation between slag and nickel metal.

To reduce a high content of nickel oxides, commonly the burden contains an excess proportion of carbon. These also increase the amount of iron that will be reduced and the final carbon content of the crude ferro-nickel. To reduce the iron and carbon content, a further refining step is necessary. To avoid further refining several process improvements have been made. For instance in the 'Ugine ferro-nickel process', no reducing agent is added. The electric furnace produces a molten ore, which is reduced to ferro-nickel by using ferro-silicon in a further ladle furnace. In the 'Falcondo ferro-nickel process', a shaft furnace is used instead of a rotary kiln. In the shaft furnace a briquetted ore is reduced with a reducing gas (low sulphur naphtha). The subsequent electric furnace is then only used to melt the metal and to separate it from the slag.

Ferro-nickel produced by the conventional process needs further refining. Besides the reduction of iron and carbon, the impurities like sulphur, silicon and phosphorus should be removed. For ferro-nickel refining a variety of equipment is available, e.g. a shaking reaction ladle, an induction furnace, an electric arc furnace and oxygen blown converters. The purified ferro-nickel is cast into ingots or granulated under water.

The off-gas from the rotary kiln, the electric arc smelting furnace and the refining step is treated by an appropriate abatement system. The dust content can be pelletised and recycled to the raw material blending station.

#### 9.1.4.3 Production of ferro-nickel from secondary raw material

FeNi can also be produced from residues that contain nickel. These residues, mostly spent catalysts from the grease production, are burned in a rotary kiln in order to concentrate the Ni content as Ni oxide in the flue dust. The off-gas is cleaned in a membrane fabric filter, where the collected dust is used as the raw material for the smelting process. The production of FeNi then takes place in a submerged electric arc furnace. The molten alloy is tapped, granulated in water and packed in drums or big bags for supply.

### 9.1.5 Ferro-vanadium

The addition of ferro-vanadium to a steel melt increases the tensile strength and the high temperature strength of carbon steel even if small amounts are added. Vanadium alloyed steel is therefore used for high speed cutting tools.

Ferro-vanadium (FeV) can be produced by a carbothermic or a metallothermic reduction of vanadium oxides assisted by the presence of iron. Because carbon is used in a carbothermic reduction, the final carbon content of the produced alloy is high. The production of ferro-vanadium by using carbon as a reducing agent is therefore only possible if there are no requirements of a low carbon content. Ferro-vanadium is usually produced by an aluminothermic reduction.

When necessary, grinding, sizing and drying can be carried out prior to charging the mix to the smelting process. The aluminothermic reduction of vanadium oxide is a self-sustaining process that can be carried out in a refractory-lined crucible. The reaction vessels used for this process can be of the following type.

- Refractory-lined crucible using a non-re-usable lining.
- Refractory-lined ring placed onto a pit that contains sand.
- Electric furnace where additional energy can be supplied either to increase the heat of reaction or to enable slag-refining operations to be carried out. The electric arc furnace is also used, because the FeV fines generated by FeV crushing can be remelted.

The smelting operation takes place in a batch process where the whole charge is transferred to the reaction vessel and ignited. After ignition, the combustion time for a common batch size of about 1 t of ferro-vanadium takes only a few minutes. Due to the short reaction time the content of vanadium oxides in the slag and the aluminium content in the metal may not reach equilibrium. The production in an electric furnace has therefore the advantage of keeping the charge in a molten state until the reaction is completely finished. The fumes from the process are exhausted and cleaned by using fabric filters or wet scrubbers.

Depending upon the process type, the slag and metal can be allowed to cool down in the crucible, or the slag and metal can be tapped together in ladles or in beds to allow separation of slag and metal and to provoke rapid cooling. Tapping of the crucible requires extraction hoods and extraction rates sufficient to evacuate the fumes and the dust escaping during the tapping. The slag from the aluminothermic process can be used for further crucible linings or crushed and sized to be used in other industries. The metal block can be air-cooled or water-cooled which facilitates further crushing. All crushing and sieving have dedicated dust extraction units, from which the dust is returned to the production process at the most appropriate point to ensure a continuous recycling of recovered products.

## 9.1.6 Molybdenite roasting and the production of ferro-molybdenum

### 9.1.6.1 Molybdenite roasting

Technical grade molybdenum trioxide ($MoO_3$) is the main raw material in the production of ferro-molybdenum and alloys that contain molybdenum as well as the starting compound for a number of other molybdenum-based products such as ammonium dimolybdate, sodium molybdate and molybdenum metal [ 104, Ullmann's Encyclopedia 1996 ]. Roasting as it is shown schematically in Figure 9.3 performs the conversion of concentrated molybdenite (molybdenum sulphide ore) into technical grade molybdenum trioxide for the metallurgical or chemical industry.

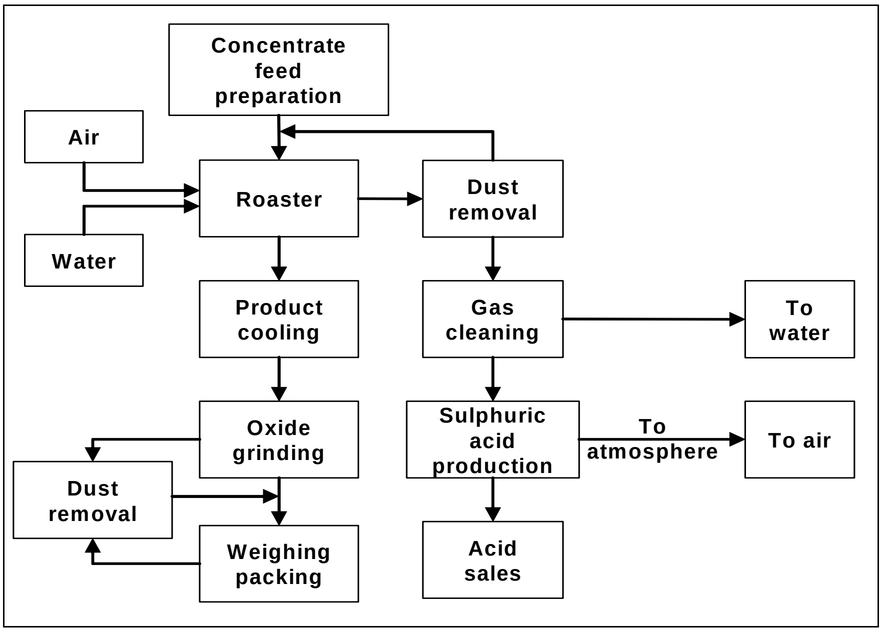


**Figure 9.3: Molybdenite roasting flow sheet**

The process of roasting molybdenite ore takes place in a multiple hearth furnace of the Nichols Herreshoff or Lurgi design. The Nichols Herreshoff type furnace is described in detail in Section 2.8.1.3. The multiple hearth furnaces consist of a number of vertically arranged hearths. In the upper part of the furnace, additional energy is added in the form of natural gas (or a liquid fuel such as diesel) in order to evaporate water and bring the feed to a roasting temperature.

The roasting process itself is exothermic and does not need additional energy unless the heat losses associated with the centre axle column cooling air, radiation from the shell of the roaster and the discharge of hot oxide from the roaster are significant. By means of induced-draught fans, the roaster operates at a negative pressure relative to the atmospheric pressure. This serves to control the inflow of ambient air for oxidation and cooling and prevents any emissions of sulphur dioxide to the environment. Airflow, transportation rate and sometimes water spray injection control the reaction rates and temperatures. The molybdenum oxide produced is discharged from the roaster and then cooled, ground to a fine powder, sampled and analysed prior to weighing and packing.

The off-gas from the process contains large amounts of sulphur dioxide and dust (up to 15 % of the concentrate feed). The dust content can be removed from the gas stream by using (multi-) cyclones and high temperature electrostatic precipitators together and recycled to the concentrate feed entering the roaster. The sulphur dioxide is normally converted into sulphuric acid in an adjacent sulphuric acid plant. The conversion of sulphur dioxide into sulphuric acid is described in detail in Section 2.11. In addition to the generation of dust and sulphur dioxide, elements such as rhenium and selenium are vaporised and are emitted. These elements can be removed from the gas stream by wet scrubbing with a subsequent treatment plant for the scrubbing liquor. Selenium and rhenium are then recovered from the ion exchangers used in the waste water treatment plant by special companies. Rhenium can also be recovered by solvent extraction.

In the toll conversion of molybdenum concentrates, batches of raw material can have high differences in Mo content (46 % - 59 %) and in other components. The roasting of batches with different grades influences the treatment of the off-gases.

### 9.1.6.2 Production of ferro-molybdenum

Ferro-molybdenum can be produced either by the carbothermic or metallothermic reduction of molybdenum trioxide. According to practical reasons like the smelting equipment used for the process and the reduced manufacturing costs, the metallothermic production of ferro-molybdenum is much more important than the carbothermic reduction. Thus the latter will not be described.

#### 9.1.6.2.1 Raw materials

The production of ferro-molybdenum is based on technical grade molybdenum trioxide ($MoO_3$) as a raw material. Besides the main raw material, molybdenum trioxide, iron oxide or mill-scale iron scrap, steel punchings or turnings are needed to produce ferro-molybdenum. Lime and fluorspar are commonly used as fluxing agents and charcoal, silicon (ferro-silicon) or aluminium, depending on the production route, are needed as a reducing agent.

#### 9.1.6.2.2 Metallothermic production of ferro-molybdenum

The metallothermic reduction is the most common process used for the production of ferro-molybdenum. Due to the higher Gibbs free energy of aluminium compared with silicon, ferro-silicon is the preferred reducing agent in order to ensure safe process conditions. However, to obtain the required heat balance for the reaction, it is necessary to use a small amount of aluminium.

The metallothermic process requires dry raw material for the process. Mill scale that arrives wet is stored in a covered bunker prior to screening and drying in order to prevent diffuse losses. Steel scrap that also arrives in bulk is off loaded and packed into containers prior to being stored. Smooth efficient smelting reactions require a blend of suitably sized raw material, this is of particular importance with respect to the oxides and the reducing agents. Fluorspar is sometimes added to improve the slag and metal separation. To get the right sized raw material, it is necessary to grind and screen ferro-silicon. All the pretreatment operations like grinding, screening, transferring and blending should be carried out by using dust control measures.

The smelting operation can be done in a number of ways, the most common are [ 125, Euro Alliages (B) 1998 ]:

- The use of long pits that contain sand where refractory-lined steel cylinders are placed to form crucibles that contain the metallothermic reaction. The reaction itself can be carried out in different ways. The 'top-fired reaction' takes place when the whole charge is placed in the crucible and then ignited from the top. Alternatively, only a part of the charge can be placed in the crucible and ignited, the remainder of the charge can then be added as the reaction proceeds (fed reactions).

- The use of refractory-lined crucibles that are placed inside a chamber that can be enclosed. As in the previous description, the reaction can then be carried out by placing all of the charge in the crucible and igniting it, or by adding only a part of the charge, initiating the reaction and then progressively adding the rest of the charge as the reaction proceeds.

The dust and fumes generated by the process must be extracted, recovered and recycled in order to assure an overall molybdenum yield of 97 - 99 % and to protect the environment. The collected dust and fumes are exhausted to a reverse air jet cleaning baghouse. The filter bags may be manufactured from special fabrics sometimes applied with additional coating to withstand high temperatures. The baghouse dust can then be fed directly back to the main smelting process. Good housekeeping is also necessary to recycle all splashings, floor sweepings, etc. in order to get an efficient overall molybdenum yield.

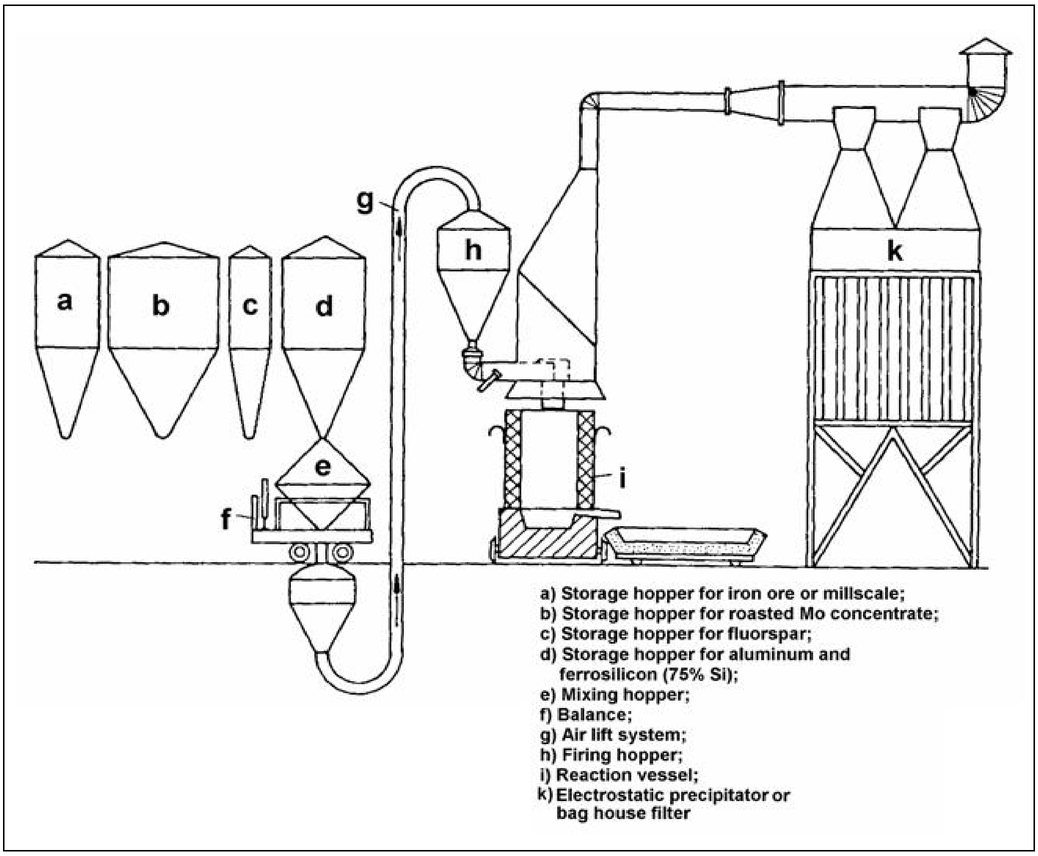


**Figure 9.4: Metallothermic firing arrangement**
[ 104, Ullmann's Encyclopedia 1996 ]

The smelting process produces an alloy block (mass) that weighs between 2.5 - 4 tonnes. After the slag is separated, the hot metal block should be cooled. This can either be achieved by natural cooling in air or by quenching in water. The cooled metal block is then broken into pieces that can be fed into an integrated crushing and screening plant to produce the wide range of product sizes used worldwide.

A process flow sheet that demonstrates the principle steps of the metallothermic ferro-molybdenum production process is presented in Figure 9.4 and Figure 9.5.

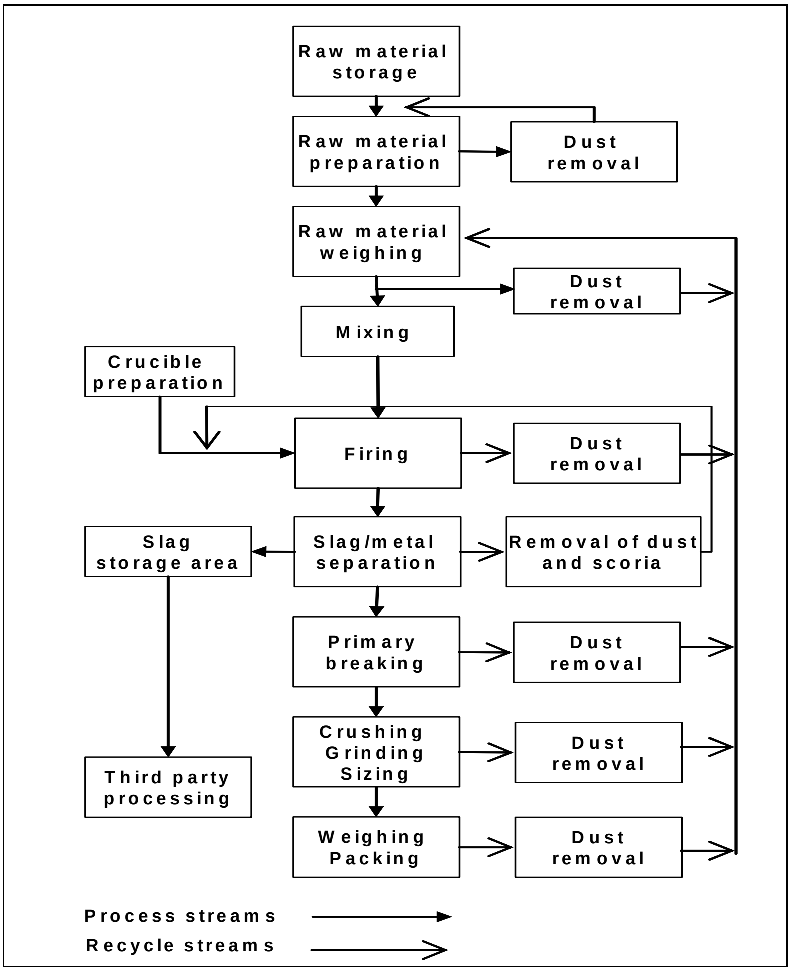


**Figure 9.5:** **Production of ferro-molybdenum by metallothermic reduction**

*What about premelting plant where nickel, vanadium oxides and molybdenum oxides are used for the production of Ferro-Molebdenum-Nickel and Ferro-Vanadium alloys which is practised in Austria [509] ?*

## 9.1.7 Ferro-tungsten

Ferro-tungsten as well as tungsten melting base (TMB) which is made from secondary raw material is mainly used to improve the properties of steel. Tungsten as an alloying element forms stable carbides and therefore increases the hot strength and wear resistance of steel. Such steel (high speed steel) is needed to produce high speed cutting tools that can be used up to temperatures of about 600 ºC. Tungsten will also increase a number of other properties like the hardness, yield strength and the ultimate tensile strength [ 104, Ullmann's Encyclopedia 1996 ].

### 9.1.7.1 Production of ferro-tungsten and tungsten melting base

Ferro-tungsten can be produced from different raw materials that contain tungsten oxides, e.g. wolframite, scheelite and hübnerite. The reduction of these minerals can be done either by carbothermic- or metallothermic reduction as well as by a combination of both.

The carbothermic process that is known as the solid block melting process takes place in an electric arc furnace. Due to the high melting temperature of ferro-tungsten, the produced alloy cannot be tapped off from the furnace. After the smelting has been started, the metal accumulates in the bottom of the furnace. When the amount of metal has reached the desired weight, the furnace is switched off. The metal ingot can then be recovered from the furnace after the refractory lining has been removed. The metal is then crushed and screened. If several furnaces are used in parallel, the production can then take place as a quasi-continuous process. The off-gases from the furnace are treated by a gas purification system in order to minimise the environmental impact and to recover the amount of tungsten trioxide in the flue dust.

A combination of the carbo- and metallothermic process using both carbon and ferro-silicon as a reducing agents are used to produce a ferro-alloy with a high tungsten content. The process is carried out in three successive stages in an electric arc furnace. In the first stage, a tungsten trioxide slag is produced that is further reduced with ferro-silicon in the following stage. The third and final stage is needed to increase the tungsten content by refining the low tungsten metal from the second stage by adding tungsten concentrates.

The metallothermic process is less economical because the process requires very pure and therefore expensive raw material. In order to keep the process self-sustaining, a mixture of silicon and aluminium is normally used as a reducing agent. The metal can be recovered from the furnace vessel after cooling and removing of the furnace linings. Metallothermic production of ferro-tungsten is today only economically viable if there are special customer requirements.

TMB is a tungsten alloy that is produced from secondary raw material. The main sources are different kinds of tungsten metal scrap. The TMB production is only a remelting and alloying process, which can take place in an electric arc furnace. The fact that more and more tungsten scrap is available on the market increases the importance of the remelting process that requires less energy than the primary smelting process.

### 9.1.8 Ferro-titanium

Ferro-titanium can be produced either from primary and secondary raw material and is used for a variety of different purposes. As an alloying element, it increases yield strength and reduces the cracking tendency. In the production of stainless steel with a high chrome and nickel content, ferro-titanium is used to bond the sulphur [ 104, Ullmann's Encyclopedia 1996 ].

For the production of ferro-titanium the primary raw materials are minerals that contain titanium oxide such as ilmenite. The reduction occurs commonly by the metallothermic process because the carbothermic reduction produces an alloy that contains too much carbon and is therefore not interesting as an alloying element in the steel industry. The production takes place as a batch process in a refractory-lined crucible or in an electric furnace depending on the process variation.

In recent years the availability of titanium scrap on the market increased and therefore the production of ferro-titanium from secondary raw material is more important. The production of ferro-titanium is achieved by melting ferrous scrap and titanium in an electric induction-melting furnace. The alloying process is a slag-free process.

Ferrous units are purchased to a specification in the form of mild steel solids. Titanium scrap is delivered to the site in container trucks. The feedstock includes lump scrap metal castings, wrought products and turnings (swarf) from machining processes. Upon receipt, materials are checked to ensure that they are not contaminated with radioactive materials. Large lumps of scrap are reduced in size by oxy-flame cutting. Swarf is chipped using a swarf pulveriser and then fed through a centrifuge to remove oil and moisture.

The titanium swarf is degreased in a rotary dryer, where the oil-bearing gases are led through a cyclone to remove dust and carryover. These gases then pass though an afterburner. Combustion gases/fumes are either recirculated through the dryer or are ducted to a second cyclone. After passing through the cyclone, sorbent (sodium bicarbonate) is introduced to neutralise the gas stream. Finally the gas passes through a ceramic filter before being discharged to the atmosphere via a stack.

Furnace charges are calculated based on the analysis of the raw materials. The materials are weighed into pans and fed into an electric induction melting furnace. A chute system is used to feed in materials during the melting operation. When melting is complete, the molten metal is tapped into an ingot mould and a stream sample is taken for analysis. After cooling, the ingot is transferred to other operations such as breaking, crushing and grinding to achieve the required product size. Figure 9.6 presents a flow diagram for the production of ferro-titanium.

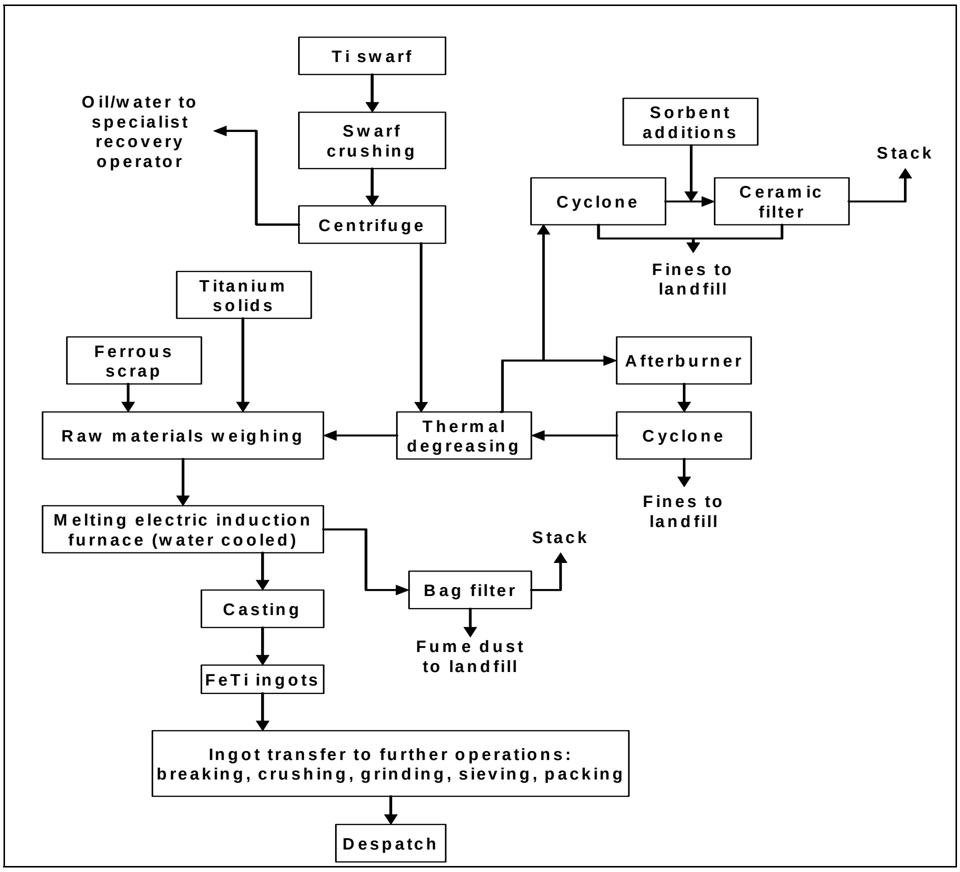


**Figure 9.6: Flow diagram of the ferro-titanium production**

### 9.1.9 Ferro-boron

Ferro-boron is mainly used as an additive in steelmaking to increase the hardenability, creep resistance and hot workability because boron-alloyed steel is oxidation-resistant up to 900 ºC. The raw materials needed to produce ferro-boron are boric oxides and boric acid. Carbon (charcoal), aluminium or magnesium are used as a reducing agent. The alloys can be produced by carbothermic or metallothermic reduction processes.

The raw materials arrive in a variety of forms, for example, drums, flexible intermediate bulk containers, pallets, stillages and polyethylene-wrapped bales. The materials are weighed out into enclosed bins at a specially designed weigh station. The bulk bags are discharged from a framework incorporating a sealing membrane, which prevents diffuse emissions. A local exhaust ventilation system vented to a filter unit furthers the removal of any dust.

The carbothermic reduction takes place in single or three-phase submerged electric arc furnaces depending on the process specification. Some variations of the carbothermic process exist. In one, boric oxides and iron oxides are reduced simultaneously with charcoal in a submerged electric arc furnace. In another process, boric acid, iron powder and charcoal are reacted in a Héroult-type electric arc furnace. Figure 9.7 shows the process for ferro-boron and boron alloy production.

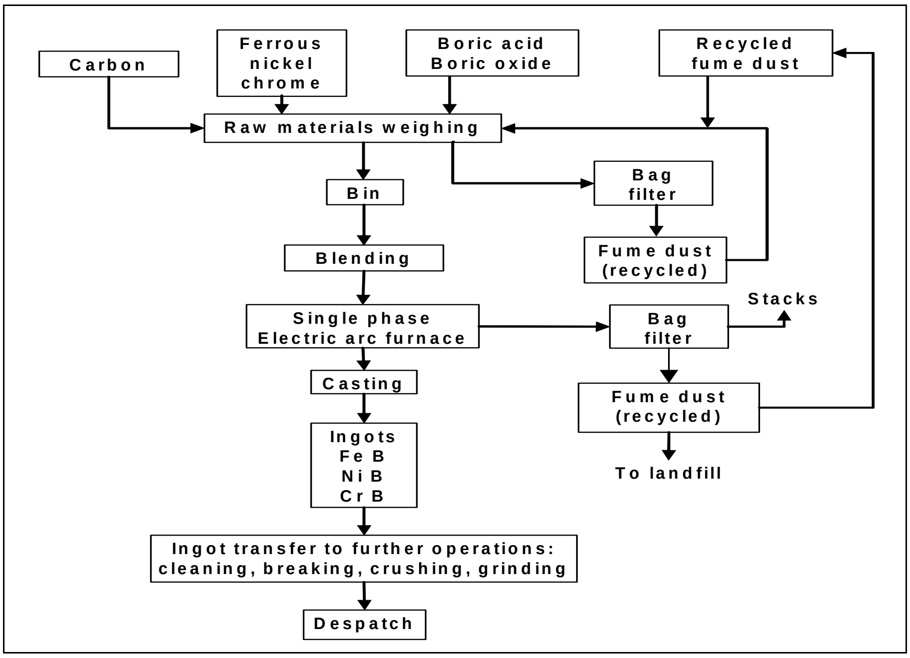


**Figure 9.7: Process for ferro-boron and boron -alloy production**

The metallothermic process uses aluminium together with a small portion of magnesium as a reducing agent. This reaction is highly exothermic and needs only a few minutes to take place in a refractory-lined crucible. The reaction can be ignited as a whole charge or as a starting mix. After the reaction is finished, the metal-alloy that builds in the bottom of the furnace can be removed mechanically. It can then be crushed and screened in order to produce the desired particle size.

### 9.1.10 Ferro-niobium

Ferro-niobium as an alloying agent improves the corrosion resistance and weld-ability of steel and prevents especially stainless chrome-nickel steel of inter-crystalline corrosion. The raw materials needed to produce ferro-niobium are ores and concentrates that contain niobium and iron oxide. The reduction occurs as an aluminothermic process. The reaction normally takes place in a refractory-lined crucible, where the whole charge can be ignited or just a part of it that then serves as a starting mixture.

Niobium can be produced from pyrochlore ore, which also contains traces of polonium which is a volatile, radioactive metal. The smelting of pyrochlore therefore requires enhanced safety and environmental procedures.

### 9.1.11 Production of ferro-alloys from secondary raw material

Due to the large number of available secondary raw materials, especially metal oxides from the production of stainless steel, the recovery of ferro-alloys, mainly ferro-chrome has become an important part of the ferro-alloy industry. The development of the various processes followed the increasing need of the stainless steel manufacturers to treat their waste products in order to reclaim the valuable metal content and to limit or prevent the dumping of waste.

The total waste treatment market of these kinds of residues from the stainless steel industry in Europe is estimated to be approximately 200000 tonnes per year corresponding to approximately 100000 tonnes of alloys. Two thirds of this market is processed and converted into metal. The market is strongly related to the development of the stainless steel industry~~ and is showing positive trends for the coming years~~.

### 9.1.11.1 Raw material and its preparation[rr66]

The typical raw materials for the production of secondary ferro-alloys are the following residues generated mainly within the production of stainless steel:
*Ask Industry if the term secondary ferro alloys is used in this context!*

- electric arc furnace (EAF) filter dust
- converter filter dust
- all kinds of scale fines
- shot blasting dust
- grinding dust.

The chemical and the physical characteristics of these raw materials vary considerably. However they might be described as shown in Table 9.2:

| Element | Content |
|---|---|
| $Cr_2O_3$ | 10 - 25 % |
| NiO | 2 - 15 % |
| $MoO_3$ | 0 - 5 % |
| $Fe_2O_3$ | 30 - 65 % |
| CaO | 1 - 30 % |
| $Al_2O_3$ | 0.5 - 4 % |
| $SiO_2$ | 1 - 15 % |
| MgO | 1 - 5 % |
| ZnO | 1 - 20 % |
| PbO | 0.2 - 1 % |
| CdO | 0.001 - 0.05 % |
| CuO | 0.1 - 3 % |
| S | 0.2 - 0.5 % |
| Cl | 0.1 - 1 % |
| F | 0 - 3 % |
| Hg | 0 - 15 ppm |

**Table 9.2: Typical amounts of metal oxides in secondary raw material**

The residues are mostly oxidised materials with a smaller, variable fraction of metals. They come mostly from surface treatment operations such as grinding, shot blasting, etc. The grain size of the raw material is typically between 1.0 - 3~~-~~0 µm and some materials are agglomerated and compacted.
~~[ 255, VDI (D) 2576 2008 ].~~*Check whether 30 µm is correct.*

The moisture content in the raw material might vary between 0 - 35 % due to different gas-cleaning or other separation steps installed at the steel mills. This requires, to a certain extent, a flexible handling and conveying equipment as well as drying equipment.

Owing to the various sources and qualities of residues, the economic viability of the activity requires a minimum content of alloying elements: Ni, Cr and if it can be valued, Mo. Residues from the manufacture of austenitic (18-8 or better) stainless steel offer an appropriate content of typically >3 % Ni and >12 % Cr, while a large proportion of residues from ferritic stainless steel production (17 % Cr) are still dumped for processing cost reasons.

The product range of the single steelworks mainly influences the composition of the waste products by the technology employed and by the raw materials fed. Two major issues in this relation are, e.g. the amount of lime in the filter dust and its zinc content. The lime content is mainly influenced by the different operations in the steel plant itself and the quality of the lime. The quality of the lime, i.e. its proportion of fines, influences the total quantity of lime present in the filter-dust. The zinc content in the filter dust and other metals, e.g. Pb, Cd, Hg, is mainly dependent on the quality of the scrap feed for the electric arc furnace. If there is a high portion of scrap feed that contains galvanised scrap, the entire zinc content is collected in the filter dust.

PCDD/F may be present in the furnace filter dust. The presence and the quantity of PCDD/F is dependent on the quality of the scrap feed in the stainless steel melt shops and the manner in which the off-gas is treated. Plastic impurities (chlorine compounds) support the formation of PCDD/F in the filter dust.

The quantity of raw material necessary to produce the ferro-alloy varies considerably because of differing metal contents in the feed. Typically, the reclamation produces 400 - 600 kg per metal per tonne of dry raw material feed.

### 9.1.11.2 Preprocessing

Due to the presence of various undesired coarse elements in the raw material, e.g. filter masks, scrap pieces and refractories it is necessary to screen the raw materials. The raw material can be delivered in big bags or in bulk. The big bags are emptied in an enclosure that is equipped with separate dedusting equipment. The dry raw material is then conveyed to a vibrating screen where foreign elements are removed on a screen of >10 mm. After this step, the material is conveyed with a bucket conveyor to a silo group which is used as a buffer silo prior to the mixing step ~~[ 255, VDI (D) 2576 2008 ]~~.

When using the submerged arc furnace, the free lime contained in the raw materials is neutralised with water in a specific mixer prior to agglomeration by briquetting. After several days of curing under cover, the briquettes are mixed with other charge ingredients and fed to the furnace.

#### 9.1.11.2.1 Mixing and drying (Plasmadust process only)

After screening, the slag-forming agents are analysed in the raw materials in order to determine how much sand or lime should be added to balance the basicity of the slag. The necessary amount of slag formers are added, predominantly silica sand together with a approximately 1 - 10 % of water in a high turbulent batch mixer in order to obtain enough free-flowing micro pellets. The consumption of silica sand is dependent on the basicity of the raw material, however it is typically in the range 0 - 100 kg/tonne of dry raw material.

The aim of drying the material is to obtain a homogeneous dry feed that can be sent pneumatically to the furnace building. The indirect rotating dryer used for this purpose is heated with CO-rich process gas. The dryer is equipped with a combined gas and oil burner. After drying, the material leaves the dryer at less than 100 ºC. The material is screened again before it is conveyed to an intermediate bunker.

A filter unit is used where the mercury emissions are monitored continuously on-line. Before entering the dryer, a small amount of $Na_2S$ is added to the material to form stable mercury compounds in order to prevent the evaporation of mercury.

### 9.1.11.3 Submerged arc furnace process

The recovery process that uses a submerged electric arc furnace is very similar to the production of ferro-chrome in an electric arc furnace. One installation in the US employs a rotary hearth furnace for the pre-reduction, followed by melting in a submerged arc furnace.

The furnace off-gas is dry filtered in a conventional fabric filter. The gas is diluted by the ambient air in the open top furnace where the combustion of CO is complete. Typical composition is 90 % air (18 to 20 % excess $O_2$), 7 % $CO_2$, and 3 % $H_2O$.

Off-gas-cleaning is done in a two-stage baghouse. After cooling to below 200 ºC, furnace dust is separated in the first stage and collected for recycling or further processing. In the second stage, adsorbent granules (activated carbon or lignite coke) are injected. Volatile metals, notably mercury and to a lesser extent cadmium and lead are chemisorbed on the surface of the carbon. The absorbent also traps chlorine compounds including PCDD/F. This second stage operates below 130 ºC. The same fabric filter collects the fumes from the tapping process.

A limited amount of water is injected and vaporised in the off-gases for temperature control. Process and cooling water are close circuited, the net consumption being released as steam in the furnace flue-gases and by evaporative coolers.

Therefore, the process does not produce liquid effluents. About 60 % of the water consumption is insured by the collection of rainwater falling on the industrial site (ground and buildings).

The liquid slag is separated from the metal by gravity. The use of multiple cascades affords virtually complete separation. The low basicity of slag (0.7 to 0.8) ensures the formation of stable silicates which are non-leaching. Prior to shipment, chemical composition and leaching tests are performed to qualify each production lot. The slag is used in various construction applications after the appropriate downsizing.

The alloy is cast in iron moulds. The pigs weigh 2 to 4 tonnes each. The free flowing slag is collected in an open pit where it solidifies. After the solidification of the metal, the ingots are broken into a few large pieces with a hydraulic hammer in order to facilitate shipment and remelting. Because of its nickel content, the metal is relatively tough (not brittle) contrary to most ferro-alloys. It requires no further processing and is apt to bulk transport by truck or rail cars.
*What exactly is the product of this process????*

### 9.1.11.4 Plasmadust process

*Where is the plasma process applied?*
After using the preprocessing steps for secondary raw material in the submerged arc process, the[rr67] material is pneumatically transported by means of a closed vacuum system from the raw material preparation building to the furnace building, [ 233, Farrell Nordic Mission 2008 ].

Smelting takes place in a shaft furnace comprising a 12 m high water cooled shell with an inner diameter of approximately 2.5 m. The furnace is equipped with, for example three plasma generators providing an installed plasma heating effect of 18 $MW_{th}$. The shaft is filled with lump coke, which acts as a reducing agent. The plasma generators symmetrically placed around the lower part of the furnace to supply the energy required for the endothermic reactions. The recirculated process gas is led to the furnace through water-cooled copper tuyères. The material feed is injected through tuyères and mixed with the plasma gas (approximately 4000 - 5000 ºC) in the raceway where the reaction take place.

Coke is charged from the top of the furnace in regular intervals. The coke column acts as a reducing agent and filter for the gas being led out of the furnace. Due to the equal heat distribution in the furnace and its height a high yield can be achieved in terms of the reduction of the valuable elements Ni, Cr, Mo and Fe and a comparatively low carryover into the gas-cleaning step. Before tapping is reached, raw material feed is injected in the shaft. In regular intervals the furnace is tapped by drilling a hole at the bottom of the furnace similar to the procedure on blast furnaces. The hot metal is cast at a temperature of approximately 1400 ºC into casting beds lined with refractory material, to pigs of 3 - 4 tonnes each. This corresponds to 40 - 60 % metal yield. The alloy is enriched with carbon (4 - 6 %) and can be granulated in a water bath which benefits handling and transportation or crushed into pieces of approximately 500 - 800 kg, according to the requirements of the end users in the various steel mills.

The gas-cleaning system is equipped with a 3 step venturi scrubber combined with a wet electric precipitator (wet ESP) that is located after the third step of the venturi system. The wet ESP further cleans the process gas. After these filtering steps, the off-gas is treated to remove mercury in a selenium filter. Here, mercury vapour is bound to mercury selenide. The clean off-gas is either used for heating the dryer, supplied to a district heating system or flared. About 50 % of this energy for the district heating system is produced by direct heat exchange of cooling water from the furnace, the other 50 % are produced in a hot water boiler. About 50 % of the process gas is recirculated into the plasma generators through a compressor and used as heat transfer gas. The mercury emissions in the gas stream after the flare are measured continuously on-line [ 233, Farrell Nordic Mission 2008 ].

The slag is separated from the metal by gravity and skimming the slag from the metal. The inert slag flows into a pit where it is regularly dug out and crushed at the same time. The slag can also be granulated. Then, the slag is separated externally from metal pieces. Based on experience, the basicity is approximately 1.0 (CaO, $SiO_2$) so that this kind of slag product can be sold as a non-leachable material for road construction. Long-term large scale leaching tests have been made, in which slag from the production was exposed to rainwater during 1.5 years. Slag has proven to be a suitable material for road construction purposes due to its very low leachability of metals and characteristics similar to those of natural mineral rocks.

## 9.2 Current emission and consumption levels

~~The manufacturing processes for ferro-alloys are, in general, energy consuming processes that take place at high temperatures. The energy and raw material consumption per tonne of product varies greatly from one product to the other. Different types of materials such as carbon or silicon are used as reducing agents to remove oxygen from the ore. Large amounts of electric energy must be used in order to reach the high process temperatures in the range of 1200 - 2000 ºC that are required for the metal-producing reactions to take place. The common carbon sources are coal, coke, charcoal and wood chips; however, some of these are unsuitablefor some ferro-alloy production processes for technical reasons, while some products require very low contents of selected trace elements such as titanium.~~

~~Coal contains considerable amounts of volatile compounds, tar, sulphur and water that leave the process together with the main process gases like CO,~~ ~~$CO_2$~~ ~~and SiO. In open or semi-closed furnaces, these gases burn, react and cool in the furnace hood and off-gas channels. The temperature and oxygen levels in the off-gases of open and semi-closed furnaces produce significant amounts of~~ ~~$NO_X$~~~~. The combustion inside the furnace hood and the off-gas ducts may be imperfect due to the design of the furnace as well as the standard for operation. Imperfect combustion may produce pollutants such as PAH, PCDD/F and~~ ~~$NO_X$~~~~. Investigations have shown that the quality of the raw materials fed into the furnace is vital to the environmental performance of the process.~~

~~Dust in the off-gas is collected by cyclones, filters or wet scrubbers. Some furnaces have recovery units for energy and/or cleaning facilities for specific elements like mercury.~~

The production of ferro alloys is a source of primarily particulate matter, solid waste/by-products and consumes a considerable amount of energy. When abatement techniques are applied to reduce emissions, cross media effects occur. Generally, the sections 9.2.1 to 9.2.6 below describe the most relevant environmental issues in the ferro alloy production processes. ~~The environmental impact on air, water and land varies considerably from one product to the other, and can be classified as follows:~~

***Consumption of raw material and energy***

- raw material and energy consumption.

***Emissions to air***

- dust and fume emissions including metals
- $SO_2$, $NO_X$, CO gas $CO_2$, polycyclic aromatic hydrocarbon (PAH), VOCs, PCDD/F and volatile metals.

***Emissions of noise and vibrations***

***Solid residues, wastes and by-products***

- dust[rr68]~~, fume~~ and sludge
- slag.

***Waste water emissions***

- waste water from wet scrubbing systems
- waste water from the cooling of slag and metals[rr69] ~~granulation~~
- blowdown from cooling water cycles.

***Energy recovery***

- energy recovery in terms of the utilisation of the CO-rich off-gas from closed furnaces;
- energy recovery from the high temperature off-gas either as electrical energy or hot water for heating purposes;
- energy recovery from cooling water.

### 9.2.1 Consumption of raw material and energy

The raw material consumption mainly depends on the metal content of the ore or concentrate, the metal yield in the furnace process, the composition of the product and losses during raw material and product handling (transport, screening, etc.) and treatment (refining, solidification, crushing, packing, etc.). Higher yields result in a lower consumption of raw materials and energy per tonne of metal for a specific process. Production of special alloys may require cleaner raw materials that have less favourable process properties giving less yield and higher consumption of raw materials and energy per tonne of metal produced.

The energy consumption per tonne of metal differs greatly from one ferro-alloy to another. One reason is the difference in the chemical bonding strengths to oxygen for different elements in the ore and the temperature required for the chemical reactions to proceed. Silicon, for instance, has both a higher bonding energy and requires higher process temperatures than manganese. Other reasons are variations in the metal content of the ore or concentrate and the final product, and the metal yield that it is possible to obtain for different ferro-alloys. The latter is mostly governed by the amount of slag that is produced per tonne of metal and the amount of metal fume contained in the gases that are present in the production furnace at different temperatures.

The consumption of raw material and energy listed in this section are figures for producing one tonne of tapped liquid metal. As an example, standard ferro-silicon can be tapped directly into moulds filled with low value fines from previously crushed metal, adding several percentages to the tapped tonnage. This gives low raw material and energy consumption per tonne product sold. The production of high purity, low titanium ferro-silicon, on the other hand, requires extremely clean raw materials with less favourable process properties and post tap-hole refining, often involving both a tapping ladle and a refining ladle. The poorer raw materials give less silicon yield in the furnace process, while the post tap-hole treatment gives substantial losses both through oxidation of elements to be removed by refining, imperfect slag-metal separation and through metal that solidifies in the ladles used. The raw material and energy consumption per tonne product sold is therefore much higher for this quality. The consumption values are given as intervals covering normal variations in the metal yield.

The latent chemical combustion energy of the free carbon in the carbon materials is listed even though this carbon is used as a reducing agent for the ore in highly energy-consuming chemical reactions rather than energy production by combustion with oxygen. The substantial amount of volatile components in coal is, for instance, not possible to utilise in the silicon metal and ferro-silicon process since it does not react with the ore. Neither does it add any energy in parts of the furnace where energy is needed. The energy consumption in ferro-alloy production is therefore always given by the amount of electrical energy used per tonne tapped metal. The values in the tables are for the metal production process only, and it does not include auxiliary energy for operating various support systems like fans, heat exchangers, raw material handling, keeping ladles warm, etc. The auxiliary power normally amounts to between 5 and 10 % of the given values in Table 9.3, Table 9.4, Table 9.5, Table 9.6 and Table 9.7.

To avoid false differences between process alternatives it is important to present only the gross energy consumption. The energy sources going into the production process consist of electrical energy and latent chemical energy in the carbonaceous material. One kg of carbon has a potential gross energy content on conversion to $CO_2$ of approximately 8.8 kWh, or approximately 7.7 kWh/kg coke. If these figures are used, the gross consumption of energy for the production of bulk ferro-alloys can be calculated. The emitted gross amount of $CO_2$ will be directly proportional to the amount of coke consumed in the process.

| Raw material | HC FeCr | | | | MC FeCr | LC FeCr |
|---|---|---|---|---|---|---|
| Chromite (kg/t) | 2400 - 3000 (1) | 2300 - 2400 (2) | NA | NA | NA | 1600 |
| Reducing agent (kg/t) | 550 - 700 (1) | 500 - 550 (2) | 600 (3) | NA | NA | 675 (FeSiCr) |
| Fluxes (kg/t) | 100 - 400 (1) | 200 - 300 (2) | NA | NA | NA | 1100 |
| Others (kg/t) | Electrode<br>8 - 25<br>Remelts<br>0 - 300 | Electrode<br>7 - 10 | NA | NA | NA | Sand <100 kg<br>Si <40 kg<br>Electrode 10 kg<br>Boric acid 3k |
| Electrical energy (kWh/t) | 3800 - 4500 (1) | 3100 - 3500 (2) | 2600 - 3100 (3) | 4500 (4) | NA | 3400 (5) |
| Potential energy by using coke (kWh/t) | 4235 - 5390 (1) | 3850 - 4235 (2) | 4620 (3) | NA | NA | NR |
| Total energy input (kWh/t) | 8035 - 9890 (1) | 6950 - 7735 (2) | 7220 - 7720 (3) | NA | NA | 3400 |

NB:

(1) Consumption data of a conventional open submerged arc furnace, lumpy and fine ore without agglomeration, preheating and/or pre-reduction processes.

(2) Consumption data by using preheated pellets as raw material and no remelts.

(3) Consumption by using pre-reduced pellets as raw material. In this case the energy consumption is dependent on the grade of metallisation

(4) DC furnace without pre-reduction process

(5) The presented energy consumption refers to the conversion of FeSiCr to LC FeCr. If the production of the intermediate product - FeSiCr - is included, the electrical energy is 8050 - 9500, potential energy by using coke 5750 - 6400 and the total energy input 13800 - 15900 kWh/t LC FeCr.

The above-mentioned electricity and reducing agent consumption's are for the whole production process. The electrical energy consumption is about 95 % of the total consumption. The main part of the remaining 5 % is electrical energy needed for the off-gas treatment.

NA = data not available
NR = not relevant

**Table 9.3: Gross consumption of raw materials and energy when producing ferro-chrome** [ 226, Nordic Report 2008 ]

Generally, a higher chromium content in the alloy requires more energy for production. Coke breeze consumption will generally be in the range of 60 - 90 kg/t sinter. With sinter consumption between 2 and 2.5 tonnes per tonne of ferro-chrome, this equals to 120 - 225 kg breeze per tonne of ferro-chrome. The external energy consumption of a steel belt sinter furnace ranges between 200 - 400 kWh/t pellets. The energy comes from coke breeze and CO gas from smelting. The coke breeze consumption is 20 - 40 kg/t of pellets and the proportion of CO as external energy is about 20 - 40 %. The external energy for coke drying in a shaft furnace is about 200 kWh/tonne of coke equalling to 100 kWh/t of FeCr.

The consumption of Søderberg electrode paste ranges between 7 - 20 kg/t of FeCr, the lowest consumption is achieved when using preheated or pre-reduced and agglomerated charge.

Water is used in the production of ferro-chrome both as process water and cooling water. Process water is used for scrubbing and slag granulation. If the process water treatment is in a closed circuit, 3 – 10 $m^3$ water/t of ferro-chrome is normally used. For cooling purposes, 5 - 15 $m^3$ water/t of ferro-chrome is also used.

Oxidised steel mill waste, dust and scale are recovered using processes adopted from high carbon ferro-chrome production. The energy consumption for the metallurgical reduction is shown in Table 9.4 for typical contents of recoverable metals. Two types of furnaces are in use, conventional submerged arc furnaces and DC plasma shaft furnaces.

| Component | Conventional submerged electric arc furnace | Plasmadust process |
|---|---|---|
| Residues (kg/t ) | 1650 - 2500 | 1650 - 2500 |
| Reducing agent (kg/t) | 400 - 500 | 400 - 500 |
| Electricity (kWh/t) | 3000 - 3400 | 2800 - 3800 |
| Metal contents (output): | (%) | (%) |
| Ni | 3 - 15 | 3 - 15 |
| Cr | 15 - 25 | 15 - 25 |
| Mo | 1 - 5 | 1 - 5 |
| C | 4 - 6 | 4 - 6 |
| Si | 0.5 - 8 | 0.1 - 1 |
| Fe | Balance | Balance |
| Water ($m^3$/t) | 1.0 - 1.5 | 2.8 - 3.2 |
| Alloy recovery (output) | (%) | (%) |
| Cr | 90 - 95 | 90 - 95 |
| Ni | 90 - 98 | 90 - 98 |
| Mo | 90 - 98 | 90 - 98 |
| Fe | 90 - 98 | 90 - 98 |

**Table 9.4: Consumption data for the recovery of ferro-alloys from steel mill residues as specific input of raw materials per tonne of recovered metal**
[ 226, Nordic Report 2008 ]

The consumption of energy and raw material for the production of ferro-silicon, silicon metal CaSi are presented in terms of specific input factors as an example in Table 9.5. The amount of electrical energy that is given is for the furnace process only and refers to one tonne of liquid metal tapped from the furnace at the specified silicon yield, electric efficiency of the furnace and carbon loss from the top of the furnace.

| | Ferro-silicon (75 % Si) | Silicon metal | CaSi |
|---|---|---|---|
| Quartzite (kg/t) | 1950 | 2700 | 1500 |
| Reducing agent (kg/t) | 1200 | 1150 - 1500 | 925 |
| Electrode (kg/t) | 63 | 100 ($^2$) | 120 |
| Iron ore pellets (kg/t) | 350 | NR | NR |
| Limestone (kg/t) | NR | NR | 900 |
| Woodchips (kg/t) | 0 - 900 | 1000 - 2000 | NR |
| Electrical energy (kWh/t) | 8750 | 10800 - 12000 ($^1$) | 9500 |
| Potential energy assuming coke or coal is used (kWh/t) | 10500<br>(coke/coal) | 10120 - 13200<br>(coal) | 7122<br>(coke) |
| Total energy input (kWh/t) | 19250 | 20920 - 25200 | 16622 |

NR: not relevant
($^1$) The ideal energy consumption for the production of silicon metal is 10100 kWh/t (heat of reaction = 8 kWh/t, heat loss with the metal = 0.9 kWh/t and heat loss in the off-gas = 1.2 kWh/t).
($^2$) Some silicon producers are using a combined Søderberg/graphite electrode. The aim is to use the Søderberg technology, but reduce the iron impurities caused by the electrode casing

**Table 9.5: Consumption of raw material and energy by producing ferro-silicon, silicon and CaSi as specific input factors**
[ 226, Nordic Report 2008 ].

*Crosscheck with Nordic report. The Nordic report gives different figures including FeSi65%. Try to find out where the new data have been taken from . They are not from the Nordic report.*

A combination of the Søderberg technology and a graphite core is used for the production of silicon metal. The aim of this compound electrode is to reduce the cost of the electrode while keeping the iron impurities caused by the electrode casing at an acceptable level for the silicon metal.

The specific input factors for the production of the different sorts of ferro-manganese as well as for silico-manganese and the sinter process of manganese ores and concentrates are given in Table 9.6 below.

| **Source** | **Sinter** | **HC FeMn** | | **MC, LC FeMn (silicothermic)** | **SiMn (standard and LC SiMn)** | **Notes** |
|---|---|---|---|---|---|---|
| | | **Blast furnace** | **EAF** | | | |
| **Ore (kg/t)** | 1000 - 1300 | NR | 1900 - 2400 | 1600 - 2000 | 500 - 1700 | (1) |
| **Coke or coal (kg/t)** | 100 | NR | 410 - 500 | 200 - 300 | 400 - 600 | |
| **Gas ($m^3$/t)** | 150 - 200 | NR | NR | | NR | |
| **Electrode (kg/t)** | NR | NR | 8 - 25 | 6 - 8 | 10 - 30 | |
| **Water ($m^3$/t)** | 12 - 18 | NR | 1.5 - 40 (N3) cooling water | Cooling water | 1.5 - 40 (3) cooling water | (2) |
| **Others (kg/t)** | NR | NR | NR | Fluxes<br>800 - 1000<br>SiMn<br>700 - 1000 | FeMn slag<br>400 - 2500 | |
| **SiMn (kg/t)** | | | | 600 - 1000 | | |
| **Electricity (kWh/t)** | 100 | NR | 2200 - 3200 | 1600 - 2000 | 3800 - 6000 | |
| **Potential energy by using coke (kWh/t)** | 900 – 1000 | NR | 3800 - 4100 | 5700 – 13300 | 3100 - 5000 | |
| **Total energy input (kWh/t)** | 1000 – 1100 | NR | 6000 – 7300 | 7300 - 15300 | 6900~~6880~~ - 11~~0~~ ~~620~~000 | |

NB: Silicon can be replaced by aluminium

(1) The consumption of raw materials normally contains recycled materials such as dusts and sludge's from the abatement system

(2) The consumption of water is dependent on the water processing equipment and varies from 20 to 40 $m^3$/t in open circuits and from 1.5 to 5 $m^3$/t in closed circuits

(3) Water consumption is associated to wet dedusting

EAF = Electric Arc Furnace

NR = not relevant

**Table 9.6: Consumption data for the production of manganese ore sinter, ferro-manganese and silico-manganese as specific input factors**

[ 226, Nordic Report 2008 ] [514]

*Delete Blast furnace! Not applied any more in Europe and no data included.*

*These data have not been taken from the Nordic report. Check where they are from.*

*Check Excel spreadsheet comments from France and Industry (Euro Alliages Ines van Lierde)*

The available information about the consumption of raw material and energy for the production of various special ferro-alloys are presented in Table 9.7.

| Component | FeNi alloys | FeV | FeMo (3) | FeTi | FeB |
|---|---|---|---|---|---|
| **Metal oxides (kg/t)** | NA | 1100 - 2000 (1) | NA (3) | NA | NA |
| **Electric energy (kWh/t)** | 5300 | 2200 - 2800 | 160 - 405 | 770 | 6000 - 11000 |
| **Gas ($m^3$/t)** | 120 | NR | 148 - 155 MJ/t | 55 | 75 |
| **Water ($m^3$/t)** | 6.9 | (2) | NR | NM | 0.3 |
| **Quicklime (kg/t)** | NA | NR | 20 - 180 | NR | NR |
| **Fluorspar (kg/t)** | NR | NR | 0 - 30 | NR | NR |
| **Aluminium (kg/t)** |  | 800 - 1000 | 36 - 70 | NR | NR |
| **Metallic iron (kg/t)** | NA | 100 - 150 | 23 - 210 | (4) | NA |
| **Mill scale (kg/t)** | NR | NR | 250 - 550 | NR | NA |
| **Others (kg/t)** | NA | NA | 620 - 700 (FeSi) |  | NA |

(1) The data presented contains the amount of $V_2O_3$ and $V_2O_5$
(2) The Consumption of water is very site-specific and therefore not representative.
(3) The consumption data for the production of FeMo are based on one tonne of molybdenum.
(4) The amount of metallic iron depends upon the alloy being made, e.g. 70 % FeTi contains 700 kg of Ti and 300 kg of iron per t of alloy; whereas 40 % FeTi contains 400 kg Ti and 600 kg iron per t of alloy.
NA = data not available
NR = not relevant in this production process
NM = not measured

**Table 9.7: Consumption data for the production of special ferro-alloy as specific input factors**
[ 226, Nordic Report 2008 ]

The process of roasting molybdenite concentrates is an exothermic process since the oxidation reaction is ignited. External energy in the form of electricity will therefore only be needed for the mechanical operation of the multiple hearth furnaces. Natural gas is used to dry the concentrates and to ignite flotation oil and elevate the temperature to the point where the exothermic reactions are ignited and to remove the remaining sulphur.

## 9.2.2 Emissions to air

### 9.2.2.1 Dust and fume emissions

According to the raw material that is needed and the unit operations used, e. g. crushing, drying, sintering, reduction, tapping and product handling the most important source of environmental emissions are dust and fumes. Figure 9.8 shows the potential emission points for dust and fumes from a ferro-alloy producing plant.

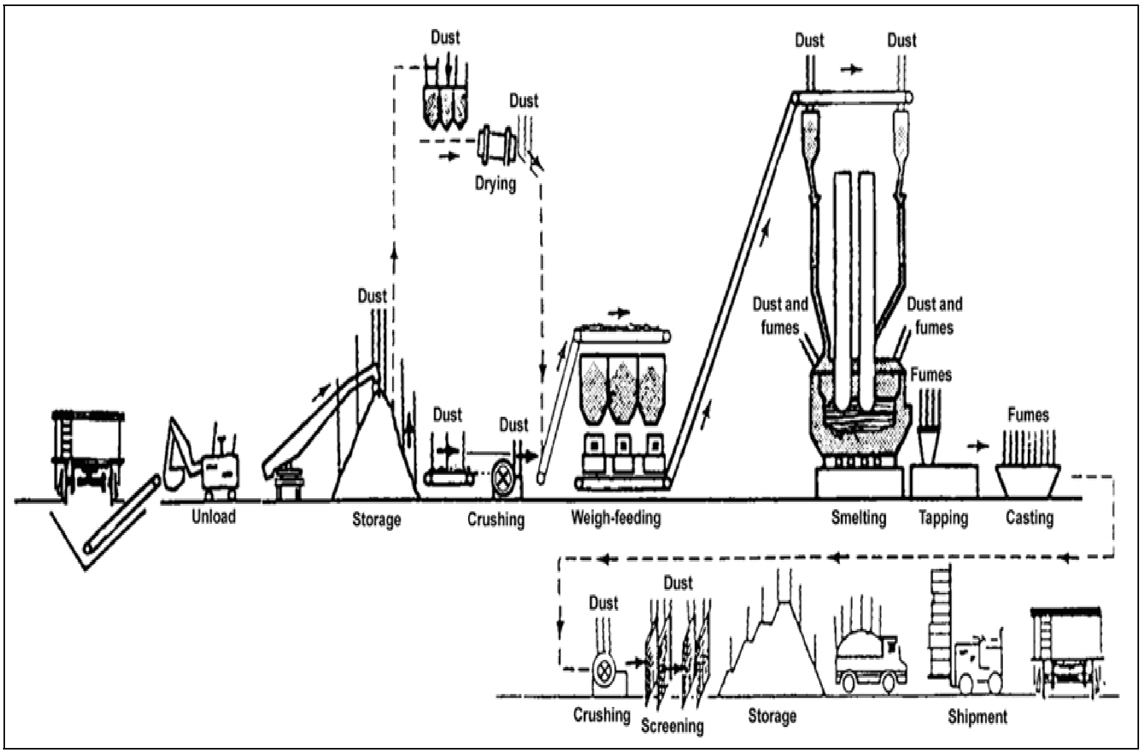


**Figure 9.8: Ferro-alloy production flow diagram showing potential points of air emissions**
[ 34, UNECE 1995 ]

Some raw materials contain a considerable amount of fines and dust. Unloading and storage of raw material can generate dust when the material falls from one conveyor to another. Dust can also be produced if the conveyor is running too fast (i.e. more than 3.5 m/s). If a front-end loader is used, dust is emitted during the whole of the journey.

The dust that is produced by the reduction process is collected by hoods or in case of a closed furnace by the furnace sealing directly and transferred to an abatement plant and dedusted (e. g. by a fabric filter or a wet scrubber[rr70]). ~~Scrubbing is used for closed furnaces [ 255, VDI (D) 2576 2008 ].~~

Tapping off-gas consists of dust and fumes from the furnace process, oxygen lancing, dust from drilling, fumes from vaporised slugs if a tapping gun is used and fumes from all exposed metal and slag surfaces. These fumes that arise from tapping contain little CO, $CO_2$ and will mainly be oxides of the metals involved in the reduction process.

Table 9.8, Table 9.9, Table 9.10 and Table 9.11 present the available emission data for the emissions of dust when producing different ferro-alloys.

| Source | HC FeCr | | MC FeCr | | LC FeCr | |
|---|---|---|---|---|---|---|
| | (kg/t) | (mg/Nm$^3$) | (kg/t) | (mg/Nm$^3$) | (kg/t) | (mg/Nm$^3$) |
| Raw material handling | 0.01 - 0.02 | f (2) | NA | f (2) | | f (2) |
| Drying | 0.01 – 0.02 (Coke) | 1 - 50 | NA | NA | 0.082 (ore) | 5 |
| Crushing | 0.002 | | NA | NA | 0.003 | 3 |
| Pelletising/sintering (4) | 0.01 - 0.02 /t pellets | 1 - 15 | NR | NR | NR | NR |
| Dosing station | 0.01 - 0.02 | 1 - 30 (4) | NA | NA | 0.024 | 5 |
| Preheating | 0.001 - 0.005 | 1 - 15 (4) | NR | NR | NR | NR |
| Smelting furnace | 0.02 - 0.1 | 1 - 100 | NA | NA | 0.101 | 8 |

| | | | | | | |
|---|---|---|---|---|---|---|
| | (1) | (4,5,6) | | | | |
| Tapping | (3) | 5 - 12<br>(4) | NA | NA | (7) | (7) |
| Casting | (3) | 5 - 12<br>(3) | NA | NA | 0.2 - 0.4<br>(4) | 3 - 15<br>(4) |
| Slag handling | NM | NM | NA | NA | 0.04 | 10 - 15 |
| Product handling (crushing, screening, storage, etc.) | 0.02 - 0.05 | r | NA | NA | NA | NA |

(1) The Cr(VI) content of the furnace dust is between 5 - 100 ppm in the closed furnace and between 1000 - 7000 ppm in the open furnace

(2) The amount of material loss caused by handling and storage of raw material is estimated to be less than 1 %.

(3) Sampling of the ventilation air leaving the furnace building including tapping and casting area over long periods of time can give an indication of the average values. These show average dust concentrations of between 5 and 12 mg/Nm$^3$.

(4) The present dust emissions are dependent on the furnace type and the used off-gas abatement technique. For instance most baghouse filters achieve less then 5 mg/Nm$^3$. Dust emissions from a sinter furnace by using a cascade wet scrubber are reported to be below 5 mg/Nm$^3$.

(5) This illustrates the range between good and pour performers.

(6) The furnace gas from a closed furnace is used as fuel after wet scrubbing The gas is flared only if a customer is temporarily not available.

(7) Included in source "smelting furnace"

NA = data not available
NR = not relevant
NM = not measured
f = diffuse dust emissions *(this should be changed to d because the emissions are diffuse dust and not fugitive.)*
r = dust is recycled back into the process

**Table 9.8: Dust emissions when producing ferro-chrome based on one tonne of produced alloy**

[ 226, Nordic Report 2008 ] *This is not the correct reference for this table.*

*Footnote 4: Where is the evidence to give such a statement. Check if any information about the performance of abatement systems in the ferro chrome production is included. This seems to be not the appropriate place to give such staements. Instead include more data about the achieved performances.*

| **Source** | **FeSi** | | **Si metal and calcium-silicon** | |
|---|---|---|---|---|
| | **(kg/t)** | **(mg/Nm$^3$)** | **(kg/t)** | **(mg/Nm$^3$)** |
| Raw material handling | f (2) | f (2) | f (2) | f (2) |
| Drying of woodchips | NM | NM | NM | NM |
| Crushing | NM | NM | NM | NM |
| Weighing dosing station | f | f | f | f |
| Smelting | 0.1 - 2 | 1 - 20<br>(1) | 0.1 - 1.5 | 1 - 20<br>(1) |
| Tapping | (N 3, 4) | (3)<br>5 - 12<br>(4) | (N 3, 4) | (3)<br>5 - 12<br>(4) |
| Casting | (4) | 5 - 12<br>(4) | (4) | 5 - 12<br>f (4) |
| Refining | (3) | (3) | (3) | (3) |
| Product crushing | 0.3 - 0.5 | r | 0.3 - 0.5 | r |

(1) Using a baghouse filter, plants are achieve dust emissions below 5 mg/Nm$^3$, corresponding to a cleaning grade of above 99.5 %. The silica fume is collected in the filter as a by-product (Micro Silica).

(2) The amount of material loss caused by handling and storage of raw material is estimated to be less than 0.2 %.

(3) If the fumes and dust from the tapping area are collected and cleaned in the baghouse the dust concentrations are in the same range as the concentration of dust emissions from the smelting furnace.

(4) Sampling of the ventilation air leaving the furnace building including the tapping and casting area over long periods of time can give an indication of the average values. These show average dust concentrations between 5 and 12 mg/Nm$^3$ and total dust emissions amounting to 0.2 - 0.6 kg/tonne of alloy produced.

NA =data not available
NR = not relevant
NM = not measured
f = diffuse dust emissions
r = dust is recycled back into the process

**Table 9.9: Dust emissions when producing ferro-silicon and silicon metal based on one tonne of produced alloy**

[ 226, Nordic Report 2008 ] *This is not the correct reference for this table.*

*Check whether the data for dust emissions are still uptodate. 20 mg/Nm$^3$ seems to be quite high. The statement in Footnote 1 is redundant here. What is needed are more data for real emission concentrations and not only the range.*
*Footnote 4 is about diffuse emissions, not only for casting of Si metal last column.*
*Footnote 4 is the same as in the previous table. Where is the reference for these data. Have the measurments been carried out at production sites for both ferro-silicon and silicon metal based and ferro-chrome?*
*Please provide data for crushing an ddrying of woodchips if relevant?*
*Refining takes place in a separate furnace. Is there also a separate dedusting? Then try to get separate data.*

| **Source** | **HC FeMn** | | | | **MC and LC FeMn** | | **Silico-manganese** | |
|---|---|---|---|---|---|---|---|---|
| | **BF** | | **EAF** | | **(kg/t)** | **(mg/Nm$^3$)** | **(kg/t)** | **(mg/Nm$^3$)** |
| | | | **(kg/t)** | **(mg/Nm$^3$)** | | | | |
| Raw material handling | NR | NR | f | f | f | f | f | <0.1 |
| Weighing dosing station | NR | NR | NA | NA | NA | NA | NA | <0.1 |
| Smelting | NR | NR | 0.1 - 0.4 | 5 - 60 (3) | NA | <25 | 0.02 - 0.4 | 5 - 60[rr71] |
| Tapping | NR | NR | NA | NA | NA | NA | NA | 3.2 |
| Casting | NR | NR | 0.05 - 0.1 | NA | 0.05 - 0.1 | NA | NA | NA |
| Refining | NR | NR | NA | NA | NA | NA | NA | NA |
| Product crushing | NR | NR | 0.1 - 0.3 | r | 0.1 - 0.3 | r | NA | r |
| Waste heat boiler | NR | NR | NR | NR | NR | NR | NR | NR |
| Electricity production | NR | NR | NR | NR | NR | NR | NR | NR |

(1) Dust emissions from an closed sealed furnace with a venturi scrubber[rr72]
(2) Dust emissions from an open furnace *(Can not find a footnote (2)*

(3) If the dedusting of the off-gases from a closed sealed furnace takes place in a cascaded wet scrubber dust emissions below 10 - 40 mg/Nm$^3$ are achieved. Some plants that are operating semi-closed furnaces using baghouses for dedusting are achieving dust emissions below 5 mg/Nm$^3$
BF = Blast Furnace
EAF = Electric Arc Furnace
NA = data not available
NR = not relevant
f = diffuse dust emissions
r = dust is recycled back into the process.

**Table 9.10: Dust emissions when producing ferro-manganese and silico-manganese based on one tonne of produced alloy**

[ 226, Nordic Report 2008 ] *This is not the correct reference for this table.*
*Check footnotes. Ask industry wheter this table is still uptodate. Check why info from [226] has not been entirely used for the silico magnese production (smelting)*

*See letter from Euro Alliages. Considering that no Blast Furnaces are operational in Euyrope for ferro-alloys production and no information is included in these table for BF delete BF column!*

| | **Fe Ni** | **FeV** | **FeMo** | **FeTi** | **FeB** | **Molybdenite roasting** |
|---|---|---|---|---|---|---|
| **Source** | **(mg/Nm$^3$)** | **(g/Nm$^3$)** | **(mg/Nm$^3$)** | **(mg/Nm$^3$)** | **(mg/Nm$^3$)** | **(mg/Nm$^3$)** |
| Raw material handling | 1 - 15 | <5 | 0.5 - 2 | 1 - 15 | 1 - 15 | 1 - 15 |
| Raw material drying | 1 - 15 | NR | 4 - 17 | 1 - 15 | 1 - 10 | NR |
| Crushing | <1 (2) | NR | 1 - 5 | | | NR |
| Pelletising | | NR | NR | | | NR |
| Sintering/roasting | | NR | NA | | | 1 - 15 |
| Dosing | | NR | 1 | | | NM |

| | | | | | | |
|---|---|---|---|---|---|---|
| Preheating | | NR | NR | | | NR |
| Smelting | 1 - 15 | <5 | 1 - 30 | 1 - 15 | 1 - 10 | NR |
| Tipping/tapping | NA | | 5 - 15 (1) | NA | NA | NR |
| Casting | | | | NA | NA | NR |
| Slag handling | NA | NA | NA | NA | NA | NR |
| Product crushing | 1 - 15 | <5 | 0.5 - 5 | NA | NA | NM |

(1) Emissions are estimated from the roof exhaust fans
(2) Data is due for the production of secondary FeNi where a modern membrane fabric filter is used. The result gives the amount of Ni oxide as part of the emitted dust from the rotary kiln.
NA = data not available
NR = not relevant
NM = not measured

**Table 9.11: Dust emissions to air (after abatement) by producing ferro-alloys**

[ 226, Nordic Report 2008 ] *This is not the correct reference for this table. Check whether Nordic countries produce these alloys!*

*What are the reference for these data? Are there measured data?*

| **Component** | **Measured concentration in stack emissions** | **Air flow rates** | **Frequency of sampling** |
|---|---|---|---|
| **Smelter total** | **mg/m$^3$** | **m$^3$/hr** | |
| Dust | 113 | 1100000 | 1/yr |
| Ni | 1.551 | | |
| Co | 0.078 | | |
| As | 0.012 | | |
| Pb | 0.049 | | |
| Cd | 0.002 | | |
| Hydrocarbon | 1322 | | |
| CO | 3262 | | |

**Table 9.12: Ferro-nickel emissions to air**

[ 356, ENIA emission data for the nickel industry 2008 ]
*Considering that Ni is high toxic and cancerongenic 113 mg dust/Nm$^3$ is quite high. Check and try to get further information.*
*The old table has been substituted by the new one. All these table are not mentioned in the text and are not introduced. This is quite confusing. Compare with the existing document.*

| **Source** | **Stack emission factor, g/ton** | **Abatement system** |
|---|---|---|
| Rotary kilns | 1.993 (2006) | Electro-precipitators |
| EAF | 20.993 (2006) | Multicyclones |
| Converter | 315 | Venturi scrubbers and bag filters |

**Table 9.13: Ferro-nickel source of emissions**

[ 356, ENIA emission data for the nickel industry 2008 ]
Clarify that (2006) means a reference year.
Is the multicyclone the last abatment step before release or are the emissions further treated?

Table 9.14 shows the measured data after dust abatement by fabric filters from different sources when producing ferro vanadium and ferro molebdenite for one site.

| | **Off-gas flow Nm3/h** | **Dust (min-max.** | **Tot. C** | **PAH (2)** | **PCDD/F** |
|---|---|---|---|---|---|

| **Source** | | **(mg/Nm$^3$)** | **(mg/Nm$^3$)** | **(µg/Nm$^3$)** | **(mg/Nm$^3$)** |
|---|---|---|---|---|---|
| Rolling scale drying | 10000 | 4.83 | NR | NR | NR |
| Mo burden preparation | 10000 | 1.74 | NR | NR | NR |
| 5 EAF (FeV) | 10870 – ca. 17000 per furnace | 0.99 – 1.36 | 1.7 – 3.3 | 23 | 0.00032 – 0.00044 |
| Thermite oven (FeMo) | 19411 | 1.43 | 2.3 – 3.8 | 35 | 0.000153 – 0.000506 |
| Product crushing<br>FeMo<br>FeV | <br>9700<br>11800 | <br>0.82<br>0.91 | NR | NR | NR |
| Slag crusher<br>FeMo<br>FeV | <br>1500<br>25000 | <br>0.99<br>2.80 | NR | NR | NR |
| Refractory crushing | 1400 | 1.03 | NR | NR | NR |
| Packing | 5400 – 8200 | 1.13 – 1.73 | NR | NR | NR |
| Diffuse emissions via the roofline (1) | 225700 – 314300 | 3.88 | NR | NR | NR |

(1~~4~~) The lower value represents furnace out of operation and the higher value represents furnace in operation
(2) 16 EPA PAH
NR = not relevant

**Table 9.14: Emissions when producing ferro vanadium and ferro molebdenite**
[509]

*Introduce a similar table for [509] FeV, FeNi, FeMoNi production in premelt plants.*

### 9.2.2.2 Other emissions to air

The most important pollutants from the production of ferro-alloys besides dust are $SO_2$, $NO_X$, CO, $CO_2$, HF, polycyclic aromatic hydrocarbon (PAH), volatile organic compounds (VOCs) and metals. The formation of PCDD/F in the combustion zone and in the cooling part of the off-gas treatment system (de novo synthesis) may be possible in open or semi-closed furnaces. $N_2O$ and $CH_4$ are emitted from sinter and pelletising plants. Mercury, if present in the ore, can also be emitted from reduction processes. The emissions can escape the process either as stack emissions or as diffuse emissions depending on the design and maintenance of the plant and the technology used. Stack emissions are normally monitored continuously or periodically and reported by on-site staff or off-site consultants to the competent authorities.

In the carbothermic process, only the fixed carbon content is used as a reducing agent, which means that volatile matter, ashes and moisture mostly leave the furnace with the off-gas and slag. *(unclear conclusion from my point of view)* –The volatile matter consists mainly of hydrocarbons and does not take part in the reaction but leaves the furnace together with the CO when the furnace is closed or burns near the surface in a semi-closed or open furnace. Closed furnaces produce higher concentrations of CO that can be used as a fuel gas in other processes.

The sulphur content in metallurgical coke varies between 0.4 and 1.0 %. 60 - 85 % of the sulphur remains in the slag and about 5 % escapes the furnace as $SO_2$. The production of silicon alloys requires different reducing agents like coal, coke, petrol-coke and charcoal. This material contains different amounts of sulphur, and typical variations are between 0.5 and 3 %. In the silicon-alloy production, this is almost slag free, nearly all sulphur escapes from the furnace as $SO_2$ or as bounded sulphur to the micro-silica. By using a reducing agent or a mixture of different carbon sources, which contains in total a high sulphur content of about 2 - 3 %, higher $SO_2$ emissions may occur.

The off-gas generated by roasting molybdenite concentrates contains large amounts of $SO_2$ that is normally cleaned in a desulphurisation plant producing sulphuric acid. Detailed information on desulphurisation plants is given in Section 2.20.6 of this document. The tail-gas from the desulphurisation plant of a molybdenite roaster contains $SO_2$ since the conversion of $SO_2$ into $SO_3$ will hardly be 100 %. The off-gas also contains a certain amount of sulphuric acid mist as well as some $SO_3$.

Metals are carried into the process as trace elements in the raw material. The metals with a high enough vapour pressure will escape as gases in the form of metal vapour, which partly condenses and oxidises to form part of the dust from the smelting furnace. Even after tapping and especially during refining, the temperature of the molten metal and slag are high enough to allow vaporisation of components both from the metal and from the slag. The fumes arising from this evaporation evolve the whole time, from the start of tapping until casting is finished. Even after the ladle is emptied, some fumes may evolve from the metal skull. During tapping most of the fumes are collected through the tapping fume collection system and cleaned.

Depending of the type of ore that is used, mercury may be emitted to air. Some plants producing SiMn have reported high mercury emissions due to a high mercury content in the raw material. Other producers of FeMn and/or SiMn may use the same raw material with a higher mercury content. Therefore, control of mercury input in the furnace and control of subsequent mercury output of the processes is advisable if such raw materials are used. In this case, the raw material needs a pretreatment to remove the mercury otherwise the mercury should be removed from the furnace off-gas by using a mercury-removal step[ 226, Nordic Report 2008 ].

There are several commercial technologies available for mercury removal from off-gases and these are reported in Section 2.20.7. Mercury removal from raw materials will involve large scale equipment. Ore dressing is only economical due to scale. For the converting step, the cleaning of the off-gas might be feasible if a satisfactory gas collection system can be installed. Sintering plants are usually built for the treatment of ore fines. If the material must be sintered due to size, mercury removal should be installed. For alloy production, online measurement and cleaning measures must be a minimum requirement.

In the production of FeMo, fluorspar may be used to improve slag and metal separation. Fluorspar is a calcium fluoride ore that is used as a flux and lowers the melting point and the viscosity of the slag resulting in an enhanced fluidity of the slag. Additionally, when mixed with lime, it reduces the phosphorus and sulphur content of the metal. Lower melting points favour the metal-slag separation, since the slag remains liquid for a longer time during the cooling. This effect together with the reduced viscosity makes it possible for small dispersed droplets to sink and coagulate in the metal phase at the bottom. However, the use of fluorspar as a fluxing agent results in emissions of fluorides within the range of 150 to 260 mg/Nm$^3$. According to the biotoxic nature of fluoride, the use of fluorspar should be minimised as far as possible. Table 9.15and Table 9.16 below present some figures of measured emissions to air when producing bulk ferro-alloys, however the data is not meant to be representative of the whole of the EU-27 industry.

| **Component** | **FeCr** | | | | **FeSi** | | **Si metal** | | **FeMn** | | | | **Silico-manganese** | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **HC FeCr** | | **MC and LC FeCr** | | | | | | **HC FeMn EAF** | | **MC and LC FeMn** | | | |
| | **(kg/t)** | **(mg/Nm$^3$)** | **(kg/t)** | **(mg/ Nm$^3$)** | **(kg/t)** | **(mg/ Nm$^3$)** | **(kg/t)** | **(mg/ Nm$^3$)** | **(kg/t)** | **(mg/Nm$^3$)** | **(kg/t)** | **(mg/ Nm$^3$)** | **(kg/t)** | **(mg/ Nm$^3$)** |
| SO$_2$ | 0.2 - 3.0 | NA | NR | NR | 20 (7) | <450 | 12 - 18 | <450 | 0.1 - 0.2 | NA | NA | NA | 0.002 - 0.1 | NA |
| CO | NM | NM | NM | NM | Traces | <200 | NM | <200 | NA | NA | NA | NA | NA | NA |
| CO$_2$ | 1200 - 2000 (1) | NA | 110 (3) | NA | 5300- (4) | 93 g/Nm$^3$ | 7500 (4) | 125 g/Nm$^3$ | 1100 - 1800 | NA | 1800 (5) | NA | 1100 - 1800 | NA |
| NO$_X$ | 0.5 - 1.5 | NA | NM | NM | 15 | 400 | 10 - 13 | <500 | NA | NA | NA | NA | NA | NA |
| HF | NM | NM | NM | NM | NM | NM | NM | NM | NA | NA | NA | NA | NA | NA |
| PCDD/F | <0.1 ng/Nm$^3$[rr73] | NA | NM | NM | 40 ng/t (8) | NA | 40 ng/t (8) | NA | NA | NA | NA | | NA | |
| Metals | Cr (in the dust) 1 - 15 % CrVI 0.1 - 0.3 % (6) | NA | Cr <0.01<br>Cr$^{6+}$ <0.002 | NA | NA | 1.0 µg Hg/Nm$^3$ (8) | NA | 1.0 µg Hg/Nm$^3$ (8) | **See Table 9.16** | | | | | |
| PAH | NM | NM | NA | NA | 0.0015 (8) | 70 µg/Nm$^3$ | 0.003 (8) | 0.02 | NA | NA | NA | NA | NA | NA |
| VOC | NM | NM | NA | NA | 0.045 (8) | 100 | 0.13 (8) | 100 | NA | NA | NA | NA | NA | NA |
| Cyanides | 0.02 - 0.05 | NA | NA | NM | NM | NM | NM | NA | NA | NA | NA | NA | NA | NA |

(1) The emissions of CO$_2$ include total emissions from the pretreatment smelting and post-furnace processes. The external use of the CO gas from the smelting furnace reduces the local emissions from the FeCr plant only.
(3) The emissions are due to 80 kg/t for natural gas-fired of dryer, ladle heating, etc. and 30 kg/t from the electrode pastes that is consumed.
(4) This CO$_2$ data contains the amount of fossil fuels as well as the amount of biological CO$_2$.
(5) This CO$_2$ data is due for the silicothermic production of LC FeMn. The CO$_2$ emissions by producing MC FeMn from HC FeMn are about 100 - 500 kg/t of alloy.
(6) The amount of Cr VI in the dust is emitted from a semi-closed furnace; cyanides = 0.2 - 0.05 from a closed furnace.
(7) The high value correspond to a production of high purity FeSi. in which a great quantity of petrol coke is used
(8) Results from comprehensive 24 h surveys of air emissions from the production of FeSi 75 and high purity Si metal. In this case it should be noted, that the data are based on relatively short measuring periods at two specific plants, and should not be taken as general for the industry. More measurements were planned within the industry and are given in Table 9.13..
NA = data not available
NR = not relevant
NM = not measured

**Table 9.15: Emissions to air (after abatement) when producing bulk ferro-alloys**

[ 226, Nordic Report 2008 ]. *This is not the correct reference for this table.*

*The data for dioxins, PAH and metal emissions have been modified according to the proposal from Laurence Cheyrou, FR, comment No. 1006. There one can find the proposal to modify the valy for dioxins from 15 ng/t to 40 µg/t. Beside that the value was modified to 40 ng/t it is entirely unclear why all these values have been altered. Furthermore it is unclear why atill footnote 8 is used which refers to a survey from the existing BREF.*

| **Emissions to air** | | | | |
|---|---|---|---|---|
| | **FeMn** | | | |
| | **HC FeMn** | | **MC and LC FeMn** | |
| | **EAF** | | | |
| | (kg/t) | (mg/Nm$^3$) | (kg/t) | (mg/Nm$^3$) |
| SO$_2$ | 0.1 - 0.2 | NA | NA | NA |
| CO | NA | NA | NA | NA |
| CO$_2$ | 1100 - 1800 | | 60 - 100 | |
| NO$_X$ | NA | NA | NA | NA |
| Hg | 0.0001 - 0.00015 | 0.001 - 0.2 | | |
| Pb | 0.0002 - 0.0004 | | | |
| As | $2\times10^{-5}$ | | | |
| Cd | $5\times10^{-6}$ | | | |
| Cr | $2\times10^{-5}$ | | | |
| Cu | $8\times10^{-5}$ | | | |
| Sum | 0.0001 | 0.0002 | | |
| Emissions to air | | | | |
| | SiMn | | | |
| | SiMn | | | |
| | (kg/t) | (mg/Nm$^3$) | | |
| SO$_2$ | 0.002 – 0.1 | NA | | |
| CO | NA | NA | | |
| CO$_2$ | 1100 - 1800 | | | |
| NO$_X$ | NA | NA | | |
| Hg | 0.00003 – 0.0001 | | | |
| Pb | 0.0002 - 0.0006 | | | |
| As | $2\times10^{-5}$ | | | |
| Cd | $5\times10^{-6}$ | | | |
| Cr | $2\times10^{-5}$ | | | |
| Cu | $8\times10^{-5}$ | | | |
| Sum | 0.0001 | 0.0002 | | |

**Table 9.16: Emission of metals from FeMn and SiMn processes (2007 data)**
[ 233, Farrell Nordic Mission 2008 ], [ 226, Nordic Report 2008 ].

The emissions to air when producing primary ferro-nickel are shown in Table 9.17.

| **Operation** | **Emissions to air** | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | **Dust/Fume** | | | **Gases** | | | | | | |
| | **Total** | **Ni** | **Others** | **SO$_2$** | **CO$_2$** | **CO** | **NO$_X$** | **H$_2$S** | **Ni(CO)$_4$** | **others** |
| Ore crushing | HL | LL | - | - | - | - | - | - | - | - |
| Drying | HL | HL | - | LL | ML | LL | | - | - | - |
| Roasting | HL | HL | - | HL | ML | LL | LL | - | - | - |
| Reductive calcination | HL | LL | - | LL | ML | LL | LL | - | - | - |
| Smelting | HL | LL | - | - | ML | ML | LL | - | - | - |
| Converting | HL | ML | SiO$_2$ | - | ML | LL | LL | - | - | - |
| Pouring | HL | LL | - | - | - | - | - | - | - | - |
| NB: LL Low level | | ML | Medium level | | HL | High level | | | | |

**Table 9.17: Emissions to air from ferro-nickel**
[ 226, Nordic Report 2008 ] *This is not the correct reference for this table.*
[ 106, Raffinot, P. 1993 ] – *why to refer to this reference???? In the existing BREF it is [tm 109, UNEP 1993]*
*This table is associated to table 9.12. It's partly a qualitative describtion of what is mentioned there. Put them together.*

Emission from a process producing of ferro-alloys are presented in Table 9.18 this uses material recovered from steel mill residues in a submerged electric arc furnace. The percentage of metals in dust will dictate the concentration of metals.

| Pollutants | Concentrations (gas and particles) (mg/Nm$^3$) |
|---|---|
| Dust | 2 - 5 |
| $SO_2$ | <100 |
| CN | 0.002 - 0.006 |
| HC | <50 |
| F | 0.1 - 1.5 |
| Cd | <0.001 |
| Cd +Hg + Ti | <0.1 |
| As | <0.003 |
| Se | <0.002 |
| Te | <0.002 |
| Zn | 2.0 |
| Pb | 0.2 |
| $CO_2$ | 1.2 - 1.5 t/t of alloy |

**Table 9.18: Emission from a process producing secondary ferro-alloys [ 226, Nordic Report 2008 ] and ~~FOR~~ for Zn and Pb??**

*Is it necessary to distinguish between secondary and primary??*

In the production of silicon and ferro-silicon, the combustion process in the smoke hood and off-gas channels may create emissions to air. The main problems are the formation of $NO_X$, PAH and PCDD/F. The preferred reporting convention is the EPA 16 as this is compatible with the PRTR reporting requirements.

These emissions may be significantly reduced by introducing an improved process design. The effects of improved design on emissions are presented in Table 9.19 and shows measured parameters for silicon and ferro-silicon production. These emissions depend upon the process method and may be imposed by the national energy regulations [ 300, Euroalliage Response 2007 ].

| Silicon | | | | | FeSi - 75 % | | |
|---|---|---|---|---|---|---|---|
| Emission | Mass per tonne of alloy | Standard charging technique | Improved charging technique | Improved charging + high temperature off-gas | Standard charging technique | Improved charging technique | Improved charging + high temperature off-gas |
| $CH_4$ | (kg/t) | 0.12 | 0.09 | | | | |
| CO | (kg/t) | 3.50 | 3.60 | 0.00 | 1.80 | 3.50 | 0.50 |
| PCDD/F | (µg/t) | 1.90 | 0.00 | 0.00 | 5.50 | 1.10 | 0.20 |
| $NO_X$ | (kg/t) | 22.30 | 11.00 | | | 7.00 | 8.30 |
| ~~$N_2O$~~ | ~~(kg/t)~~ | | | | | | |
| PAH | (g/t) | 1.86 | 0.00 | 0.00 | 1.21 | 0.01 | 0.01 |
| VOC | (kg/t) | 0.10 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |

**Table 9.19: Effects of improved design on emissions [ 226, Nordic Report 2008 ][515]**

*In [515] are also some estimations included for all the blanks. Decide whether to introduce this info in the table.*

### 9.2.3 Emissions of noise and vibrations

The heavy machinery such as crushers and large fans used in the ferro-alloy production can give rise to emissions of noise and vibration. Also the mechanical releasing of skulls from the ladles may be a source of noise.

*What about noise from the EAFs??*

### 9.2.4 Emissions to water

For the production of ferro-alloys, the emissions to water are very dependent on the process, for instance the abatement system and the type of waste water treatment used. A variety of different water collection and waste water treatment systems are used in the ferro-alloy industry. Some plants use a central waste water treatment plant in which water from different production processes as well as surface run-off water will be cleaned together. Other facilities use a separate treatment system for rainwater and special treatment processes for the different process waste water streams. The main water pollutants are suspended solids and metal compounds. The waste water is treated in order to remove dissolved metals and solids and is recycled or re-used as much as possible in the process. The possible waste water streams are:

- surface run-off and drainage water
- waste water from wet scrubbers
- waste water from slag cooling and metal granulation
- cooling water.

The contaminated water is normally led to a thickener or a settling pond to settle out the suspended solids. Precipitation steps are often used to remove metal compounds from the water. In special cases, for instance by cleaning scrubbing water from a molybdenite roasting furnace, ion exchangers are used to remove metal compounds such as selenium and rhenium from the scrubbing water.

The particles mostly consist of very fine particles, it may therefore be necessary to add a flocculent to assist settling in thickeners. After the treatment in a thickener or a settling pond, the suspended solids are usually below 40 mg/litre, which allows re-use in scrubbers as cooling water or as process water for other purposes. *(In the existing BREF it was 20 mg/liter. Where are data which leads to this amendment?)*

If a thickener, slag granulation and settling ponds are used emissions of suspended solids will correspondingly be 10 - 20 g with a total amount of Cr at about <1 g, zinc <2 g and cyanide in the range of <1 g/tonne of FeCr. For the production of LC FeCr it has been reported that the amount of Cr discharged in the waste water is < 1.0 g/tonne of product. PAH emissions to water after abatement for the production of FeMn have been reported to be in the range of 0.05 - 0.2 g/t FeMn. **REF??** *Unclear: what has the slag granulation to do with this? To what are the 10 – 20 g related to? Per tonne product?*

The contaminated waste water of the scrubber system from an alloy recovery plant is cleaned in a separate waste water treatment plant in which may also rainwater from the site may also be cleaned. The partly oxidised particles contained in the water are concentrated in a thickener and in a later step separated from free water in two filter presses. The resulting filter cake with 20 - 25 % moisture consists of the following main constituents:

| | |
|---|---|
| ZnO | 30 - 40 % |
| $SiO_2$ | 10 - 15 % |
| CaO | 5 - 15 % |
| FeO | 5 - 7 % |
| PbO | 3 - 5 % |
| Hg | 0.001 %. |

The amount of dry cake generated is 200 - 400 kg/tonne of alloy.

This filter cake is shipped in regular intervals for zinc and lead recycling either to the ISF (Imperial Smelting Furnace) or the Waeltz process.

There is a bleed off from the scrubber system of approximately 0.5 - 2 $m^3$/tonne of ferro-alloys recovered. This bleed off is cleaned in several steps as follows:

- cyanide removal
- reduction of $Cr_6$+ to $Cr_3$+
- precipitation of metal hydroxides at a high pH together with the oxidisation of cyanides
- precipitation of fluoride and cleaning the water from particles in a sand filter.

The emissions to water from the recovery ferro-alloys from steel mill residues using the Plasmadust process with a wet scrubber as the abatement technique are presented in Table 9.20.

| Component | (g/t) |
|---|---|
| As | 0.002 |
| Cr | 0.02 - 0.06 |
| Ni | 0.03 - 0.08 |
| Zn | 0.06 - 0.16 |
| Cu | 0.03 - 0.08 |
| Cd | 0.006 - 0.03 |
| Pb | 0.006 - 0.03 |
| Hg | 0 - 0.005 |
| F | 9.0 - 28.0 |
| N | 12 - 64 |
| CN | 0 - 0.08 |

**Table 9.20: Emissions to water from the recovery of ferro-alloys from steel mill residues using the Plasmadust process with a wet scrubber as the abatement technique**

[ 350, Arc Fume process 2009 ]

Data reported for a waste water treatment plant for a molybdenite roaster is presented in Table 9.21.

| $H_2SO_4$ (kg/t) | HF (kg/t) | Mo (g/t) | Bi (g/t) | Pb (g/t) | Cu (g/t) | Zn (g/t) | Sn (g/t) | COD (kg/t) | Re (g/t) | As (g/t) | Se (g/t) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 32.9 to 114.7 | 0.3 | 25.9 to 319.3 | 0.03 | 0.29 | 0.05 to 2.4 | 1.72 to 12 | 0.03 | 0.42 | 0.007 to 7.10 | 0.26 to 2.1 | 0.29 to 1.2 |
| NB: Elements based on 1 tonne Mo produced as molybdenum trioxide. | | | | | | | | | | | |

**Table 9.21: Emissions to water from roasting molybdenite**

*Where are these data from? All values increased except the one for Re???*
*Try to find this information.*
*Try to find examples for ferro alloy plants where real water streams occur and treatment takes place. And introduce relavant concentration data.*
*Data needed!*

### 9.2.5 By-products, process residues and waste

The production of ferro-alloys is related to the generation of a number of by-products, residues and wastes, which are also listed in the European Waste Catalogue (Council Decision 94/3/EEC). *This has been replaced by a new directive 75/442/EEC (see Section 5.2.4)* The most important process-specific residues are filter dusts, sludge from wet scrubbers, slag from the reduction process, used furnace linings and packaging material like drums or big bags. These residues are partly sold as by-products, recycled to the process or in cases of wastes without economic utility, transported to a deposit or a disposal site. The amount of slag and filter dust or sludge generated per tonne of produced ferro-alloy and their possibilities of valorisation are shown in Table 9.22 and Table 9.23.

| Ferro-alloy | | Slag/t of alloy | Analytical composition | Recycling, re-use and discharge |
|---|---|---|---|---|
| FeCr | HC FeCr | 1.0 – 1.7 t/t | Mixture of spinel. MgO, $Al_2O_3$, forsterite, 2MgO, $SiO_2$ and $Cr_2O_3$ (3 - 15 %) Slag is chemically very stable | The low basicity of slag (0.7 to 1.0) insures the formation of stable silicates, which are non-leachable. Crushed lump and granulated slag are used as building material and road construction materials. Slag can be used also as a sandblasting grit, and for the production of refractory castables |
| | MC FeCr | NA | NA | |
| | LC FeCr | 1 t/t | CaO 44 - 45 %<br>$SiO_2$ 23 - 33 %<br>MgO 9 - 13 %<br>$Al_2O_3$ 5 - 9 %<br>$Cr_2O_3$ 2.5 - 6.5 %<br>FeO 0.6 - 1.2 % | The slag will be landfilled |
| Alloy recovery from steel mill residues | | 0.4 - 1.2 t/t | CaO 25 - 40 %<br>$SiO_2$ 35 - 50 %<br>MgO 3 - 15 %<br>$Al_2O_3$ 1 - 35 %<br>$Cr_2O_3$ <3 %<br>$Fe_2O_3$ <2 %<br>NiO <0.1 % | The low basicity of slag (0.7 to 1.0) insures the formation of stable silicates, which are non-leachable. The slag is used in various construction applications. |
| Silicon metal FeSi | | 20 - 30 kg/t | Si/FeSi 20 - 30 %<br>$SiO_2$ 5 - 20 %<br>SiC 20 - 40 %<br>CaO 25 - 40 %<br>$Al_2O_3$ 3 - 35 % | The production of silicon metal and FeSi is almost a slag-free process (small amounts of quartz are transformed into slag, <1 %). The slag will go to a landfill. During refining of silicon metal and FeSi, some small amounts of refining slag is produced The slag will go to landfill |
| Calcium-silicon | | 0.4 - 0.6 t/t | $SiO_2$ 10 - 20 %<br>SiC 15 - 25 %<br>CaO 50 - 60 %<br>$Al_2O_3$ 5 - 10 %<br>$CaC_2$ 3 - 8 % | All the slag is recycled to the furnace |
| FeMn | HC FeMn | Electric arc furnace 1.0 - 1.7 t/t | NA | Standard exhausted slag (low content of MnO) is used as a construction material.<br>Rich slag (high content of MnO) is sold as raw material for the production of silico-manganese or other metallurgical applications |
| | | 1.6 - 1.9 t/t | NA | |
| | MC FeMn | 1.6 - 1.9 t/t | NA | |
| | LC FeMn | NA | | |
| SiMn | | 0.9 - 2.2 t/t | Mn0 2 - 17 %.<br>$SiO_2$ 30 - 50 %<br>CaO 15 - 30 %<br>$Al_2O_3$ 9 - 30 %<br>MgO 3 - 15 %<br>$K_2O$ 0 - 2 %<br>BaO 0 - 2 %<br>S 0 - 1.5 %<br>Fe <1 % | Slag is used as a construction material |
| FeNi | | NA | NA | Slag is sold as secondary raw material to the process industry, e.g. for the production of refractories |
| FeV | | 2.6 - 3 t/t | NA | Depending on the composition, the slag is sold for further processing or deposited in a landfill |
| FeMo | | 1.5 - 2 t/t (1) | NA | Slag can be used as a construction material |
| FeW, FeTi, FeB | | NA | NA | |
| FeNb | | 1.9 t/t | NA | |

**Table 9.22: Generation, recycling, re-use and discharge of ferro-alloy slag**
[ 226, Nordic Report 2008 ] [512]

*Unclear for yellow highlighted. Why is the EAF for FeMn production emphasised? All production is via the EAF route since the Blast furnace is shut down. Emphasising is misleading here. Two slag values for HC FeMn mentioned. Why? In the old BREF the rate for slag from LC FeMn was 1.6 to 1.9. Maybe the right way would be:*

| | | | | |
|---|---|---|---|---|
| FeMn | HC FeMn | 1.0 - 1.7 t/t<br>(in [512] 0.4 – 0.8 t/t | NA | Standard exhausted slag (low content of MnO) is used as a construction material.<br>Rich slag (high content of MnO) is sold as raw material for the production of silico-manganese or other metallurgical applications |
| | MC FeMn | 1.6 - 1.9 t/t | NA | |
| | LC FeMn | 1.6 - 1.9 t/t | NA | |

*Attached to [512]*

| **Ferro-alloy** | | **Dust or sludge/t of alloy** | **Recycling, re-use and discharge** |
|---|---|---|---|
| FeCr | HC FeCr | 20 – 80 kg/t (1) | Dust from the furnace will be landfilled. Dust from crushing and screening is remelted in the furnace, or is used in stainless steel production. Dust from the raw material transport systems, coke drying, agglomeration and dosing station can be recycled back into the processes. Sludge from wet scrubber may contain PAH and metals and then will need to be discharged on a hazardous waste landfill. About 8 - 10 kg/t of coarser dust with high chromium content that is collected in a waste heat boiler after a semi-closed furnace can easily be recirculated to the furnace after agglomeration |
| | MC FeCr | NA | |
| | LC FeCr | 70 kg/t | Dust is recycled back to the smelting furnace |
| Alloy recovery from steel mill residues | | 100 - 500 kg/t. | Furnace dust is high in ZnO (20 - 60 %) and PbO (2 - 6 %). It is pelletised and recycled by the Zn industry (I.F. smelter, or by using the Waelz process as an intermediate concentration step. Sludge from wet scrubber is recycled in the Waelz process to recover Zn and Pb |
| FeSi | | 200 - 300 kg/t | Silica fume (micro-silica) is collected in the fabric filter and sold as a by-product. Micro-silica is used as a cement additive, which increases the strength of the concrete and leads to a very smooth surface that prevents the concrete from water infiltration |
| Silicon metal | | 300 - 400 kg/t | |
| FeMn | HC FeMn | 30 – 50 kg/t | Dust and sludge are recycled, valued in other industries or discharged to a landfill. Sludge from wet scrubber will contain PAH and metals and need to be treated in a waste water system or discharged on a hazardous waste landfill |
| | MC FeMn | 30 – 50 kg/t | Dust and sludge are recycled, valued in other industries or discharged to a landfill |
| | LC FeMn | EAF<br>30 – 50 kg/t | Dust and sludge are recycled, valued in other industries or discharged to a landfill |
| SiMn | | 30 – 60 kg/t | Dust and sludge are recycled, valued in other industries or discharged to a landfill<br>Sludge from wet scrubbers will contain PAH and metals and should be disposed of at a hazardous waste landfill |
| FeNi | | NA | |
| FeV | | NA | Dust is recycled to the smelting process or partly be discharged to a landfill |
| Molybdenite roasting | | NA | Off-gas leaving the roaster contains dust up to 15 % of the concentrate feed. Most of the dust and sludge from the off-gas-cleaning is recycled to the concentrate feed |
| FeMo | | NA | Dust is recycled to the smelting process or sent to special waste disposal or processed to recover Mo |
| FeW, FeTi, FeB, FeNb | | NA | Dust from the furnace is discharged to a landfill except for some fen |

(1) The composition of the dust or sludge varies depending on the used smelting furnace and the raw materials.

**Table 9.23: Generation, recycling, re-use and discharge of dust and sludge from the air abatement system**

[ 226, Nordic Report 2008 ]

*The tables 9.22 and 9.23 are not consistent with tables 9.33 and 9.34 in sction 9.4.3. I consider it not necessary to mention them twice. If they are included twice they should be consistent. First choice: Merge and mention them only in section 9.2.5.*

## 9.2.6 Energy recovery

The production of ferro-alloys is a high energy consuming process because high temperatures are needed for the reduction of metal oxides and smelting. Factors affecting the energy consumption are, among other things, the quality of raw materials and their pretreatment before smelting, the utilisation of reaction energies, and the heat content of the processes. The energy used in the process can be supplied as electrical energy or fossil fuel in the form of coal, coke charcoal or sometimes natural gas.

In the case of SiMn production, the introduction of metallic Si can decrease the energy consumed [ 243, French comments on MnFe alloys 2008 ].

The energy that is used melts the charge and heats the furnace including the off-gas. *(this reads strange. The energy is used to heat the furnace?)* In a semi-closed furnace, heat generally escapes with the off-gas but can be recovered in a heat exchanger. When a closed furnace is used and CO, $CH_4$ and $H_2$ are produced from fossil fuel and so the heat content and fuel value of the off-gas is available. Energy can be recovered as hot water for district heating and there is at least one example where the heat from slag cooling water is used for this purpose.

If carbon is used as a reducing agent, the process gases produced in the smelting process contain significant concentrations of CO which can be used as a secondary fuel and transferred by means of pipelines within the plant area like any other fuel gas. It can be used by direct burning for instance in the sinter-furnace and for drying or preheating the furnace charge as well as for energy recovery in the form of hot water, steam and/or electricity.

Recovery of energy from ferro-alloy smelting furnaces is site-specific as it relies on the technical and economic feasibility. There are several examples of successful energy recovery.

Figure 9.9 below shows the energy flow in a 10 $MW_e$ submerged electric arc furnace for the production of silicon metal.

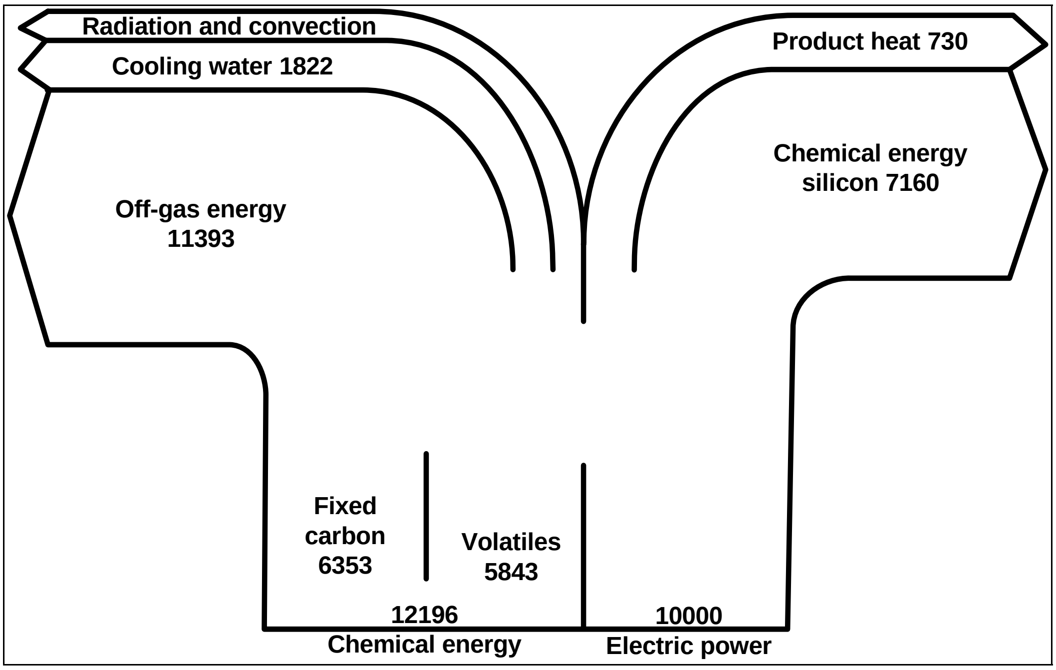


**Figure 9.9: Energy flow (in $MW_{th}$) in a 10 $MW_e$ silicon furnace**
[ 149, Schei, A, et al. 1998 ]

*What exactly is meant by volatiles in this context??*

Figure 9.9 shows that there is a large amount of waste energy from the silicon and ferro-silicon processes. The figure also shows, that volatiles from the reduction materials give a significant contribution to the energy input. The viability of energy recover is a site-specific issue depending on potential savings and use of the energy.

The best way to recover energy is to produce heat energy. The temperature from the furnace is determined by the total off-gas from the furnace and may vary from 200 to 750 °C. Due to lack of (economically) feasible usage of heat energy, some installations recover energy as electrical energy. This gives a lower energy recovery.

Often energy recovery efficiency is defined as the amount of energy recovered in relation to the electrical energy input to the furnace as shown in Table 9.24:

| **Applicability** | **Electric power recovery (%) (¹)** | **Heat energy recovery (%) (¹) (hot water or steam):** |
|---|---|---|
| Existing plants | 22 | 70 |
| Optimised new plants | 30 - 35 | 70 - 100 |
| (¹) Recovery is related to electrical input to the reduction furnace. The heat energy in the off-gas may be in the order of 20 % higher than the electrical energy. | | |

**Table 9.24: Energy recovery efficiency for silicon and FeSi furnaces**
[ 226, Nordic Report 2008 ]

If a semi-closed submerged electric arc furnace is used for the production of FeCr, FeSi, silicon metal, SiMn or FeMn, the CO gas from the smelting process burns in air thus creating a hot off-gas. Therefore the semi-closed furnaces are sometimes equipped with a waste heat boiler as an integrated energy recovery system. The waste heat boiler generates superheated steam that can be sold to neighbouring mills or used for electricity production in a back pressure turbine.

During the production of FeCr, FeMn or SiMn in a closed electric arc furnace, the off-gas contains a very high percentage of CO, which is collected without being burned above the charge surface. This CO is a high quality fuel that is favourably being used for electricity production or supplied to a neighbouring industrial plant as a secondary fuel or as a synthesis gas that serves as a raw material in chemical processes. A typical composition of a CO-rich gas, formed in a closed furnace producing HC FeCr contains 75 - 90 % CO, 2 - 15 % $H_2$, 2 - 10 % $CO_2$, 2 - 5 % $N_2$ and <5 % $H_2O$.

Table 9.25 and Table 9.26 give an overview about the different possibilities of energy recovery and the use of the recovered energy.

| **Ferro-alloy** | **Number of plants** | **Electrical energy used (GWh/yr)** | **Possible recovery (GWh/yr)** | | | **Actual recovery (GWh/y)r** | | |
|---|---|---|---|---|---|---|---|---|
| | | | **Electrical energy** | **Thermal energy** | **Total** | **Electrical energy** | **Thermal energy** | **Total** |
| FeSi | 9 | 4940 | 856 | 1024 | 1880 | 115 | 183 | 298 |
| Si metal | 3 | 1250 | 163 | 215 | 378 | | 1 | 1 |
| FeMn SiMn | 4 (¹) | 2290 | 100 | 790 | 890 | 90 | 386 | 476 |
| Total | 16 | 8480 | 1119 | 2029 | 3148 | 205 | 570 | 595 (²) |
| NB: Energy recovery data of 16 Norwegian ferro-alloy plants. [ 156, VDI (D) 1976 ]<br>(¹) Gas is partly used as fuel or synthetic gas<br>(²) From the reported 16 ferro-alloy plants in 1989, energy has been recovered by 8 plants | | | | | | | | |

**Table 9.25: Overview of energy recovery in the Norwegian ferro-alloys industry in 1989**
[ 156, VDI (D) 1976 ] **[ 226, Nordic Report 2008 ].**

*Data in green are new and from [226] Caption is wrong. Since new data have been introduced these data can not display the situation in 1989.*

*This is Reference [156]: VDI (D) (2008)."Biological Waste Gas Purification - 1 Bioscrubbers and 2 Trickle Bed Reactors". How should I find this information if it is not properly referenced????*
*If you compare this with the existing BREF you see that most of the data are from there (table 9.19). Only the FeMnSiMn data have been changed. Even at that time the reference was wrong.*

*The total 595 has been taken from the existing BREF. But the sum of 205 and 570 is 775!!!*

*From the reported 16 ferro-alloy plants in 1989, energy has been recovered by 8 plants. CO or heat recovery?*

*Check Nordic report. Good examples. Euro Alliages stated that energy recovery is not applicable to these plants, but 8 from 16 have applied energy recovery in 1989. Check how the situation has changed since then. Increase or decrease or?*

| **Ferro-alloy** | **HC FeCr** | | **HC FeMn** | | **SiMn** | | **FeSi** | **Si** |
|---|---|---|---|---|---|---|---|---|
| Furnace type | **Semi-closed EAF** | **Closed EAF** | **Semi-closed EAF** | **Closed EAF** | **Semi-closed EAF** | **Closed EAF** | **Semi-closed EAF** | **Semi-closed EAF** |
| Drying | | ■ | ■ | ■ | ■ | ■ | | |
| Ladle heating | | ■ | | ■ | | ■ | | |
| Sintering | | ■ | | ■ | | ■ | | |
| Preheating | | ■ | | ■ | | ■ | | |
| Hot water | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ |
| Steam | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ |
| Electricity | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ |
| Neighbouring Mills | | ■ | | ■ | | ■ | | ■ |

NB: Energy recovery is not always used, because local conditions for instance local prices of energy, periods of production and the absence of possible customers should be taken into account.

**Table 9.26: Energy re-use when producing bulk ferro-alloys**

*Check whether these estimations are realistical.*

## 9.3 Techniques to consider in the determination of BAT

The sections of this document entitled 'Techniques to consider in the determination of BAT' set out techniques considered generally to have potential for achieving a high level of environmental protection in the industries within the scope of the document. The background to the way the techniques are described is given in Section 2.1.2 and Table 2.2.

This section presents a number of techniques for the prevention or reduction of emissions and residues as well as techniques for reducing the overall energy consumption. They are all commercially available. Examples are given in order to demonstrate techniques which illustrate a high environmental performance. The techniques that are given as examples depend on information provided by the industry, European Member States and the valuation of the European IPPC Bureau. The general techniques described in Chapter 2 as 'common processes' apply to a large extent, to the processes in this sector and influence the manner in which the main and associated processes are controlled and operated.

### 9.3.1 Materials, storage and handling

The raw materials used for the production of ferro-alloys are basically ores, concentrates, reducing agents, solid fuels and additives. The main environmental impact by storage and handling of these materials are diffuse dust emissions and the contamination of surface water and soil cased by wash out from rainwater *This is the original text from the existing BREF. Reference [255] has not been used.*

**Description**

To prevent contamination, raw materials are preferably stored on hard surfaces where indoor and outdoor storage may be used, depending on the potentially dusty nature and the chemical properties of the materials. To keep the materials clean, the storage area can also be divided into different storage bays. Dry fine-grained materials should be stored and handled inside where closed silos, bins and hoppers are used to prevent diffuse emissions to the environment as well as to the workspace. Excessive dusting can also be prevented by water spraying of dry fine materials ~~[ 290, EC 2006 ].~~ *This is the original text from the existing BREF. Reference [290] which is the EFS BREF has not been used.*

Closed conveyors and transfer systems are used for the handling of dusty fine materials, where extraction and filtration equipment is used for dusting delivery points. The dust-laden air from the silos, closed conveyors and charging systems are cleaned by using fabric filters, which may be monitored by measuring the pressure drop to control the cleaning mechanism. Some plants use crushers or agglomeration equipment to obtain the desired size of the charging material. Fabric filters clean the suction air of crushers and agglomeration equipment. Wet grinding, filtering and pelletising systems are also suitable to prevent dust emissions. Crushing of wet slag can be performed outdoors if dust is not produced. If dust is produced, it should be collected in a fabric filter. In these cases, the water is recycled. The crushing facilities are built in a manner that noise emissions and vibration are minimised. The collected dust is recycled to the charging system, which may need an additional agglomeration step.

**Achieved environmental benefits**

Prevention and capture of dust is achieved.

**Cross-media effects**

No data was reported.

**Operational data**

Given in the descriptions of the process above.

**Applicability**

These techniques are applicable to most installations.

**Economics**
No data was reported.

**Driving force for implementation**
Environmental impact and energy costs due to lost material.

**Example plants**
UK, ES, DE.

**Reference literature**
*This is the original text from the existing BREF. Reference [255] has not been used.* ~~,~~[ 290, EC 2006 ].

## 9.3.2 Pretreatment techniques

High-grade ores especially for the production of FeCr are generally not readily available as lump material. Upgrading low grade ores by wet grinding and upgrading by wet gravitational methods (heavy media separation, jig washing, spiral washing, wash tables, etc.), to remove gangue minerals and increase, for instance, the $Cr_2O_3$ content, is common practice worldwide. Most of these methods give a fine-grained, high grade product that must be dewatered by filtering, and agglomerated by briquetting, sintering or pelletising/sintering before smelting.

The reducibility of different ores is quite different. Generally speaking for the production of FeCr, podiform ores are easily reduced, stratiform ores not as easily. For this reason, podiform ores most often will give a chromium recovery in excess of 90 %, while some of the stratiform ores have below 80 % recovery in conventional type production routes. This is the case with South African ores. With the DC plasma process, recovery is reportedly above 90 %. This compensates for the higher consumption of electrical energy needed to increase the process temperature to achieve faster reduction. Another way of increasing the reduction rate of stratiform ores is to increase the reaction surface. This can be achieved by grinding the ore to a very fine size and pelletising/sintering. For podiform ores, the recovery benefits of these alternative process routes will not be of the same magnitude.

Primary raw material like coke or secondary raw material such as titanium turnings and metal scrap need to be dried before using them in the process. In some cases coke drying is important to remove moisture, and depending on the climate, snow and ice ~~[ 255, VDI (D) 2576 2008 ].~~
*(This the original text from the existing BREF and not from the used reference)*

### 9.3.2.1 Drying of coke in a shaft furnace

**Description**
A shaft furnace is used for coke drying in a ferro-chrome production process. The furnace uses CO-rich off-gas from the smelting furnace as a fuel. For the abatement equipment, a fabric filter or a wet scrubber can be used [ 138, Niemelä, P. 1999 ].

**Achieved environmental benefits**
A shaft furnace generates less dust and fines[rr74]. The use of CO-rich off-gas as a fuel reduces the overall energy consumption of the process. The energy content of the CO used for drying is 550 - 700 MJ [ 138, Niemelä, P. 1999 ].

**Cross-media effects**
No data was reported.

**Operational data**

No data has been reported.

**Applicability**
The technique is applicable to all new and existing plants which use wet quenched coke and there is a CO-rich off-gas available from the furnaces.

**Economics**
No data has been reported.

**Driving force for implementation**
Reduced energy consumption and reduced emissions.

**Example plants**
FI.

**Reference literature**
[ 138, Niemelä, P. 1999 ].

#### 9.3.2.2 Degreasing of titanium swarf for the production of ferro-titanium

Metal scrap, turnings and swarf sometimes have to be liberated from oil and cutting liquids, which may take place by drying in a rotary kiln. This technique shows a titanium swarf degreasing plant that is used in the production of secondary ferro-titanium [ 159, Coulton, G. 1999 ].

**Description**
The degreasing system removes oil and water from titanium turnings and swarf so that they can be safely melted in an electric induction furnace. Swarf is degreased in a rotary dryer which is designed to distribute the swarf through a flow of combustion gases recycled from an afterburner. Material is fed into the degreaser by a belt conveyor, and after degreasing, is collected in hoppers prior to melting.

Ducting carries the oil-bearing gases away from the dryer and through a cyclone to remove dust and carryover. These gases then pass through the afterburner, which is heated by a gas-fired burner. The afterburner was designed to allow complete combustion of the oil vapour and destruction of volatile organic compounds. Combustion gases/fumes are either recirculated through the dryer or are ducted to a second cyclone. Dampers control the proportion of gas recycled. From the cyclone, the gas stream enters the filtration plant and sodium bicarbonate is injected into the ducting prior to the filter unit to neutralist any acidic gases that may be present and to prevent corrosion damage to the filtration plant. The gas cleaning system for a degreasing plant is shown in Figure 9.10.

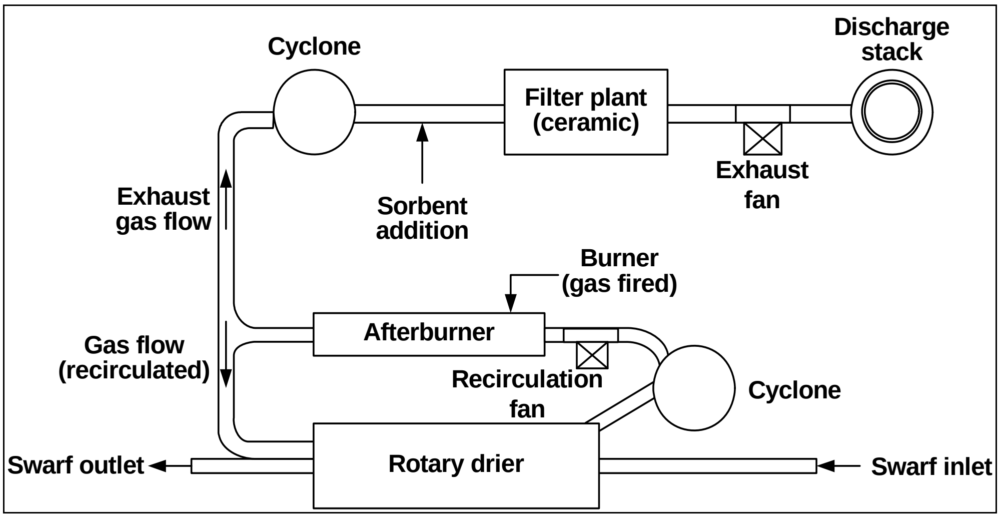


**Figure 9.10:** **Gas cleaning system for a de-greasing plant**

### Achieved environmental benefits

[ 159, Coulton, G. 1999 ]

Emissions to air

| | |
|---|---|
| Dust: - | below 5 mg/Nm$^3$ |
| Volatile organic compounds (VOC): | destroyed in the afterburner,<br>VOCs below the permit level of 20 mg/Nm$^3$ |

Emissions to water

None

Emissions to land

Waste fume dusts from the process are taken to a licensed landfill site. The quantity of fume dust generated will depend on the quantity and quality of the swarf being processed.

### Cross-media effects

The nature of the operation is such that the emissions are to air, rather than to either of the other two environmental media.

For most applications, the metals industry uses a fabric filter plant to control airborne emissions. For this application, a ceramic filter was chosen due to the high temperature of the waste gas stream. The ceramic filter provides good filtration with the lowest environmental impact.

Wet scrubbing systems were considered, but rejected. A wet type of arrestment such as a venturi scrubber would result in a sludge waste that would be more difficult and costly to dispose of, and would contain a significant proportion of water. The plume from the main stack would also be wet and not so well dispersed.

### Operational data

[ 159, Coulton, G. 1999 ]

Maximum temperature of gases entering the filter plant is 350 ºC. The filter is rated at approximately 7000 Nm$^3$/h at 350 ºC and contains 576 ceramic filters. The filters are tubular and manufactured from calcium or alumina silicate. The cleaning cycle is fully automated and cleaning is achieved by means of a reverse air pulse system. Dust emissions from the stack are continuously monitored and any deviation above a preset level will signal an alarm. The fume *(what is meant by fume plant?)* plant achieves dust emission levels below 5 mg/Nm$^3$.

The plant uses the following utilities:

- Gas: the amount of gas consumed varies widely depending upon the density of the material being processed and the amount of oil and moisture contamination present. The average consumption is typically 374 $m^3$/tonne of swarf processed.
- Electricity: the plant is not independently metered. However, it is calculated that electricity consumption is typically 180 kWh/tonne of swarf processed.
- Water: none is used.

**Applicability**
This technique is applicable to new and existing plants.

**Economics**

Project Costs [ 159, Coulton, G. 1999 ]
The rotary dryer and afterburner was installed in 1993.
The cost in 1998 = EUR 0.607 M
Cyclone, ducting, (ceramic filter) filtration plant installed in 1998 = EUR 0.410 M
Estimated overall project cost = EUR 1.017 M

**Driving for implementation**
Reduction of emissions.

**Example plants**
UK.

**Reference literature**
[ 159, Coulton, G. 1999 ].

## 9.3.3 Sintering

*(I think sintering is not the BAT. BAT is steel belt sintering against shaft sintering or a grate furnace. But ask industry if this is true. Also direct burning of recovered CO could be considered as BAT)*
As already mentioned, a large number of ores and concentrates are only available as fines. To use these fines, some plants, especially those for the production of HC FeCr, HC FeMn and SiMn use sintered pellets as a raw material in the furnace. The most important reason to sinter fines is to obtain a better porosity of the burden with easier penetration and elimination of gas generated by the reduction reactions. Sintering can take place in shaft, grate or in steel belt sintering furnaces, where the steel belt furnace provides several economic and environmental advantages.

### 9.3.3.1 Steel belt sintering furnace

**Description**
The steel belt sintering furnace is used to sinter chromite pellets in the production of FeCr. The steel belt sintering furnace is closed. The off-gases from the sintering furnace and the dusting points can be cleaned by a low pressure wet scrubber or a fabric filter. The operation of the process is controlled by a computerised control system. The process is shown in Figure 9.11.

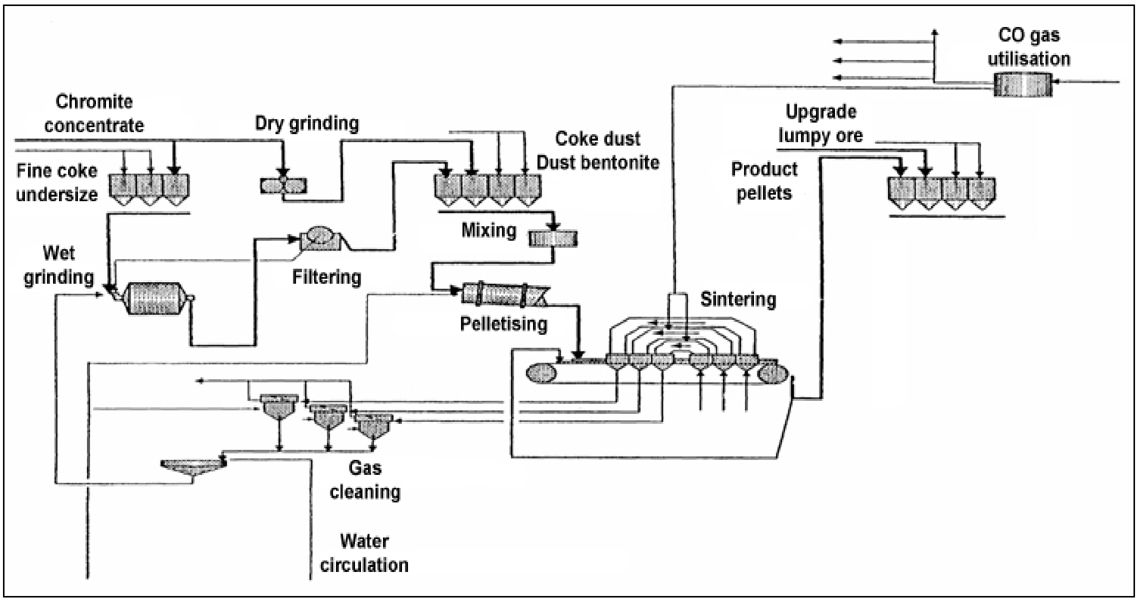


**Figure 9.11: Steel belt sinter furnace**
[ 138, Niemelä, P. 1999 ]

### Achieved environmental benefits

[ 138, Niemelä, P. 1999 ]
The external energy consumption in a steel belt sintering furnace is lower compared to a shaft and a grate furnace. As a consequence, the generation of $CO_2$ and $SO_2$ emissions are lower. The sludge from the off-gas treatment can be recycled back to the wet grinding step.

Emissions of dust are:

| | |
|---|---|
| • wet scrubber | <10 mg/Nm$^3$ |
| • cascade wet scrubber | <5 mg/Nm$^3$ |
| • fabric filter | <1 - 10 mg/Nm$^3$. |

Dioxins: << 0.1 ng ITE/Nm$^3$
$SO_2$: 145 mg/Nm$^3$[rr75]

### Cross-media effects

The use of CO gas as a fuel reduces the external energy required for the sinter process, which results in less generation of $CO_2$, and reduces the impact of greenhouse gases to the atmosphere if the savings of external energy resources are taken into account. The wet scrubber generates a waste water that can be recycled to the wet grinding step.

### Operational data

Energy consumption is 700 - 1400 MJ/t of pellets. CO from the smelter is used as a fuel together with coke fines.

### Applicability

This technique is applicable to all new and existing plants where sintered pellets are used as a raw material for the furnace. The use of CO as a fuel is only possible for plants using a closed furnace.

### Economics

No data has been reported.

### Driving force for implementation

Reduction in emissions and energy consumption.

**Example plants**

Torino, Finland~~FI.~~

**Reference literature**

[ 138, Niemelä, P. 1999 ].

## 9.3.4 Pre-reduction and preheating

### 9.3.4.1 Pre-reduction of chromite and manganese ores

**Description**

Pre-reduction of chromite and manganese ore reduces the specific electrical energy consumption and increases the productivity of the smelting furnace at the same time [ 140, Ferro-Alloy-Expert-Group 1998 ]. In FeCr production, chromite ore fines are pelletised with coke as a reducing agent and fired in a rotary kiln. A pulverised coal/CO/oil burner heats the kiln. Waste heat from the kiln is recovered in a waste-heat recovery boiler to generate steam. The exhaust gas is cleaned in a fabric filter[rr76]. The pre-reduced pellets are stored in a completely sealed surge hopper designed to prevent re-oxidation. The reduced material is then charged hot to the furnace, which combines preheating and pre-reduction. It has been reported, that the fully implemented and continuously operated pre-reduction technique in a Japanese ferro-chrome plant decreases the energy consumption down to about 2000 - 2100 kWh/t of FeCr. For Mn ore, the pre-reduction stage can be achieved in the furnace itself leading to important energy savings. The weakness of a pre-reduction process is the potential formation of accretions in the kiln. Worldwide there are only two plants using this pre-reduction process and one plant using the Krupp-Codir pre-reducing technique. *(This is the situation 10 years ago! Any changes?)*

The electricity consumption of the smelting furnace can be decreased by preheating the feed materials. Preheating for instance as it is used in the production of FeCr increases the productivity of the smelting furnace at the same time [ 243, French comments on MnFe alloys 2008 ]. *(Preheating is not included in the heading. The way the section in the existing BREF has been restructured does not fit to the headings)*

The shaft furnace is used to preheat the charging material for the production of FeCr in a closed electric arc furnace *(Question: Does this mean a shaft fiunace is exclusively used in combination with EAF? In the aforementioned example a rotary kiln is used but nothing is said about the type of meting furnace. Can it be a EAF as well? Then this statement about the shaftfurnace should be limited to one example.)* . The shaft type furnace has the advantage that crushing up of charge material and dusting is lower. The utilisation of fuel energy for instance CO from the smelting furnace or natural gas is higher and less maintenance work is needed.

**Achieved environmental benefits**

Preheating decreases the energy consumption. By preheating the charge to 700 ºC, the moisture and a major part of the volatiles can be removed before the material is charged into the electric furnace. Thus the formation of reduction gases in the furnace is stable.

**Cross-media effects**

The use of CO gas as a fuel reduces the electrical energy required for the subsequent smelting process. This results in less generation of $CO_2$, and reduces the impact of greenhouse gases to the atmosphere if the savings of electrical energy are taken into account. The comparison of a shaft kiln has been made with a rotary kiln.

**Operational data**

The electrical energy consumption of the subsequent smelting furnace is reduced by 70 - 90 kWh per 100 ºC increase in the preheating temperature for the smelting furnace.

**Applicability**
This technique is applicable to new and existing plants. The use of CO as a fuel is only possible for plants using closed furnaces.

**Economics**
No data has been reported.

**Driving force for implementation**
Reduction in energy consumption

**Example plants**
FR

**Reference literature**
[ 140, Ferro-Alloy-Expert-Group 1998 ], [ 243, French comments on MnFe alloys 2008 ], [ 111, Shunan Denko, Japan 1998 ].

### 9.3.5 Reduction processes

**Description**
In the production of ferro-alloys, the most important stage is the reduction of metal oxides and alloying with the iron present in the process. Depending on the reducing agent, different types of smelting systems (such as the electric arc furnace, the blast furnace or a reaction crucible) are used. Electric arc furnaces are normally operated submerged as a closed, semi-closed or open type. The concept of the different smelting systems are influenced by the desired flexibility in the production, the range of raw material, the possibilities of energy recovery and the environmental performance. The different techniques to be considered for the recovery of energy are very dependent on the smelting system used and on local conditions such as energy prices, periods of production and the presence of potential customers.

The different furnaces used for the production of ferro-alloys have been described earlier in Chapter 1 and are listed in Table 9.27 that summarises the advantages and disadvantages of the various systems.

| Smelting system | Produced alloys | Gas collection and abatement | Advantages | Disadvantages |
|---|---|---|---|---|
| Open submerged arc furnace with three electrodes | FeCr, FeMn, SiMn, FeSi, FeNi<br>Si-metal, alloy recovery | Hooded and cleaned in a fabric filter | Robust, simple design<br>Low investment and maintenance cost<br>Can use almost any raw material and can perform pre-reduction<br>Easy control of the smelting process can be obtained<br>Hot water production | High electrical energy consumption (filter)<br>No heat recovery except hot water production<br>Large off-gas volumes<br>Need of large pollution control systems<br>Higher environmental impact due to the off-gas volume and the heat supplied to the ambient air |
| Open submerged arc furnace with a single electrode | Special ferro-alloys FeV, FeB | Hooded and cleaned in a fabric filter | Robust, simple design, high production flexibility<br>Low investment and maintenance cost<br>Can use almost any raw material<br>Can remelt fines and perform pre-reduction | The open furnace with a single electrode is normally used in the production of special alloys for small quantities. The above-mentioned disadvantages are therefore relatively lower |
| Semi-closed submerged arc furnace | FeCr, FeMn, SiMn, FeNi<br>FeSi,<br>Si-metal alloy recovery<br>Special ferro-alloys | Hooded and cleaned in a fabric filter | Large flexibility in raw materials<br>Energy recovery as electrical energy and/or steam<br>Hot water production<br>Smaller off-gas smaller filter plant<br>Easy control of the smelting process<br>Reduced environmental impact | Relative high energy consumption if no pre-reduction<br>More complex system<br>Higher maintenance cost<br>Can use a limited amount of fines without agglomeration |
| Closed submerged arc furnace | FeCr, FeMn, Si Mn, FeNi, Special ferro-alloys | Sealed furnace with wet scrubber or a dry wire-cloth filter | Low environmental impact<br>Energy recovery in the form of CO-rich gas as a secondary fuel<br>Low off-gas volume<br>Fairly simple system | Well sized lumpy or agglomerated raw materials<br>Off-gas consists of CO (explosive and poisonous)<br>Wet gas-cleaning system<br>Waste water and sludge need to be treated or re-used |
| Closed submerged arc furnace with preheating in a rotary kiln | FeCr | Sealed furnace with a wet scrubber | Low electrical energy consumption<br>Energy efficient<br>Low environmental impact<br>Increase the furnace capacity | Need stricter amounts of well sized hard lumpy ore or concentrates have to be agglomerated<br>Agglomeration or pelletising plant<br>Higher investment cost<br>Little flexibility in the choice of raw material<br>Complex system<br>Wet gas-cleaning system |
| Closed submerged arc furnace with a preheating shaft furnace | FeCr | Sealed furnace with a wet scrubber | More flexibility in raw material supply<br>Low energy consumption<br>Energy recovery<br>Low environmental impact<br>Increased productivity of the furnace | Need well sized hard lumpy ore or agglomerated raw material<br>Wet gas-cleaning system |

| Smelting system | Produced alloys | Gas collection and abatement | Advantages | Disadvantages |
|---|---|---|---|---|
| Closed submerged arc furnace with a pre-reduction in a rotary kiln | FeCr | Sealed furnace with a wet scrubber | Very low electrical energy consumption<br>Heat recovery, fully utilisation of off-gases<br>Higher coal consumption lower coke consumption<br>Increased productivity of the furnace | Higher investment cost<br>Wet gas-cleaning system<br>Very complex system<br>No flexibility in raw material supply<br>Relatively high maintenance cost<br>Possibility of accretion formation |
| Plasma furnace | FeCr | Sealed furnace | Possibility to use any ore<br>Use of fines without agglomeration<br>Energy recovery<br>Use of coal instead of coke | Higher investment cost<br>High energy consumption<br>Complex system<br>Lower operating time<br>CO in a pressurised system |
| DC Furnace | FeCr | Sealed furnace | Use of fines without agglomeration<br>Low investment cost<br>Higher energy density | Injection with unknown difficulties<br>Problems with the bottom electrode when overheated<br>Need of prebaked electrodes |
| Refractory lined crucible | Special alloys, FeMo | Hooded and a fabric filter | Low investment cost<br>High flexibility in the production | Higher off-gas volume<br>Less effective gas collection system |
| | | Enclosed in a reaction chamber connected to a fabric filter | Low investment cost<br>High flexibility in the production<br>Effective fume collection system<br>Less off-gas volume | Slightly higher investment costs |
| Multiple hearth furnace | Molybdenite roasting | Wet scrubber | Proven technology<br>Sulphuric acid can be produced | |
| Plasmadust process | Alloy recovery | Sealed furnace | Use of fines without agglomeration<br>Energy recovery<br>High energy density<br>High flexibility in the production | Higher investment cost<br>High energy consumption<br>Complex system<br>CO in a pressurised system<br>Wet gas-cleaning system |
| For Mn and Ferro-manganese, a mercury removal stage should be incorporated. These are described in detail in Chapter 2. | | | | |

**Table 9.27: Summary of advantages and disadvantages of the smelting systems used in the ferro-alloy industry**
[ 140, Ferro-Alloy-Expert-Group 1998 ]

**Achieved environmental benefits**
Described in Table 9.27.

**Cross-media effects**
The use of CO gas as a fuel reduces the electrical energy required for the subsequent smelting process. This results in less generation of $CO_2$, and reduces the impact of greenhouse gases to the atmosphere if the savings of external production of electrical energy are taken into account. The comparison of a shaft kiln has been done with a rotary kiln. Burning of CO generates $CO_2$.

**Operational data**
Taking account of the above advantages and disadvantages, the smelting systems to consider are:

- open furnace for special applications and small capacities connected to a fabric filter
- semi-closed furnace connected to a fabric filter
- closed furnace systems in different applications cleaned by a wet scrubber or dry cleaning system
- blast furnace if the waste energy is recovered
- reaction crucibles with an appropriate hooding system connected to a fabric filter
- reaction crucibles in a closed chamber connected with a fabric filter
- multiple hearth furnace for molybdenite roasting with dust removal and acid recovery.

The open furnace for producing bulk ferro-alloys is not a technique to be considered in the determination of BAT. The main reasons are the higher electrical energy consumption due to the higher off-gas volume to be cleaned in the filter-house. This higher off-gas volume induces, even with a high standard baghouse, a larger amount of fine dust emitted to the environment. In addition, the energy used to operate an open furnace cannot be recovered [ 140, Ferro-Alloy-Expert-Group 1998 ].

**Applicability**
These techniques are applicable to new and existing plants.

**Driving force for implementation**
No data has been reported.

**Example plants**
FR, FI, ES, DE.

**Reference literature**
[ 140, Ferro-Alloy-Expert-Group 1998 ].

## 9.3.6 Gas collection and abatement

### 9.3.6.1 Hooding systems for the collection for tapping and casting fume from an electric arc furnace

**Description**
The use of hoods for tapping and casting is also a technique to consider. Tapping fume will consists of fumes from oxygen lancing, dust from drilling, fumes from the vaporised slugs if a tapping gun is used and fumes from all exposed metal and slag surfaces. These fumes will consist mainly of oxides of the metals that are involved in the smelting process. The design of the hooding system should take account of access for charging and other furnace operations and the way the source of process gases change during the process cycle [ 140, Ferro-Alloy-Expert-Group 1998 ].

The design of appropriate hooding systems to collect fume from the tapping and casting areas is very much dependent on the site-specific arrangements of the tapping and casting. Therefore a large number of different hooding designs exist. The cleaning equipment, which today is normally used for tapping fumes, is a fabric filter. This can be a separate filter, or a filter that also cleans the fumes from metal casting or the furnace off-gas. The hot gases can also be collected and used to preheat the furnace charge.

An example of a hooding system used for the collection of tapping and casting fumes is shown below in Figure 9.12.

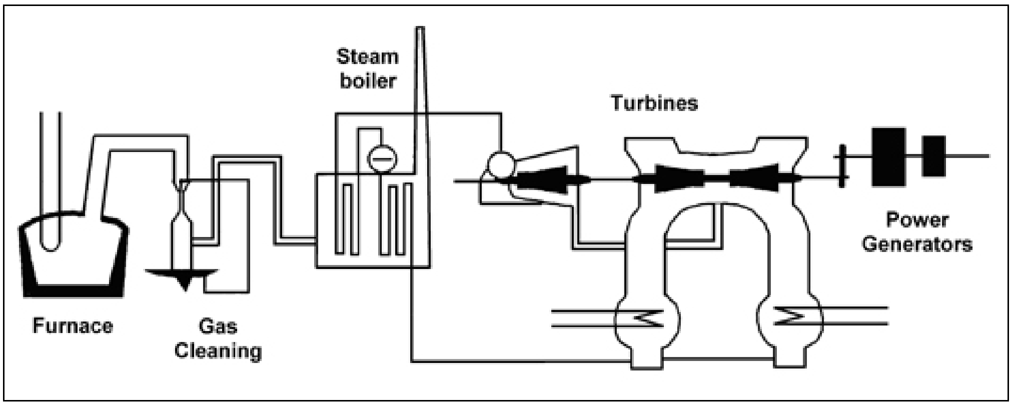


**Figure 9.12: Collection of tapping and casting fume**

*This picture is not the correct picture to demonstrate the collection of fumes from tapping and casting.*
*This picture is about Direct use of the CO gas for the production of electrical energy, see also figure 9.14.*

**Achieved environmental benefits**
Reducing the diffuse emissions from the tapping and casting area and minimisation of the uncontrolled fumes, dust and smoke that leave the furnace building with the ventilation air. The fabric filter can achieve dust emissions below 5 mg/Nm$^3$. Reducing of diffuse emissions in a furnace building results also is better working conditions.

**Cross-media effects**
The application of evacuation and treatment of gases requires extra energy consumption due to the use of powerful fans.

**Operational data**
Sampling of the ventilation air leaving the furnace building including tapping and casting area over long periods of time can give an indication of the average values. These show average dust concentrations between 5 and 12 mg/Nm$^3$ and total dust emissions amounting to 0.2 - 0.6 kg/tonne of produced alloy. This amount of dust can significantly be reduced.

**Applicability**
This technique is applicable to all new and existing plants.

**Economics**
No data has been reported.

**Driving force for implementation**

Reduction in diffuse emissions.

**Example plants**
FR.

#### Reference literature

[ 140, Ferro-Alloy-Expert-Group 1998 ] [ 255, VDI (D) 2576 2008 ].

### 9.3.6.2 Hooding system for the dedusting of tap-holes and runners from a sealed arc furnace

*(I don't think that you can simply replace the device in the heading from blast furnace to sealed electric arc furnace and keep in the figure the blast furnace. Check wether blast furnaces are still applied. As far as I know they are not. Try to get other data and figures for the tapping of ferro alloys. The info here came from SFPO and was for the French BF which is shut down since 2003. How can DE, NO, SE be mentioned?)*

#### Description

The dedusting equipment is composed of various hoods located above the tap-hole of the blast furnace, the main metal runner and the device where the liquid metal is poured into the torpedo ladle. The collected fume is cleaned in a separate fabric filter. The hooding system (view from the top of the furnace) is shown in Figure 9.13.

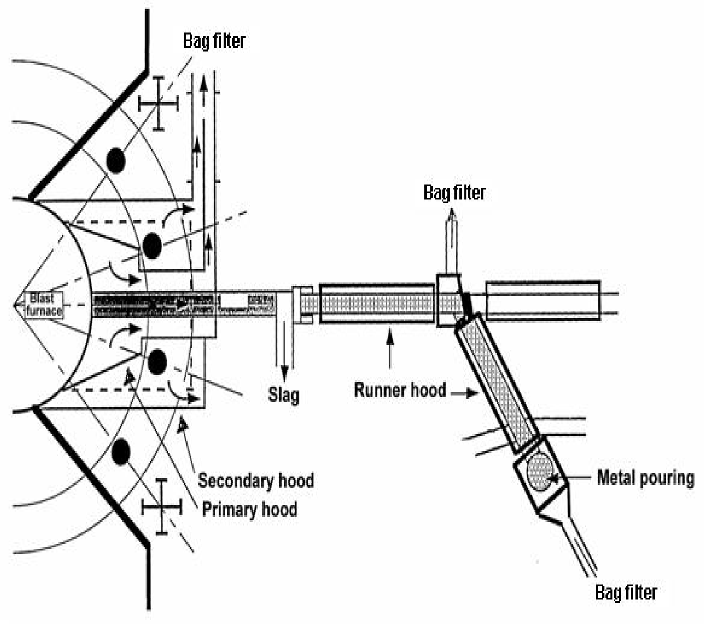


**Figure 9.13: Hooding system for a blast furnace**
[ 192, SFPO 1999 ]

#### Achieved environmental benefits

Reducing the diffuse emissions from the tapping and pouring area and minimisation of the uncontrolled fumes, dust and smoke that leave the furnace building with the ventilation air. Reducing of diffuse emissions in a furnace building results also is better working conditions.

#### Cross-media effects

The application of evacuation and treatment of gases requires extra energy consumption due to the use of powerful fans

**Operational data**
Collection efficiency:

- main hood: 96 %
- hood corresponding to the pouring of metal in the ladle: 86 %
- runner hood: 100 %
- flowrate: 310000 $Nm^3/h$
- measured dust emissions after abatement (fabric filter): <5 $mg/Nm^3$.

**Applicability**
This technique is applicable to all new and existing furnaces.

**Economics**
Investment cost is about EUR 1.0 million.

**Driving force for implementation**
Reduction in diffuse emissions and energy consumption.

**Example plants**
DE, NO, SE.

**Reference literature**
[ 192, SFPO 1999 ].

### 9.3.6.3 Abatement techniques

**Descriptions**
The techniques for fume collection and abatement discussed in Chapter 2 of this document are techniques to consider for the production of ferro-alloys. Fabric filters and wet scrubbers are normally used for dedusting the process off-gases. In the ferro-chromium and alloy recovery industries, scrubbed gases that contain CO are used as a fuel gas in other processes and are not emitted.

A number of different fabric filter designs exist that use different kinds of filter materials. In[rr77] principle, all achieve low emission values with dust emissions below 5 $mg/Nm^3$. The use of membrane filtration techniques (surface filtration) results in an increased bag life, a high temperature limit (up to 260 ºC) and relatively low maintenance costs combined with dust emissions in the range of 5 $mg/Nm^3$. There are different suppliers in Europe who are able to provide fabric filters with membrane filter bags. The membrane filter bags consist of an ultrafine expanded PTFE membrane laminated to a backing material. The particles in the off-gas stream are captured on the bag surface. Rather than forming a cake on the inside or penetrating into the bag fabric, particles are repelled from the membrane thus forming a smaller cake.

Baghouse filters in many cases in the ferro-alloy and metallurgical industry, are pressure filters with fans on the dirty fume/gas side. Experience shows that a closed suction filter with fans on the clean gas side works better than an over-pressure filter. This combines the advantages of gentle bag cleaning that means longer bag life of approximately 10 years and lower operating and maintenance costs.

By recovering ferro-alloys from steel mill residues in a sealed arc furnace, the off-gas-cleaning is performed in a two-stage baghouse. In the first stage, furnace dust is collected for recycling or further processing. In the second stage, absorbent granules (activated carbon or lignite coke) is injected. Volatile metals notably mercury and to a lesser extent cadmium and lead is chemisorbed on the surface of the carbon. Due to the highly toxic nature of mercury and cadmium emissions of these metals below 0.2 $mg/Nm^3$ can be achieved. The absorbent also traps chlorine compounds including PCDD/F. In the closed plasma dust process a three step venturi scrubber combined with a wet electrostatic precipitator and a selenium filter may be used. The selenium filter removes mercury from the off-gas.

Wet scrubbers are techniques to consider when closed furnaces produce CO-rich off-gas that should be washed and dedusted at very high temperatures. Modern wet scrubbers achieve dust emissions below 10 mg/Nm$^3$. With coarser dust, even achieved dust concentrations of 4 mg/Nm$^3$ by using a cascade scrubber to clean the off-gas from a sinter furnace have been reported.

Venturi scrubbers used to clean the off-gas from a closed HC FeCr furnace achieve emissions below 50 mg/Nm$^3$ with average values below 20 mg/Nm$^3$ due to very fine dust that is produced in the furnace. This is not emitted directly to the atmosphere as the CO-rich gas is used as a fuel[rr78].

The disadvantages of the wet scrubber are normally the slightly higher dust emissions and the washing liquid and sludge that needs a further treatment. Compared with a bag-filter that is normally used for a semi-closed furnace, the wet scrubber even with the higher dust emissions do not result in an higher environmental impact due to the reduced off-gas volume from a closed furnace. One case has been reported where a closed ferro-alloy furnace is provided with a wire-cloth filter instead of a wet cleaning system. This filter recovers heat from the exhaust gases and eliminates the need of a scrubbing unit. The collected dust is pelletised and then returned to the furnace, and the cleaned gas is burned in a boiler unit.

The waste gas leaving the molybdenite roaster contains high amounts of dust that is removed by (multi)cyclones in combination with a dry ESP. The collected dust is recycled to the concentrate feed. The gas contains also up to 2.5 % of sulphur dioxide, small amounts of unburned hydrocarbons and sulphur trioxide and some highly volatile metals. To remove these pollutants after dedusting, the gas is washed and cooled in wet scrubbers in order to produce a clean sulphur dioxide gas that can be converted to concentrated sulphuric acid.

Some ores, for example manganese ores, have an increased mercury concentration. The volatile mercury is released in the processes and methods are needed to reduce the emissions and to take care of the mercury. Additional information concerning mercury cleaning techniques is provided in Section 2.9.2.8.

**Achieved environmental benefits**
Effective gas-cleaning and lower instances of abatement plant failure, the collected dusts are returned to the process. Energy is also recovered.

**Cross-media effects**
No data has been reported.

**Operational data**
Given in the description above.

**Applicability**
These techniques are applicable to new and existing plants. Improved fabrics can be used in existing filter houses.

**Economics**
No data has been reported.

**Driving force for implementation**
Reduction in energy consumption and environmental pressures.

**Example plants**

NO, FI, SW.

**Reference literature**
[ 141, Elkem Asa 1998 ], [ 197, Kantola, E. 1999 ], [ 199, EnviroSense 1995 ], [ 226, Nordic Report 2008 ] [ 255, VDI (D) 2576 2008 ].

### 9.3.7 Process control

The principles of process control discussed in Section 2.5 are applicable to the production processes used in this metal group. Some of the furnaces and processes are capable of improvement by the adoption of many of these techniques. Computerised control systems are used for instance in the production of FeSi and Si metal in order to follow and control the generation of silica fumes.

### 9.3.8 Post furnace operations

**Description**
Using a pneumatic or hydraulic drill normally opens the tap-hole of the smelting furnace. Oxygen lancing is also used, either as the only method or as a back up or complement to drilling. A tapping gun helps to remove blockages, but slugs that contain lead and zinc should only be used if an appropriate hood is installed to remove tapping fumes. This is necessary because lead and particularly zinc vaporise at the tap-hole and create fumes that pollute the working area and the ventilation air. The tap-hole is closed after tapping using a mud gun or shutting paste/clay [ 226, Nordic Report 2008 ].

The most frequently used technique for tapping is cascade tapping. In this case, the metal and slag are tapped together in the same vessel. The lower density slag floats on the top of the bath and overflows via a weir into a separate ladle as the bath fills.

Slag is granulated in a granulator, by pouring directly into a water bath or by spraying water onto a slag pit or teeming station. These techniques all reduce emissions of fumes and dust. The water used needs treatment in a settler to remove particles and heat can also be recovered. The water is used again as quenching water. Slag is processed where possible to recover metal.

The generation of very fine powder (dust) that is collected in the fabric filter used for dedusting the furnace off-gases may create problems in the handling, storage and transport of powders. *This sentence is unclear: Is the generation of fine powder addressed or the dedusting of the furnace off-gas or both concerning the handling of these dusts?*

**Achieved environmental benefits**
The environmental benefits are the prevention of diffuse emissions of metals, dust and other compounds.

**Cross-media effects**
None are reported.

**Operational data**
None are available.

**Applicability**
The processes and the techniques are suitable ~~-~~for use with new and existing installations.

**Economics**
None was provided but the processes are operating economically.

**Driving force for implementation**

The reduction of emissions and saving raw materials.

**Example plants**
Plants in DE, AT, FR, BE, PL and NL.

**Reference literature**
[ 196, Finkeldei, L. 1999 ], [ 233, Farrell Nordic Mission 2008 ].

#### 9.3.8.1 Densification of silica powder and other dust collected in fabric filters from silicon or ferro-silicon smelting furnaces

**Description**
To handle silica fumes (micro-silica) and other ferro-alloy filter dust, a micro-pelletisation step has been reported to densify the material. The process transforms a powder into small spheres of about 0.5 - 1 mm in diameter.

**Achieved environmental benefits**
Higher bulk density reduces the environmental impact of transportation. This means less air pollution and fewer noise problems from truck traffic.

**Cross-media effects**
No data has been reported.

**Operational data**
The bulk density of raw silica dust is less than 0.2 t/m$^3$. The process of micro-pelletisation increases the bulk density to 0.5 - 0.6 t/m$^3$. These reduce the transport costs by about 65 % and also reduce the environmental impact of transportation.

**Applicability**
This technique is applicable to new and existing plants where silica fume, SiMn powder, filter dust from FeCr production, furnace dust and manganese and ferro oxides need to be handled.

**Economics**
No data has been reported.

**Driving force for implementation**
Reduction in energy consumption.

**Example plants**
NO.

**Reference literature**
[ 141, Elkem Asa 1998 ].

### 9.3.9 Waste water

Existing treatment systems are reported to be of a high standard. Where necessary, waste water should be treated to remove dissolved metals and solids. The techniques listed in Section 2.12 are the techniques to consider. In a number of installations, cooling water and treated waste water including rainwater are re-used or recycled within the processes.

Water treatment is needed in the processes with wet scrubbers and granulation processes, because suspended solids should be removed before the water is recirculated. To reach acceptable values of harmful components, it may in some cases, be necessary to polish the bleed that should be taken from the scrubbing water cycle. This may achieved by using sand filters, carbon filters or by adding suitable chemicals to precipitate harmful compounds.

## 9.3.10 By-products, process residues and waste

The processes and recycling routes that were discussed earlier as applied methods in Section 9.1 and 9.2 are all techniques to consider in the determination of BAT. The most important factors to reduce the environmental impact of residues are process-integrated measures that result in the generation of fewer residues. If the amount of process residues is minimised by using primary measures, the remaining amount should be recycled or re-used as much as possible. The specific feed materials will influence the final process choice. The techniques discussed in Section 2.13 should also be considered in conjunction with these processes.

## 9.3.11 Techniques to reduce the overall energy consumption

### 9.3.11.1 Techniques for energy efficiency

*All included section for energy efficiency describe more or less the same and include the same devices. Combine and improve readability.*

As already mentioned in Section 9.2.1, the production of ferro-alloys is an energy-consuming process. For the processes producing HC FeCr or HC FeMn in closed furnaces, coke consumption is in the range of 420 - 520 kg/tonne. Pre-reduction of the ore using coal or other carbonaceous materials as an energy source and as a reducing agent will lower both the amount of coke and electric power in the reduction furnace, but might also increase the total consumption of carbonaceous materials and the gross energy consumption of the process as a whole [ 149, Schei, A, et al. 1998 ].

**Description**

If carbon is assumed to be converted into CO, i.e. no reduction is done by CO gas, the carbon could theoretically be recovered as CO gas [ 255, VDI (D) 2576 2008 ]. This can be used as a fuel by burning it above the top of a semi-closed furnace to heat the furnace roof, or by collection in a closed furnace and use as a fuel in other processes. The quantity of CO would be between 770 and 1050 kg/tonne of FeCr produced equivalent to between 2160 and 2950 kWh/tonne. In reality, these figures would probably be 5 - 15 % lower. The resulting amount of $CO_2$ produced by the furnace process alone would amount to 1200 - 1650 kg/tonne.

For instance in a Norwegian FeCr plant the balance for CO gas recovery and utilisation in 1998 was reported and is shown in Table 9.28. The plant is no longer in production.

| Energy recovery and Utilisation | Energy (kWh/t) |
|---|---|
| Total recoverable energy | 2090 |
| Total recovered energy, ~~included~~ including internal use 190 kWh/t (sintering, coke drying, ladle heating) | 1460 |
| Flared | 630 |

**Table 9.28: Recoverable and total recovered energy**
[ 149, Schei, A, et al. 1998 ]

Recoverable energy in this case is not a theoretical figure, but is the amount of CO gases used internally and externally plus flared excess gas. The total energy balance for the whole plant is shown in Table 9.29.

| Energy consumption and recovery | Energy |
|---|---|

| | (kWh/t) |
|---|---|
| Electrical energy | 4060 |
| Potential energy in coke | 4430 |
| Recovered CO gas, including internal energy use 190 kWh/t | 1460 |
| Total plant energy consumption: | 7220 |

**Table 9.29: Total energy balance for a FeCr smelter**
[ 149, Schei, A, et al. 1998 ]

A similar balance for other process routes cannot be made due to the lack of sufficiently detailed information. However, an approximate balance can be made, which includes only fuel or process energy consumption figures, i.e. electrical energy and coke and gas used as fuels, as shown in Table 9.30. It does not include a comparison of the consumption of reducing agent and the energy recovery efficiencies of CO gas.

| Energy source | Conventional process (1) (kWh/t) | Sintering and closed furnace (kWh/t) | Closed furnace and pelletising/ sintering preheating(3) (kWh/t) |
|---|---|---|---|
| Electricity | 3800 - 4500 | 4060 | 3100 - 3500 |
| Sintering | 0 | 880 (2) | 0 |
| Pelletising/ sintering | 0 | 0 | 275 - 500(3) |
| Preheating | 0 | 0 | 500 - 700 (4) |
| Other | 0 - 2700 | 190 | 100 - 200 |
| Total | 3800 - 7200 | 5130 | 3975 - 4900 |

(1) Conventional open, semi-closed or closed furnace with lump ore and/or briquettes/fines.
(2) Energy from coke breeze used in the sintering process.
(3) Assuming 60 % of the ore is pellets.
(4) Preheating to 700 °C.

**Table 9.30: Comparison of electrical and fuel energy consumption**

Table 9.30 shows that the difference in process energy consumption between production alternatives is not very big. Indeed, the "conventional" process routes may have an advantage if a considerable part of the recoverable energy can be sold externally. Most often plants do not have external energy customers. Choosing a process route that can utilise recovered heat, either for added process steps that increase efficiency and output, or for electricity generation, will then be advisable options.

An important point of the closed furnace process that uses pelletising/sintering and preheating is to minimise the use of fossil carbon per tonne of produced alloy, which will also minimise the specific $CO_2$ emissions. However, the pelletising/sintering will only reduce the impact of greenhouse gases if an alternative, less energy efficient process leads to a deficiency of CO gas.

Ore quality is also an important factor for energy consumption. Of primary importance is the content of metal oxide and the non-ferrous metal to iron ratio, which should both be as high as possible. The content of gangue minerals should be as low as possible in the ore or the ore mix (this will partly be a consequence of a high amount of metal oxide), and of a composition to minimise use of slag additives. This will lower the slag amount, and thus the proportion of the electrical power necessary to melt the slag.

Concerning the energy usage, the disadvantage of the smelting furnaces used without energy recovery is the high amount of energy lost as CO in the off-gas and/or as waste heat in the off-gas. For instance, by producing FeSi and silicon metal, only about 32 % of the energy consumed is chemical energy in the product. That means about 68 % of the energy is lost as heat in the furnace off-gas. Energy can be recovered from the cooling cycles as hot water and from the off-gas as heat which can be transferred into high pressure steam and subsequently into electrical energy or by using the CO content directly as a secondary fuel.

There are some direct plant improvements that can be made to reduce energy consumption, such as running the process with a high metal yield or improving the furnace design to achieve lower energy loss. In addition to the direct plant improvements, about 15 - 20 % of the electric energy consumed by the electric arc furnace can be recovered as electricity by an energy recovery system. This percentage is considerably higher for a system that produces electricity and uses the thermal energy of the furnace cooling and the off-gas. This will be as well the case if the CO gas is utilised directly as a secondary fuel in order to replace fossil fuels.

**Achieved environmental benefits**
The use of the CO gas reduces the overall power and coke consumption of the process, which consequently minimises the impact of global warming by burning fossil fuel.

**Cross-media effects**
No data has been reported.

**Operational data**
By using a closed, sealed furnace, the volume of the off-gas can be reduced by a factor of 50 - 75 and by the factor of 10 - 20 in case of a semi-closed furnace. The investment cost for the off-gas-cleaning systems for closed furnaces are much lower than for open furnaces. The cleaned CO gas can be used as fuel for raw material preheating, coke drying and similar processes, substituting oil or other fossil fuels. Energy can be recovered from semi-closed furnaces in the form of steam or hot water [ 149, Schei, A, et al. 1998 ].

**Applicability**
These techniques are applicable to sealed and semi-sealed furnaces where high concentrations of CO are produced.

**Economics**
The high investment costs are offset to a large extent by the energy savings and the income from the energy that is sold.

**Driving force for implementation**
Reduction in energy consumption.

**Example plants**
FI, NO.

**Reference literature**
[ 233, Farrell Nordic Mission 2008 ], [ 149, Schei, A, et al. 1998 ] [ 255, VDI (D) 2576 2008 ].

#### 9.3.11.2 Energy recovery and utilisation of the CO from a closed electric arc furnace

**Description**
The main part of the process is a closed electric arc furnace, which generates a CO-rich off-gas (70 - 90 % of CO). The off-gas is cleaned by using a wet scrubber before it can be used as a secondary fuel. One possibility is the combustion with air in a stream boiler. The steam is fed to a set of high pressure and low pressure turbines. The energy is then recovered as electricity (See Figure 9.14).

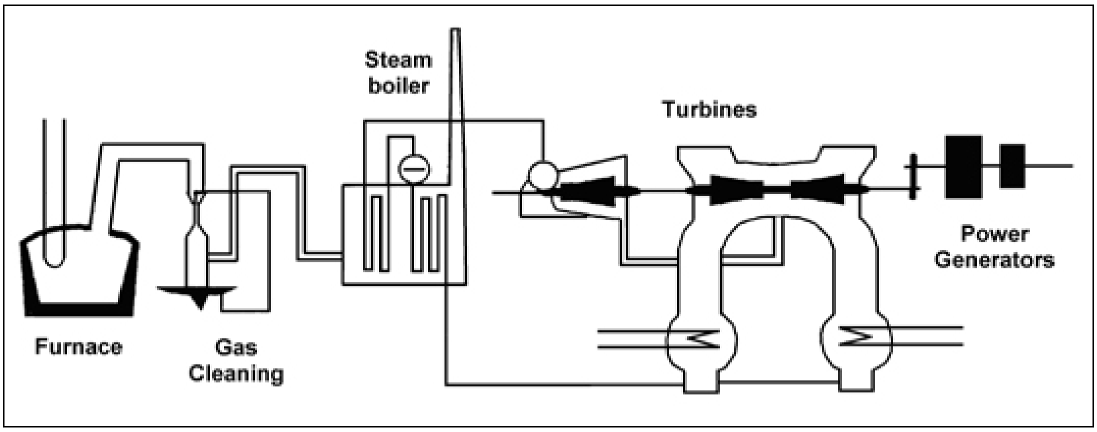


**Figure 9.14: Direct use of the CO gas for the production of electrical energy**
[ 148, Kolbeinsen, L. et al. 1995 ], [ 154, Lindstad, T. et al. 1994 ]

Besides the production of electricity, the CO gas can be used for drying and heating of ladles and can also be transferred by means of pipelines in the plant area and used as a secondary fuel for many purposes. The best utilities are achieved in direct burning replacing fossil fuels, e.g. heavy oil or coal. In the production of FeCr, FeMn and SiMn, CO gas can be used for the drying of coke and other raw materials. CO gas can as well be used as a fuel in the steel belt sintering furnace in order to reduce the primary energy consumption of the furnace. By producing FeCr, the CO gas is used to preheat the charge material, which cut the consumption of electric energy by 70 - 90 kWh per a 100 ºC increase in the preheating temperature. It can also be used in an adjacent stainless steel plant. [ 138, Niemelä, P. 1999 ].

The CO-rich gas can also be cleaned and then supplied as a synthetic gas to a neighbouring steel or chemical plant, in which the gas serves as a raw material.

In a semi-closed furnace[rr79], the CO gas from the smelting furnace burns in the suction air thus creating a hot off-gas of about 400 - 800 ºC which can also reach peaks up to 1200 ºC. The furnaces can be equipped with an integrated energy recovery system, which contains the following components:

- exhaust hood with furnace ducting
- waste-heat boiler
- feed-water system
- heat distribution system or steam turbine with generator and condenser.

**Achieved environmental benefits**
The recovery of electric energy from the CO gas reduces the overall energy consumption of the process, which consequently minimises the impact of global warming by emitting $CO_2$ from burning fossil fuel. The recovered energy replaces in most cases fossil fuel like oil or coal and reduces therefore at the same time the emissions of $SO_2$ at the same time.

**Cross-media effects**
No data has been reported.

**Operational data:**
[ 148, Kolbeinsen, L. et al. 1995 ], [ 154, Lindstad, T. et al. 1994 ]
Steam produced: 35 - 40 tonnes/h.
Energy recovery: 70 GWh/yr = 13.5 % of the electrical energy input.

**Applicability**
This technique is applicable to new and existing plants producing FeCr, FeMn and SiMn in closed furnaces.

**Economics**

A cost indication is about EUR 0.025 per kWh (7 % real interest rate and 15 years lifetime.

**Driving force for implementation**

Reduction in energy consumption.

**Example plants**

NO.

**Reference literature**

[ 148, Kolbeinsen, L. et al. 1995 ], [ 154, Lindstad, T. et al. 1994 ].

#### 9.3.11.3 Energy recovery for a semi-closed electric arc furnace

**Description**

The energy in hot off-gases from the furnace processes can be recovered in a waste heat boiler, which produces superheated steam. Relatively conventional water pipe boilers with super heater, economiser and condenser sections are used, combined with an efficient cleaning system to keep the heating surfaces clean in the heavily dust-polluted flue-gas.

The furnace top hood is highly exposed to the internal furnace heat, and is conventionally cooled with a water piping system covered by a ceramic lining. About 25 % of the furnace heat emissions are lost to the top hood cooling water. For energy recovery, the top hood may be cooled by unshielded high-pressure water piping, producing steam to the recovery boiler system. Such hoods exist and contribute substantially to energy recovery.

The steam can be used in a back-pressure turbine in order to produce electricity or can also be sold to a neighbouring mill. The recovery system can be designed to produce hot water, which can be used by a local heating system (See Figure 9.15).

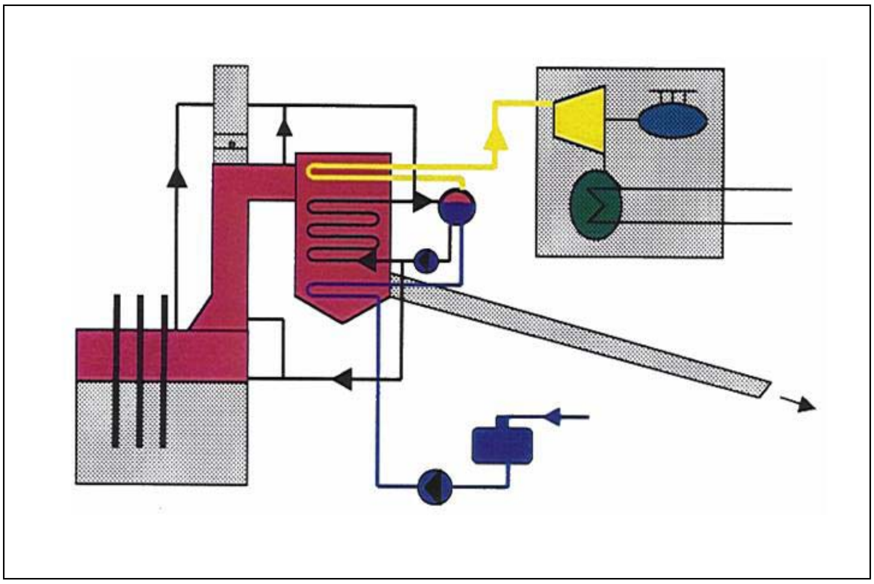


**Figure 9.15: Energy recovery from a semi-closed furnace**

*Without any description or legend this figure is not very meaningful.*

**Achieved environmental benefits**

The recovery of energy from the hot off-gas reduces the overall energy consumption of the process, which consequently minimises/reduces the impact of global warming by emitting $CO_2$ from burning fossil fuel. The off-gas energy can present a large available, partly unexploited energy source that can provide new electricity without pollution or additional $CO_2$ emissions.

The recovered energy replaces, in most cases fossil fuel-like oil or coal and therefore reduces the emissions at the same time. The energy recovery produces no pollution, as the flue-gas composition is not changed by the recovery. The emission of hot cooling air and water from the plant are reduced. The energy recovery creates no visual changes of the landscape.

**Cross-media effects**
No data has been reported.

**Operational data**
The off-gas energy can be used to produce electrical power, heat energy or both. If the waste heat is utilised as electrical power, the recovery is up to 28 - 30 % of the energy consumption. Alternately, the steam can be drained at mean pressure and can be used for district heating, and the recovery will increase to approximately 80 - 90 %. But then only 20 % of the waste heat can be recovered as electrical power. The demand of district heating often varies through the year and the most efficient solution is the co-generation of electric power and heat energy to supply heat energy only when needed.

**Applicability**
The technology is in general applicable to both new and existing plants. Energy recovery is beneficial to existing plants when the energy can be produced in a manner that can be used by the plant or its neighbours.

**Economics**
There are two economic case studies, which have been reported. The following results should be seen as an cost indication because exact cost data is very much dependent on the specific circumstances of the plant.

**a) First Case:**
A plant with three furnaces and a total electric power consumption of about 117 $MW_e$ has been taken into account. The furnaces are equipped with hoods of the conventional type. Net recovered electric energy is 317.6 GWh/yr, which equals 32.9 % of the power consumption. Annuity depreciation for the investment of EUR 43.1 million over 15 years at 7 % interest result in a capital cost of EUR 4.73 million/yr. The electricity cost is approximately EUR 0.016 - 0.017/kWh.

| | |
|---|---|
| • capital cost | EUR 4.73 million |
| • manning (5.5 Man-years) | EUR 0.25 million |
| • total | EUR 5.76 million. |

**b) Second Case:**
FeSi production with an electricity consumption of 60 $MW_e$ uses a semi-closed furnace with an off-gas temperature of 750 ºC. The waste heat boiler consists of three sections and each section has four economisers, two evaporators and two super heaters. The gas exits the boiler at approximately 170 ºC. The superheated steam produced is fed to a multistage turbine. The generator produces 17 $MW_e$ of electric power equal to 90 GWh/yr, which corresponds to 28 % of the flue-gas energy and 16.5 % of the electric power consumption in the furnace. The investment costs for the recovery plant was about EUR 11.7 million in 1987 (20 Years annuity, 11.5 % interest, electricity cost EUR 0.02/kWh)

| | |
|---|---|
| • capital cost | EUR 1.81 million |
| • operation and maintenance, | EUR 0.45 million |
| • manning (5.5 Man-years) | EUR 0.25 million |
| • total | EUR 2.51 million. |

**Driving force for implementation**
Reduction in energy consumption.

**Example plants**
NO.

**Reference literature**
[ 183, ABB 1999 ], [ 184, Elkem 1999 ], [ 148, Kolbeinsen, L. et al. 1995 ], [ 149, Schei, A, et al. 1998 ], [ 154, Lindstad, T. et al. 1994 ], [ 196, Finkeldei, L. 1999 ].

### 9.3.11.4 Energy recovery from a furnace off-gas

*The whole example here has been changed. Before it was a specific description of a blast furnace to produce HCFeMn in a blast furnace and the associated CO recovery and usage in the hot stoves.*

*Now this section talks about sealed furnaces in general and not a word about Ferro alloys. The included percentagesdo not make sense any more since the corresponding and needed explanation has been deleted.*

*Who proposed this?? Ask industry.*

**Description**
The production of ferro-alloys especially in sealed furnaces can result in the generation of a large amount of CO-rich off-gas. This CO gas can partly be used as a secondary fuel to preheat the blast in the hot stoves or as fuel for a neighbouring plant.

An example of energy recovery is given in Figure 9.16.

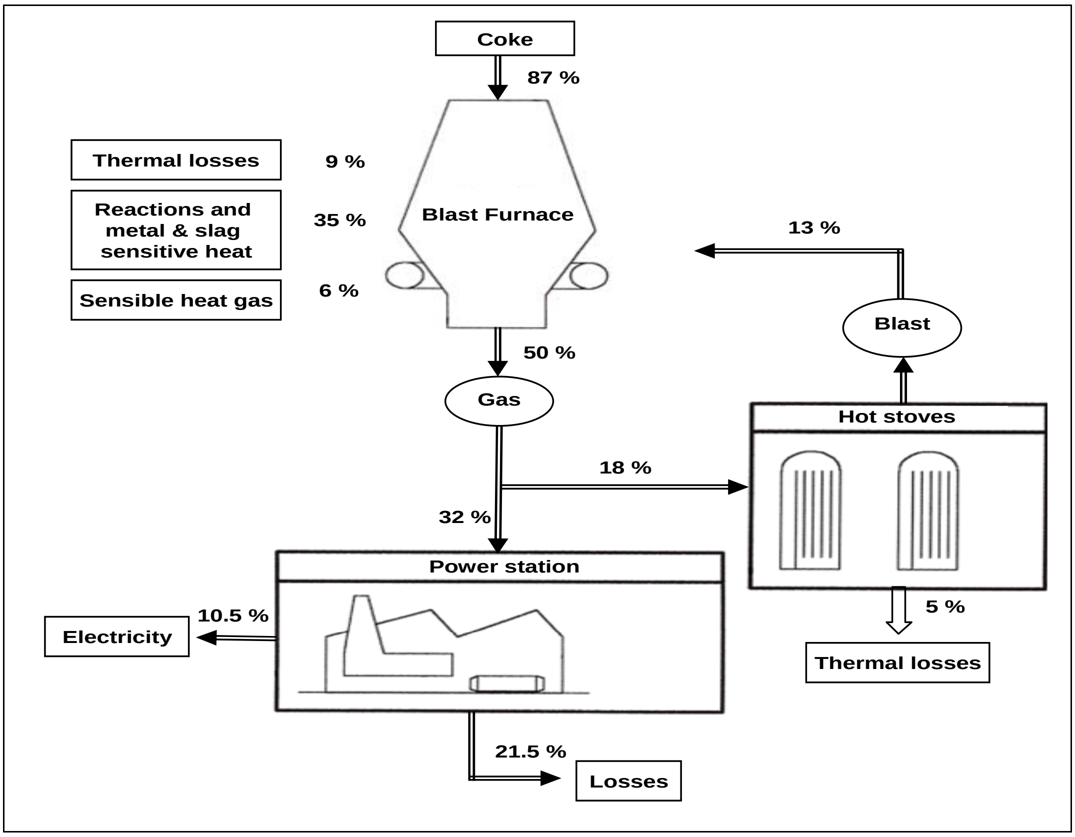


**Figure 9.16: Example of energy recovery**

**Achieved environmental benefits**
The use of the CO gas reduces the overall power and coke consumption of the process, which consequently minimises the impact of global warming by burning fossil fuel. Off-gases are

cleaned and dust is returned to the process. The use of modern burners will reduce the $NO_X$ emissions.

**Cross-media effects**
No data has been reported.

**Operational data**
By using a closed, sealed furnace, the volume of the off-gas can be reduced by a factor of 50 - 75 % and by the factor of 10 - 20 % in the case of a semi-closed furnace. The investment cost for the off-gas-cleaning systems for closed furnaces are much lower than for open furnaces. The cleaned CO gas can be used as fuel for raw material preheating, coke drying and similar processes, substituting oil or other fossil fuels. Energy can be recovered from semi-closed furnaces in the form of steam or hot water.

**Applicability**
This technique is applicable to sealed and semi-sealed furnaces where high concentrations of CO are produced.

*An energy recovery system means a high capital investment. Taking local conditions, such as local energy prices, periods of production and the absence of potential customers into account, the returns of investments may in several cases not be high enough to justify such investments from an economic point of view[rr80].*

**Economics**
The high investment costs are saved to a large extent by the energy savings and the income from the energy that is sold.

**Driving force for implementation**
Reduction in energy consumption

**Example plants**
FI.

**Reference literature**
[ 192, SFPO 1999 ], [ 196, Finkeldei, L. 1999 ], [ 297, European Commission 2001 ].

For the production of FeSi and Si metal it has been reported that a smelting furnace, which slowly rotates may contribute to the reduction of the overall energy consumption by about 10 % and increases the metal yield.

~~An energy recovery system means a high capital investment. Taking local conditions, such as local energy prices, periods of production and the absence of potential customers into account, the returns of investments may in several cases not be high enough to justify such investments from an economic point of view.~~

## 9.4 Best Available Techniques

In understanding this section and its contents, the attention of the reader is drawn back to the Preface of this document and in particular the fifth section of the Preface: ‘How to understand and use this document’. The techniques and associated emission and/or consumption levels, or ranges of levels, presented in this section have been assessed through an iterative process involving the following steps:

- identification of the key environmental issues for the sector which for the production of ferro-alloys are: dust and fume, CO and $CO_2$ gas, $SO_2$, energy recovery, waste water, residues such as filter dust, sludge and slag;
- examination of the techniques most relevant to address these key issues;
- identification of the best environmental performance levels, on the basis of the available data in the European Union and worldwide;
- examination of the conditions under which these performance levels were achieved; such as costs, cross-media effects, and the main driving forces involved in implementation of the techniques;
- selection of the best available techniques (BAT) and the associated emission and/or consumption levels for this sector in a general sense, all according to Article 2(12) and Annex IV to the Directive.

Expert judgement by the European IPPC Bureau and the relevant Technical Working Group (TWG) has played a key role in each of these steps and in the way in which the information is presented here.

On the basis of this assessment, best available techniques, and as far as possible emission and consumption levels associated with their use, are presented in this section that are considered to be appropriate to the sector as a whole and in many cases reflect the current performance of some installations within the sector. Where emission and consumption levels 'associated with best available techniques' are presented, this is to be understood as meaning that those levels represent the environmental performance that could be anticipated as a result of the application, in this sector, of the techniques described, bearing in mind the balance of costs and advantages inherent within the definition of BAT. However, they are neither emission nor consumption limit values and should not be understood as such. In some cases, it may be technically possible to achieve better emission or consumption levels but due to the costs involved or cross-media considerations, they are not considered to be appropriate as BAT for the sector as a whole. However, such levels may be considered to be justified in more specific cases where there are special driving forces.

The emission and consumption levels associated with the use of BAT have to be seen together with any specified reference conditions (e.g. averaging periods).

The concept of ‘levels associated with BAT’ described above is to be distinguished from the term ‘achievable level’ used elsewhere in this document. Where a level is described as ‘achievable’ using a particular technique or combination of techniques, this should be understood to mean that the level may be expected to be achieved over a substantial period of time in a well maintained and operated installation or process using those techniques.

Where available, data concerning costs have been given together with the description of the techniques presented in the previous sections. These give a rough indication about the magnitude of the costs involved. However, the actual cost of applying a technique will depend strongly on the specific situation regarding, for example, taxes, fees, subsidies, and the technical characteristics of the installation concerned. It is not possible to evaluate such site-specific factors fully in this document. In the absence of data concerning costs, conclusions on economic viability of techniques are drawn from observations on existing installations.

The BAT (including the associated emission and consumption levels) given in this section are 'BAT in a general sense' (i.e. considered to be appropriate to the sector as a whole). It is intended that they are a reference point against which to judge the current performance of an existing installation or to judge a proposal for a new installation. In this way, they will assist in the determination of appropriate 'BAT-based' conditions for the installation or in the establishment of general binding rules under Article 9([8]) of the IPPC Directive. It is foreseen that new installations can be designed to perform at or even better than the BAT levels presented in this section. It is also considered that existing installations could move towards the BAT levels presented in this section or do better, subject to the technical and economic applicability of the techniques in each case.

While the BAT reference documents do not set legally binding standards, they are meant to give information for the guidance of industry, Member States and the public on achievable emission and consumption levels when using specified techniques. The appropriate permit conditions for any specific case will need to be determined taking into account the objectives of the IPPC Directive and the local considerations.

**Recommendation to help users/readers of this document:**

It is strongly recommended that this section on BAT be read in conjunction with the sections of this document that describe the techniques to consider in the determination of BAT. The applicability of the techniques and measures are reported in these sections and should be taken into account at a local level. To help the reader, references to the appropriate sections are included in the description of BAT.

If not otherwise mentioned, BAT associated emission and consumption levels given in this section are expressed as follows:

- for pollutants emitted to air (except dioxins): expressed on a daily average basis with standard conditions of 273 K, 101.3 kPa, measured oxygen content and dry gas with the plant operating normally under steady-state conditions and no dilution of the gases;
- for dioxins: expressed as the average over the sampling period which should preferably be a minimum of 6 hours;
- for waste water: based on qualified random samples or 24 hour flow proportional composite samples.

As described in the Preface, this document does not propose emission limit values. The best available techniques and the ranges of emission or consumption levels associated with best available techniques (BAT-AEL ranges) are related to installations with different sizes, different kinds of operation and different raw materials. In this document, special local considerations cannot be taken fully into account. The determination of appropriate permit conditions will involve taking account of local, site-specific factors such as the technical characteristics of the installation concerned, its geographical location and the local environmental conditions. In the case of existing installations, the economic and technical viability of upgrading them also should be taken into account. Even the single objective of ensuring a high level of protection for the environment as a whole will often involve making trade-off judgements between different types of environmental impact, and these judgements will often be influenced by local considerations.

Although an attempt is made to address some of these issues, it is not possible for them to be considered fully in this document. The techniques and emission and consumption levels presented here will therefore not necessarily be appropriate for all installations. On the other hand, the obligation to ensure a high level of environmental protection including the minimisation of long-distance or transboundary pollution implies that permit conditions cannot be set on the basis of purely local considerations. It is therefore of the utmost importance that the information contained in this document be fully taken into account.

Section 2.20 to this document reports BAT for the following common processes and the following sections should be referred to for those techniques that are BAT:

- environmental management systems (EMS) (Section 2.20.1)
- material handling and storage (Section 2.20.2)
- process control (Section 2.20.3)
- fume and gas collection (Section 2.20.4)
- the prevention and the destruction of PCDD/F (Section2.20.5)
- sulphur dioxide removal (Section 2.20.6)
- the removal of mercury (Section 2.20.7)
- effluent treatment and water re-use (Section 2.20.8)
- energy efficiency (Section 2.20.9)
- intermediate products, process residues and wastes (Section 2.20.10)
- emission monitoring (Section 2.20.11)
- prevention of the formation of $NO_X$ (Section 2.20.12)
- removal of dust and particles (Section 2.20.13)

BAT for the production of ferro-alloys is the combination of the generally applicable techniques reported in Section 2.20 and the specific techniques indicated in this section.

## 9.4.1 Prevention and treatment of emissions to air

### 9.4.1.1 Pretreatment techniques

**a) BAT is to prevent diffuse emissions and optimise the use of energy by using the techniques given in Sections 9.3.2, .9.3.3, and 9.3.4 and the following techniques:**

- use of a shaft furnace for coke drying with the use of recovered energy or the CO-rich off-gas from the smelting furnace as a secondary fuel;
- use of a rotary kiln for drying or degreasing of secondary raw material such as turnings or metal scrap and to recycle the hot air back to the burner; *Where is this from? This is not what is described in 9.3.2.2 where the hot air from the afterburner is partly recycled to the burner.*
- use of an afterburner for the degreasing of secondary raw material in order to destroy VOC;
- use of wet grinding, filtering and pelletising to produce an increased specific surface area of chromite.

*In Section 9.3.2.2 is only one example for titanium swarf degreasing. This is not sufficient to conclude on a general treatment as in bullets 2 and 3.*

### 9.4.1.2 Sintering

*I consider it to be difficult to combine diffuse emission prevention and energy optimisation inone BAT again and again and simply to cross-refer to complete sections.*

**a) BAT is to prevent diffuse emissions and optimise the use of energy by using the techniques given in Sections 2.4.3 and 9.36 for sintering.**

*9.36 does not exist. Probably 9.3.3.*

### 9.4.1.3 Pre-reduction and preheating

*I consider it to be difficult to combine diffuse emission prevention and energy optimisation inone BAT again and again and simply to cross-refer to complete sections.*

**a) BAT is to prevent diffuse emissions and optimise the use of energy by preheating the charge materials (see Section 9.3.4).**

### 9.4.1.4 Reduction process

**a) BAT is to prevent diffuse emissions and optimise the use of energy by using the techniques given in Table 9.31 depending on the ferro-alloys produced and the environmental impact of the processes (see Section 9.1).**

**b) BAT is to reduce diffuse emissions from existing open or semi-closed furnaces by undertaking CFD studies to assess the viability of retrofitting with an appropriate hood.**
*CFD= Computerised fluid dynamics*
*To include CFD a specific section about CFD should be introduced.*

### 9.4.1.5 Post furnace operations

**a) BAT is to prevent diffuse emissions and optimise the use of energy by using one of the techniques presented in Section 9.3.8.**
*(All included post furnaces operation have nothing to do with energy optimisation)*

| **Smelting furnace** | **Ferro-alloy production** | **Technique** | | **Comments** |
|---|---|---|---|---|
| | | **Abatement technique** | **Energy recovery** | |
| Semi-closed electric arc furnace | HC FeCr | Fabric filter | Heat and electric energy can be recovered | |
| | FeSi, Si-metal | Fabric filter | Heat and~~,~~ electrical ~~and~~ energy can be recovered | |
| | HC FeMn, SiMn | Fabric filter | Heat and electric energy can be recovered | |
| | Other ferro-alloys produced by carbothermic reduction;<br>Alloy recovery from steel mill residues | Two-stage fabric filter with injection of activated carbon or a three step venturi scrubber and wet ESP and mercury removal by a selenium filter | Heat and electric energy can be recovered | Special ferro-alloys are normally produced only in small amounts, therefore the energy that can be recovered is low compared to bulk ferro-alloys.<br>Semi-closed furnaces can be used also for the production of FeV where fines need to be remelted. |
| Closed electric arc furnace | HC FeCr | Wet scrubber or dry cleaning system | Energy can be recovered from CO that can be used as secondary fuel | Closed furnaces are operated in connection with different pretreatment and peripheral techniques, such as sinter plants, preheating furnaces, etc. These techniques may all have a positive influence on the environmental impact, especially if CO-rich off-gas from the smelting furnace is used as a fuel |
| | HC FeMn, SiMn | Wet scrubber or dry cleaning system | Energy can be recovered from CO that can be used as secondary fuel | |
| | Other ferro-alloys produced by carbothermic reduction, but not FeSi and Si-metal | Wet scrubber<br>Fabric filter | Energy can be recovered from CO that can be used as secondary fuel | Special ferro-alloys are normally produced only in small amounts, therefore the energy that can be recovered is low compared to bulk ferro-alloys. FeSi and Si-metal cannot yet be produced in a closed furnace. |
| Refractory lined crucible enclosed in a reaction chamber | Ferro-alloys produced by metallothermic reduction | Fabric filter | Energy recovery is not practised | Recovery of heat energy will not be practised, because the metallothermic reduction takes place as a batch process, which needs only a short reaction time.<br>According to the bio-toxic nature of fluoride, the use of fluorspar by producing FeMo should be minimised as much as possible or replaced. |
| Multiple hearth furnace | Roasting of molybdenite concentrate | (Multi)cyclones with dry ESP, wet scrubber and a sulphuric acid plant | Energy can be recovered where there is a use for the energy produced | The (multi)cyclones and the dry ESP serve as a dust catcher where the dust is recycled back to the furnace, for the final dedusting, a wet scrubber is used |
| Plasma Dust process | Alloy recovery from steel mill residues | A three step venturi scrubber and a wet ESP and a mercury removal by a selenium filter | Energy can be recovered from CO that can be used as secondary fuel | |

**Table 9.31: Smelting furnaces considered BAT for the production of ferro-alloys**

### 9.4.1.6 Fume and gas collection and abatement

**a) BAT is to prevent and control emissions of dust, metals, PAH, total organic carbon, sulphur dioxide and PCDD/F to air and by using the techniques given in Table 9.32 or a combination of them (see Section 9.2.2.1.2).**

**The emission levels given in Table 9.32 are the BAT-AELs.**

| Pollutant | Techniques | BAT-AELs | Comments |
|---|---|---|---|
| Dust | Fabric or ceramic filter<br>Cascade scrubber | <1 - 5 mg/Nm$^3$ | A bag burst detection system should be used.<br>(See Sections 2.9.2.2.4, 2.9.2.2.6 and 2.20.13) |
| Metals | Fabric or ceramic filter *(Examples for plants?)* | <0.2 mg/Nm$^3$ | The concentration of metals is linked to the concentration of dust and the proportion of the metals as part of the dust (see Section 9.2.2.2) |
| Vaporised metal (Hg, Cd, and Pb) | Two-stage fabric filter with a bag burst detection system and injection of activated carbon or a three step venturi scrubber, wet ESP and a mercury removal stage (see Section 2.20.7) | <0.1 mg/Nm$^3$ | By recovering ferro-alloys from steel mill residues, Hg, Cd and Pb can be emitted (see Section 9.2.2.2) |
| PAH (EPA 16) | | <50 µg/Nm$^3$ | (see Section 9.2.2.2) |
| Total organic carbon as C | Semi-closed furnace?? *What about closed furnaces??* | <5 mg/Nm$^3$ | (see Sections 2.9.2.6 and 9.2.2.2) |
| $SO_2$ *Where are these techniques applied, introduce examples!!! Who proposed to introduce requirements for $SO_2$?* | Alkali semi-dry scrubber and fabric filter. Wet alkali or double alkali scrubbers using lime, magnesium hydroxide, sodium hydroxide. | <50 to 400 mg/Nm$^3$ | Potential cross-media effects from energy use, waste water and solid residues together with the ability to re-use scrubber products will influence the choice of the technique used (see Section 2.11.3.4) |
| | Fabric filter with dry lime injection into cool gas or control of the sulphur content of the raw materials | 100 to 500 mg/Nm$^3$ | Part of the reacted lime can be used as a fluxing agent. (see Section 2.11.3.6) |
| $SO_2$ from molybdenite roasting | Sulphuric acid plant (single or double contact plant) | See Section 2.20.6 | The performance of the gas treatment plant depends upon the individual raw material batch and the furnace loading and therefore influence the conversion efficiency. |
| PCDD/F *Where are these techniques applied, introduce examples!!! Who proposed to introduce requirements for Dioxine?* | High efficiency dust removal system. Afterburner followed by quenching. adsorption by activated carbon, oxidation catalyst | <0.1 ng I-TEQ/Nm$^3$ | Treatment of a clean dedusted gas is required to achieve low levels.<br>(See Sections 2.10.2.1 and 2.20.5) |

NB: Collected emissions only. BAT-AELs are given as daily averages based on steady-state operation or, in cases where continuous monitoring is not practicable as the average over the sampling period. For PCDD/F, the BAT-AEL is the average over the sampling period which should preferably be a minimum of six hours.

**Table 9.32: BAT and BAT-AELs to prevent and control emissions to air from ferro-alloy processes**

Venturi scrubbers are used to clean the off gas from a closed ferro-alloys furnace. The Co-rich off gas is not emitted directly to the atmosphere but is used as secondary fuel.

**b) BAT is to prevent and control emissions of dust, metals and sulphur dioxide from the smelting of sulphide concentrates using one of the techniques reported in Section 2.11.3**.

**The emission levels given in** Error! Reference source not found. **for new or retrofitted sulphuric acid plants and** Error! Reference source not found. **for existing sulphuric acid plants are the BAT-AELs.**

## 9.4.2 Effluent treatment and water re-use

**a) BAT is to prevent and control emissions of metals to waste water by using the techniques given in Sections 2.20.8 and 9.2.4**[rr81]**.**

**The emissions given in Table 9.33 are the BAT-AELs.**

| **Component** | **BAT-AELs (mg/l)** |
|---|---|
| Cu | 0.2 to 0.5 |
| Pb | 0.2 to 0.5 |
| Ni | 0.2 to 0.5 |
| Zn | 0.2 to 1.0 |
| As | 0.1 to 0.2 |
| $Cr^{total}$ | 0.1 to 0.2 |
| $Cr^{VI}$ | 0.01 to 0.05 |
| Cd | 0.1 to 0.2 |
| Hg | 0.01 to 0.05 |
| NB: BAT-AELs are based on qualified random samples or twenty four hour flow proportional composite samples. | |

**Table 9.33: BAT-AELs for emissions to water**

## 9.4.3 By-products, process residues and waste

Specific techniques for the refractory metals sector are given here.

**a) BAT for recycling and re-use of intermediate products and process residues (slag, filter dust and sludge) in ferro-alloy production is to use the techniques given in Table 9.34 and Table 9.35. If recycling or re-use is not economically possible, secure disposal should be used.**

| **Ferro-alloy** | | **Techniques** |
|---|---|---|
| FeCr | HC FeCr | Use of crushed lump and granulated slag as building material and road construction material.<br>Use of slag as a sandblasting grid, and for the production of refractory castables |
| | MC and LC FeCr | Use of slag as far as possible |

| Ferro-alloy | | Techniques |
|---|---|---|
| Alloy recovery from steel mill residues | | Production of low basicity slag to ensure the formation of stable silicates which are non-leachable. The slag can be used in various construction applications |
| Calcium-silicon | | Recycling slag to the furnace |
| FeMn | HC FeMn | Use of rich slag (high content of MnO) as raw material for the production of silico-manganese or other metallurgical applications |
| | | Use of standard exhausted slag (low content of MnO) as a construction material |
| | MC FeMn | Use of slag as raw material in the production of silico-manganese or other metallurgical applications |
| | LC FeMn | Use of slag can as raw material in the production of silico-manganese or other metallurgical applications |
| SiMn | | Use of slag as a construction material |
| FeV | | Use of slag as secondary raw material in the process industry, e.g. for the production of refractories or in the steel industry |
| FeMo | | Use of slag for further processing |
| NB: Analysis of residual materials before transfer to other sites so that the correct disposal or recovery routes can be used. | | |

**Table 9.34:** **BAT for the recycling and re-use of intermediate products and process residues (slag and filter dust) from the production of ferro-alloys**

| Ferro-alloy | | Techniques |
|---|---|---|
| FeCr | HC FeCr | Recycle dust from crushing raw material transport and handling as well as the dust and sludge from the pretreatment processes<br>Remelt the dust from FeCr product handling in the furnace or used in stainless steel production<br>Solidify filter dust using ferrous sulphate which reduces Cr VI to CrIII |
| | MC and LC FeCr | Recycled dust back to the smelting furnace<br>Solidify filter dust using ferrous sulphate which reduces Cr VI to CrIII |
| Alloy recovery from steel mill residues | | Recycle filter cake from the sludge treatment in the Plasmadust process either to the ISP (Imperial Smelting Process} or to a Waelz kiln |
| FeSi | | Use micro-silica as a cement additive. |
| Silicon metal Calcium-silicon | | |
| FeMn | HC FeMn | Agglomerate and recycle manganese rich dust to the furnace or use as raw material for the production of silico-manganese in an electric arc furnace. |
| | MC FeMn | Recycle dust and sludge in the process or in other industries |
| | LC FeMn | |
| SiMn | | Recycle dust and sludge in the process or in other industries |
| FeNi | | Recycle dust and sludge in the process or in other industries |
| FeV | | Recycle dust and sludge in the process or in other industries. FeV fines are remelted |
| Molybdenite roasting | | Recycle dust to the roaster and sludge from the off-gas-cleaning to the concentrate feed |
| FeMo | | Recycle dust and sludge in the process or in other industries |
| NB: Analysis of residual materials before transfer to other sites so that the correct disposal or recovery routes can be used | | |

**Table 9.35:** **BAT for the recycling and re-use of intermediate products and process residues (filter dust and sludge) from the production of ferro-alloys**

## 9.4.4 Energy efficiency

Specific techniques for the ferro-alloys sector are given here.

**a) BAT for ferro-alloy production is to use the techniques given Table 9.36 in a new or substantially changed plant.**

| Ferro-alloy | Furnace | Energy medium | Techniques |
|---|---|---|---|
| FeCr | Closed | CO gas | Production of electrical energy<br>Utilisation of CO as fuel in neighbouring plants<br>Direct burning for drying, sintering, preheating and ladle heating, etc.<br>Use in a integrated FeCr and stainless steel plant |
|  | Semi-closed | Heat | Production of electrical energy<br>Production of high pressure steam and utilisation in own or neighbouring plants<br>Production of hot water |
| FeSi<br>Si-metal | Semi-closed | Heat | Pre-reduction is the most effective stage for energy recovery<br>Production of electrical energy<br>Production of high pressure steam and utilisation in own or neighbouring plants<br>Production of hot water |
| FeMn<br>SiMn | Closed | CO gas | Pre-reduction is the most effective stage for energy recovery<br>Production of electrical energy<br>Utilisation of CO as a raw material in neighbouring plants<br>Direct burning for drying, sintering preheating ladle heating, etc. |
|  | Semi-closed | Heat | Production of electrical energy<br>Production of high pressure steam and utilisation in own or neighbouring plants<br>Production of hot water |
| FeNi | Semi-closed | Heat | Production of electrical energy<br>Production of high pressure steam and utilisation in own or neighbouring plants<br>Production of hot water |
| FeV | Special ferro-alloys are normally produced in small amounts compared to bulk ferro-alloys. The energy recovery from the excess process heat is difficult and may not justify a high investment for an energy recovery system.<br>Energy recovery may be viable if there is a use for the heat generated |  |  |
| FeMo |  |  |  |
| FeW |  |  |  |
| FeTi |  |  |  |
| FeB |  |  |  |
| FeNb |  |  |  |
| NB: Combining the different recovery techniques can increase the overall efficiency of an energy recovery system. |  |  |  |

**Table 9.36: BAT for energy recovery in the production of ferro-alloys**

## 9.5 Emerging techniques

The following techniques are emerging techniques, which means that these techniques are not fully implemented in the ferro-alloy industry:

- the rotary hearth furnace for pre-reducing chromite;
- coal/oxygen or smelt-reduction processes using coal with oxygen or oxygen-enriched air to provide the entire energy requirement for smelting chromite to ferro-chrome;
- closed furnace operation for the production of ferro-silicon and silicon metal (not been successfully been developed);
- the fluidised bed roaster for molybdenite roasting;
- recycling of slag from silicon production processes to reduce energy and raw material consumption in the production of SiMn [ 244, French comments on SiMn 2008 ].

# 10 PROCESSES TO PRODUCE ALKALI AND ALKALINE EARTH METALS

The alkali metals (lithium, sodium, potassium, rubidium, caesium and francium) form Group 1a in the periodic table of the elements. The alkaline earth metals (calcium, strontium and magnesium) form Group 2a and have similar properties and are therefore covered by this sector.

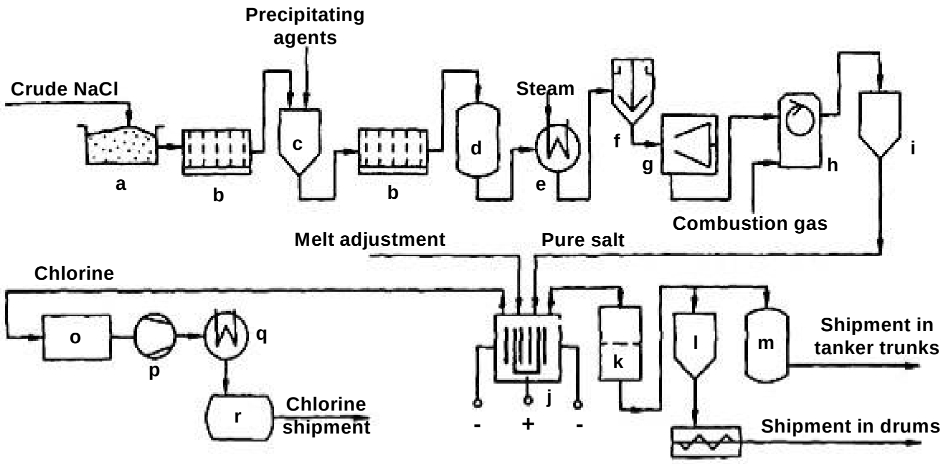
There are very few companies within the EU that produce alkali and alkaline earth metals; the processes used are therefore limited but are representative of the techniques used worldwide. There are two producers of sodium metal and one producer of lithium in the EU. Only one company produces calcium and strontium metal and there are two companies that produce magnesium metal.

## 10.1 Applied processes and techniques

### 10.1.1 Sodium metal

Sodium metal is produced by the electrolysis of fused sodium chloride (NaCl). Calcium and barium chlorides ($CaCl_2$ and $BaCl_2$) are added to the NaCl to form a eutectic mixture, which melts at 580 °C [ 103, Farrell, F. 1998 ].

A flow sheet of sodium metal production is presented in Figure 10.1, where the electrolytic cell is the main part of the process.



a) Dissolution vessel; b) Filter; c) Precipitation vessel; d) Vessel for pure brine; e) Evaporator; f) Thickener; g) Centrifuge; h) Rotary dryer; i) Pure salt bunker; j) Electrolysis cell; k) Sodium filter; l) Sodium storage; m) Sodium tank; n) Casting; o) Chlorine purification; p) Chlorine compressor; q) Liquefier; r) Chlorine storage vessel

**Figure 10.1: Flow sheet of sodium metal production**
[ 104, Ullmann's Encyclopedia 1996 ]

Downs cells are used and have a special cylindrical anode and a circular concentric cathode separated from the anode by a steel mesh diaphragm. Each cell has a loosely fitting top and normally has four pairs of electrodes. Energy from electrolysis is sufficient to keep the electrolyte molten and no additional heating is needed. The cell voltage is 6.2 to 7 V and this is used to monitor and control the process. Raw materials are received as crystals and are dried in a rotary dryer before use; dust is extracted and scrubbed. The sodium chloride concentration in the cell bath is held in the desired range by continuously feeding salt to the cells at the same rate as it is electrolysed to form sodium and chlorine, thus maintaining a constant cell bath level. Sodium and chlorine are collected, under the surface of the cell bath, in separate compartments of a collector assembly. The chlorine is drawn off continuously under a very slight vacuum, to a chlorine plant, where it is normally liquefied and passed to the liquid chlorine storage tanks. The sodium is forced, by the weight of the bath above the collector assembly, up a finned riser pipe where it continuously overflows across a weir into receivers. These are tapped every two hours into larger, portable 24 hour receivers.

A small amount of the calcium chloride in the cells is also electrolysed, along with the sodium chloride, forming calcium and chlorine. A portion of this metallic calcium is carried out of the cells as an impurity in the sodium and separates as the metal cools. This calcium chloride in the cell bath is replaced by adding dry granular calcium chloride to the cells daily. The barium chloride is not electrolysed. Filters remove calcium by-product from the sodium and the purified sodium from the filters is transferred by vacuum to the intermediate storage tanks, and thence under gravity to final storage tanks.

A typical Downs cell for the electrolytic production of sodium metal is shown in Figure 10.2.

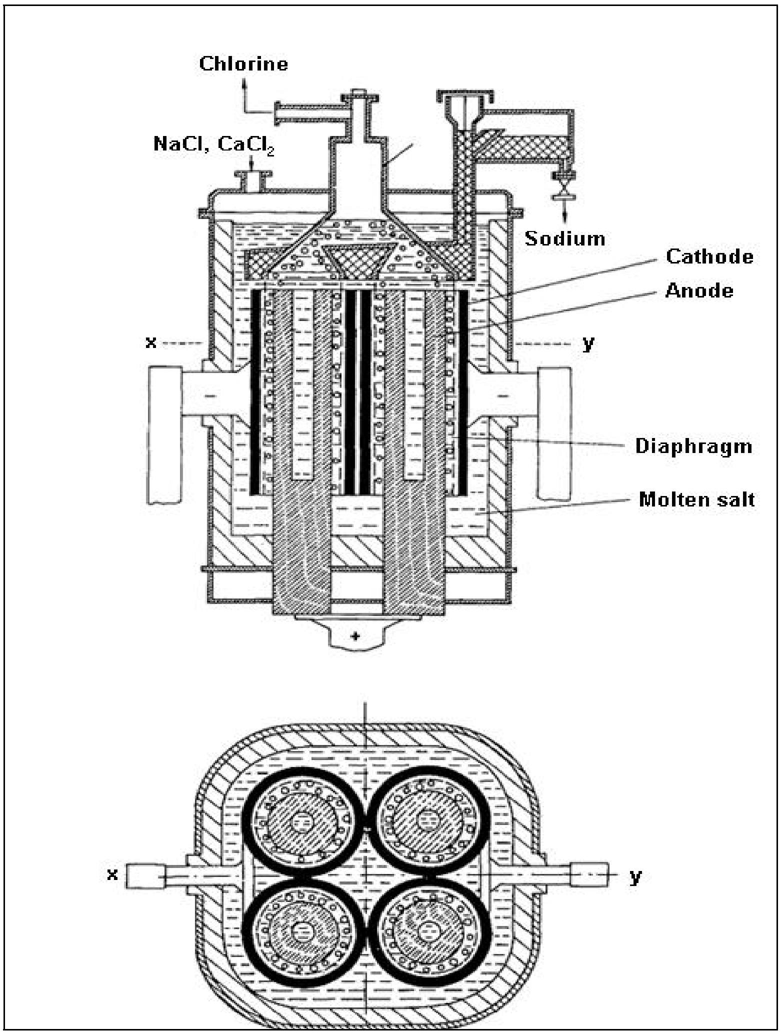


**Figure 10.2: The Downs cell**
[ 104, Ullmann's Encyclopedia 1996 ]

Filter cake from the sodium cleaning stage is pressed to remove sodium and is then washed, dissolving it away as an alkaline effluent. This is used as a reagent to treat other site effluents. Other solid wastes arise from sediment in storage tanks these are burnt on an open hearth and fumes are collected and scrubbed in a two-stage water scrubber. This scrubber discharges into a third stage using HCl which also treats fumes from the filter cake wash [ 352, MSA proposals for sodium 2010 ].

### 10.1.2 Lithium metal

Lithium metal is produced by the electrolysis of a molten, eutectic mixture of lithium chloride (LiCl) and potassium chloride (KCl) at 450 °C [ 103, Farrell, F. 1998 ]. Lithium carbonate is collected in IBCs and is converted into LiCl; the solution is concentrated and crystallised. Waste lithium hydroxide waste can also be converted. LiCl crystals are dried before they are drummed for manual feeding into the cells. There is some local dust extraction at handling points. KCl is not electrolysed at the voltage used (4 to 5 volts) and only LiCl is added to the cells during operation.

Cells are rectangular baths each having five pairs of electrodes (a cylindrical carbon anode and a concentric circular steel cathode). There is no membrane in this process and this is likely to reduce the efficiency of electrolysis, as a portion of the lithium liberated (from the inside surface of the cathode) will react with chlorine to reform LiCl. Cells can be heated by gas burners for startup and winter use but normally sufficient heat is generated by electrolysis to keep the bath molten. Cell life is ~7 years and is prompted by wear of the weir plate.

Molten lithium is produced and accumulates at the front of the cell and is skimmed off manually using a fine mesh skimmer into a handheld ladle. The metal is then immediately cast into small moulds (~350 mm × 50 mm × 50 mm), no metal fumes are produced but the filled moulds are immediately covered by a mineral oil to prevent oxidation. This causes oil fumes, which are extracted into a vertical lip captor and emitted untreated through a stack along with other fumes extracted from the cell room that contain alkali, dust and chlorine. Lithium bar can also be produced in small quantities using a hand-operated hydraulic press.

Chlorine produced by the cell room is collected by partial vacuum and is absorbed in caustic soda to produce sodium hypochlorite, which is sold. Two absorption columns are used, one on standby for emergency use.

The applied current and voltage control the process. Rectifier trips are easily handled and only cause a problem during skimming when current induced stirring of the electrolyte stops. Other problems arise from the presence of sodium as an impurity in the electrolyte as it is electrolysed and separates from Li as it cools. Na forms small mushrooms on the metal surface and these ignite and may cause the ingot to burn. The sodium content of the raw material is controlled to prevent this.

There are no emissions to water; mother liquor from crystallisation is recirculated.

### 10.1.3 Potassium metal

Potassium metal is produced on an industrial scale only by the reduction of potassium chloride with sodium metal. In the continuous production, a fractional distillation is incorporated into a reaction column packed with molten potassium chloride. By feeding sodium into the columns, a vapour mixture of sodium and potassium is fractionated. Potassium metal is then obtained by distillation of the vapour mixture using air as a coolant [ 104, Ullmann's Encyclopedia 1996 ].

### 10.1.4 Calcium and strontium metal

Calcium and strontium metal are used for a variety of purposes. Calcium as an alloying element improves the quality of steels especially the mechanical properties like formability, drawing and machinability. Because of its strong ability to form oxides and sulphites, calcium is important in the production of ultraclean steel. Calcium metal may also be used for lead de-bismuthation. Strontium metal is needed in aluminium refining as well as for the rafination of steel slag.

### 10.1.4.1 Calcium metal

Calcium metal can be produced by electrolysis or metallothermic reduction, but the only process used in the EU is the high temperature vacuum reduction of calcium oxide with aluminium using the metallothermic process. A short description of the electrolysis process is also given.

#### 10.1.4.1.1 The electrolytic process

The basic electrolytic cell is a graphite-lined vessel filled with partially molten calcium chloride maintained at a temperature above the melting point of $CaCl_2$, but below the melting point of calcium metal. Calcium metal forms as a solid deposit in a water-cooled anode. This calcium contains 15 - 25 % of entrapped salts and should be remelted to reduce the impurity levels.

#### 10.1.4.1.2 The metallothermic process

The production of calcium metal depends on a small finite equilibrium of calcium vapour in the range of 1000 to 1200 ºC. The calcium vapour is then transferred with a vacuum pump to a cooled region of the reactor where condensation takes place. This shifts the equilibrium at the reaction site and allows more calcium vapour to be formed.

Lime is ground in order to get a small particle size material that is dry blended with the desired amount of aluminium. The mixture of both is compacted into briquettes to ensure good contact of reactants. The briquettes are then heated in an electric resistance furnace up to about 1300 ºC. Due to the vacuum in the furnace, a condensed block that contains more than 95 % calcium metal is formed in the cooled part of the furnace. These blocks of calcium metal and calcium aluminate residue are removed from the furnace. For some applications, calcium metal should be reduced in size, which can be done by using special grinders adapted to the characteristics of calcium. A characteristic flow diagram of the production of calcium metal is shown below in Figure 10.3.

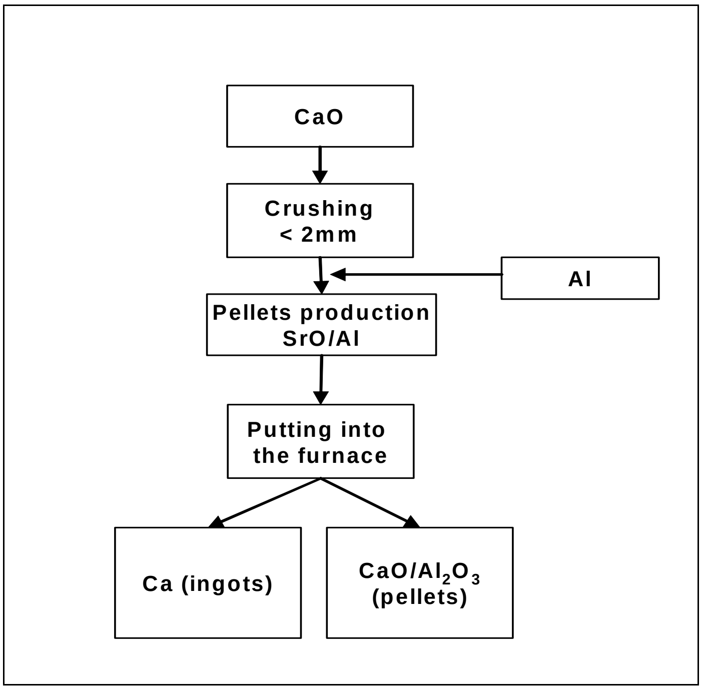


**Figure 10.3: Flow diagram of the production of calcium metal**

### 10.1.4.2 Strontium metal

Strontium metal is produced in the European Union only by thermal reduction of strontium oxide with aluminium as a reducing agent. The reaction is conducted in a similar way to the production of calcium metal in a vacuum furnace. The vaporised metal is condensed in a cooler part of the furnace. The blocks of strontium metal and strontium aluminate residue are removed from the furnace. Strontium metal then is sold as such without any additional grinding. A characteristic flow diagram of the production of strontium metal is shown in Figure 10.4.

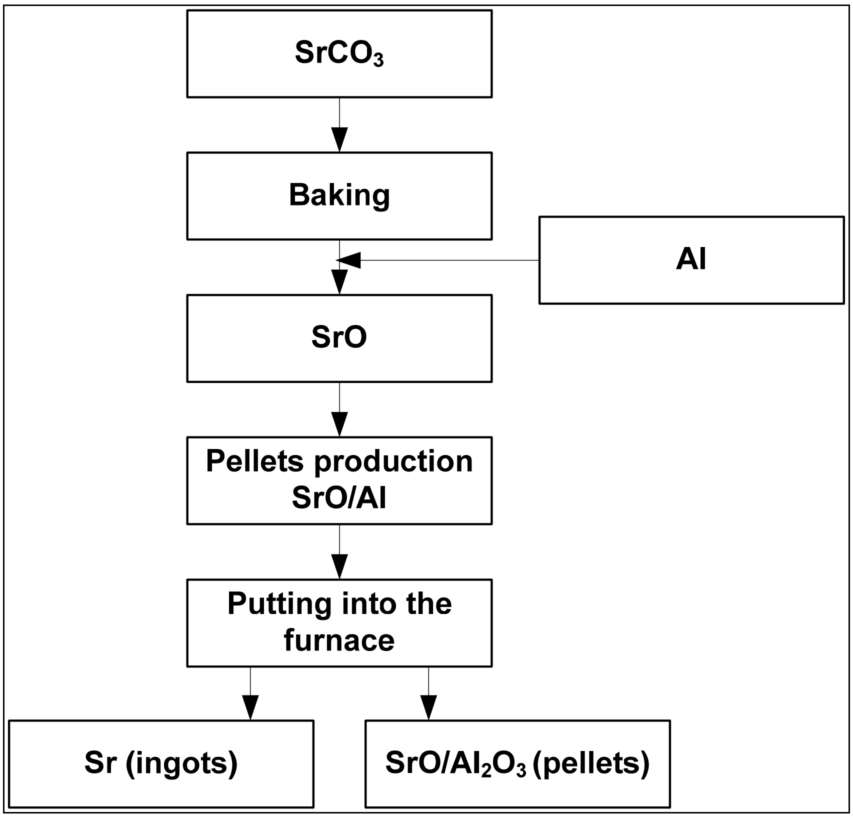


**Figure 10.4: Flow diagram of the production of strontium metal**

## 10.1.5 Magnesium metal

Magnesium metal and magnesium alloys have widespread use in different industrial sectors, for instance as an alloying element in aluminium as well as in automotive, telecommunication or electrical applications. Magnesium can also be used for cathodic protection of pipelines, tanks and bridges.

Magnesium can be produced either by electrolysis or by a thermal reduction process. The raw materials used are dolomite, magnesite, carnalite, brines or seawater, depending on the process. Magnesium will also be recovered and produced from a variety of secondary raw materials that contain magnesium.

### 10.1.5.1 Production of primary magnesium by thermal reduction

In the thermal reduction process, calcined dolomite is reacted with ferro-silicon sometimes together with aluminium in a furnace or retort vessel. The calcination process takes place by de-carbonisation and dehydration of dolomite limestone. For the calcination process for dolime, a rotating or vertical furnace can be used. A schematic overview of the thermal reduction process is give Figure 10.5.

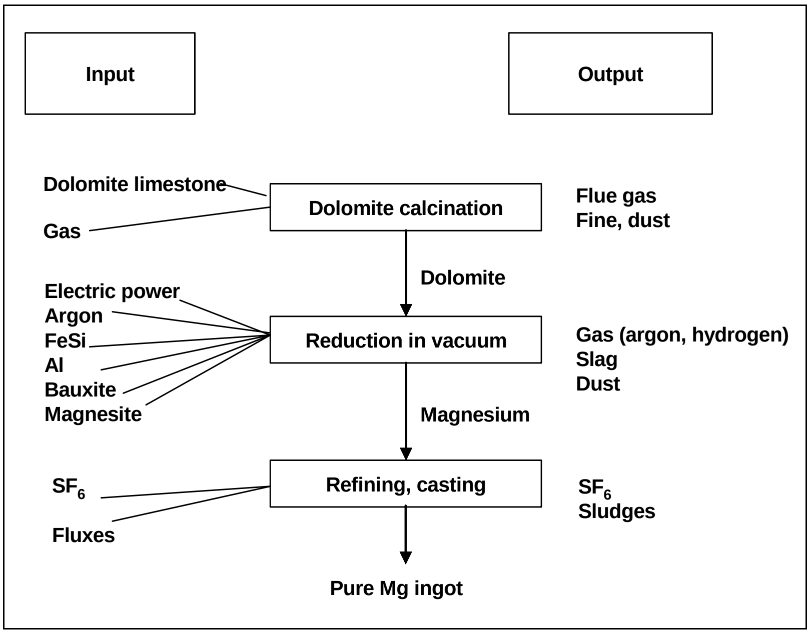


**Figure 10.5: Schematic flow sheet of the thermal reduction process to produce magnesium metal**

The metallothermic process is operated under vacuum and produces magnesium vapour, which is subsequently condensed into liquid or solid form. This operation is carried out in a furnace electrically heated by the Joule effect where the liquid slag acts as a resistor between the electrode and a carbonaceous bottom lining. The reduction is carried out at 1700 ºC and 6 kPa pressure. Reducing agents and oxides are introduced continuously over the slag. Argon is also introduced to form an inert atmosphere. The magnesium is condensed in a condenser cooled by water (crucible). This crucible is taken apart when it is full, and then transported to the foundry to produce magnesium ingots.

#### 10.1.5.2 Electrolytic production of primary magnesium

The electrolytic process produces magnesium by the electrolysis of magnesium chloride, which can be produced from various raw materials. The production from dolomite and seawater is described, as practised by a European producer. The dolomite, which is brought to the plant, is calcined in a gas suspension calciner. The feed is introduced through cyclones countercurrently to the hot exhaust gases, then calcined to dolime in a reactor fired with gas.

The dolime is slaked with seawater to produce a precipitated magnesium hydroxide. Prior to the slaking, the seawater is de-carbonated by stripping with air after acidification with hydrochloric acid. The magnesium hydroxide is concentrated by reducing the water content in a thickener. The resulting magnesium hydroxide pulp is fed to a rotary kiln and calcined to a light burnt magnesium oxide. The magnesium oxide is then mixed with carbon and pelletised.

The pellets are fed into the chlorinators, which are brick-lined shaft furnaces. The chlorinators are charged from the top, and the chlorine gas that is recycled from the electrolysis stage is introduced near the bottom. The reaction in the furnace converts the magnesium oxide into magnesium chloride, which in the molten form is purified by passing over the carbon resistors countercurrently to the incoming chorine gas. The liquid magnesium chloride is withdrawn from the furnace and transferred via closed vessels to the electrolysis stage.

Magnesium chloride is electrolysed in the electrolytic cells at 300 - 400 kA into liquid magnesium metal. The magnesium metal is withdrawn from the cells and transported in closed vessels to the cast-house where the metal is cast as pure magnesium or as magnesium alloys in ingots. To prevent the metal from oxidation by the surrounding air, the use of sulphur hexafluoride ($SF_6$) in the casting process can protect the metal surface.

The off-gas from the chlorination furnaces is treated in a series of wet scrubbers and wet electrostatic precipitators before finally being subjected to incineration. $SO_2$ gas is added to the off-gas between scrubbing stages to convert $Cl_2$ into HCl and thereby enhance the efficiency of the scrubber.

The contaminated water streams mainly from the chlorination off-gas treatment are treated in a two-stage water treatment plant. The first stage consists of a flocculation and solids separation, the second stage cleaning by activated carbon. The process of magnesium production by electrolysis is shown in Figure 10.6.

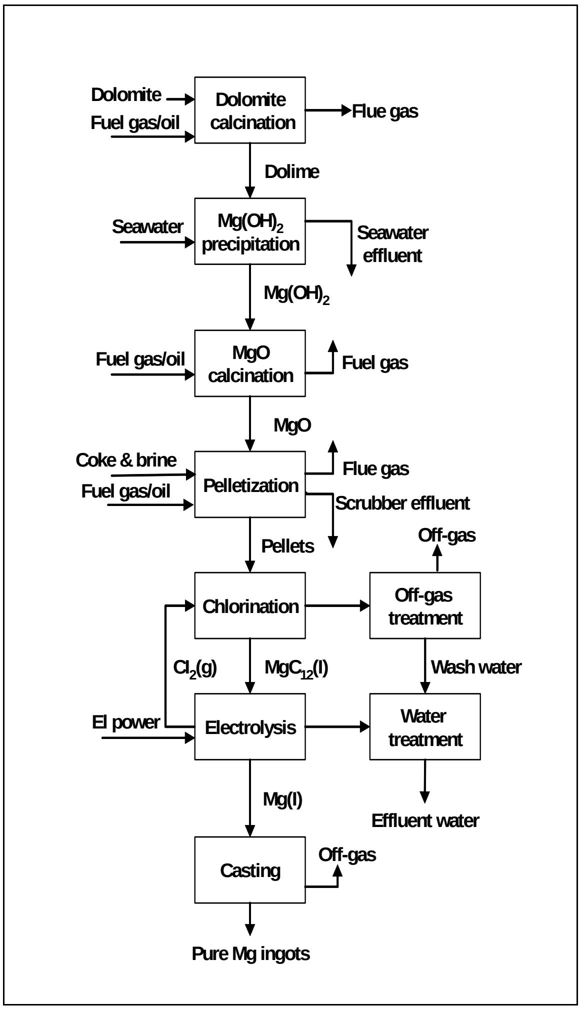


**Figure 10.6: Process flow diagram of magnesium production by electrolysis**

### 10.1.5.3 Production of magnesium from secondary raw material

Due to the increasing availability of magnesium scrap and other secondary raw material that contain magnesium, the production of secondary magnesium becomes more and more important. Scrap magnesium alloys may be directly recycled in house or sent to an external recycling facility. According to the quality, recyclable magnesium materials can be classified as shown in Table 10.1.

| Type of secondary raw material | Classification | Description |
|---|---|---|
| Magnesium scrap | Type 1 A | High grade clean scrap, e.g. scrap castings, biscuits, etc. |
| | Type 1 B | Clean scrap with a high surface area, e.g. thin castings, flashings, etc. |
| | Type 2 | Clean scrap with steel/aluminium inserts. No copper or brass contamination. If the copper or brass is contaminated, the scrap is treated as a special case |
| | Type 3 | Scrap castings, painted with/without inserts of steel/aluminium. No copper or brass contamination. If the copper or brass is contaminated, the scrap is treated as a special case |
| Other material that contains magnesium | Type 4 | Unclean metal scrap e. g. oily, wet or other contamination<br>The material may contain:<br>• silicon contamination, e.g. tumbling, beads, sand, etc.<br>• aluminium alloys<br>• copper-contaminated alloys<br>• non-magnesium sweepings |
| | Type 5 A | Chips, swarf or machinings which are clean, dry and uncontaminated |
| | Type 5 B | Chips, swarf or machinings which are oily and/or wet |
| | Type 6 A | Flux-free residues, e.g. crucible sludge, dross, etc., which should be dry and silica-free (sand free) |
| | Type 6 B | Flux residues, e.g. crucible sludge, dross, etc., which should be dry and silica free (sand free) |

**Table 10.1: Definition of magnesium scrap and materials for recycling**

Typical secondary magnesium production is shown in Figure 10.7.

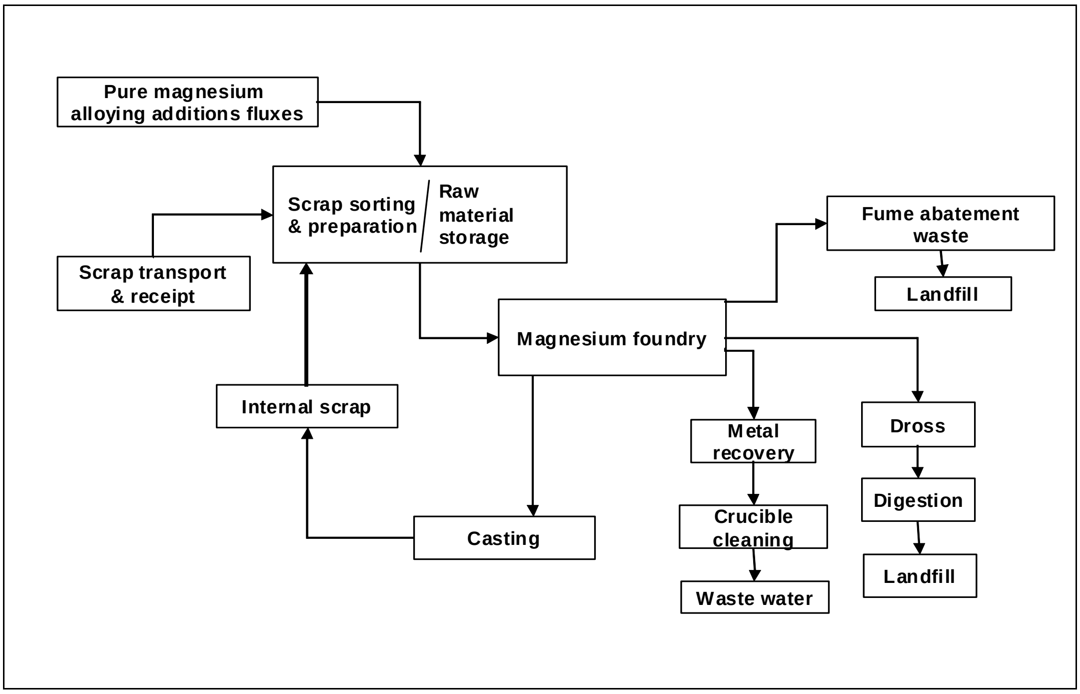


**Figure 10.7: Flow sheet of a production process for secondary magnesium**

The process begins with the receipt of the different secondary raw materials. After a quality control to define the type of scrap, it is stored separately in order to define the most appropriate way of recycling. The sorted raw material is then sent to the melting shop. Magnesium melting and alloying is carried out in indirect gas or electric furnaces. Fluxes or inert blanketing gases are used. Sulphur hexafluoride ($SF_6$) may be used but the European Council and Parliament adopted Regulation (EC) 842/2006 on certain fluorinated greenhouse gases (the F-Gas Regulation). This Regulation entered into force on 4 July 2007 and, inter alia, prohibits the use of SF6 in magnesium die casting as of 1 January 2008, except where the quantity involved is below 850 kg per year (Art 8([1])).

The melted metal is then cast into secondary magnesium ingots of semi-finished products.

## 10.2 Current emission and consumption levels

The production of alkali metals as well as calcium, strontium and magnesium metal causes environmental impacts to air, water and land, where the most significant emissions can be classified in principle as follows.

***Consumption of raw material and energy***

- Raw material and energy consumption

***Emissions to air***

- Dust from the dolomite and the magnesium oxide calcination.
- Chlorine and HCl as part of the cell gases and the cell room ventilation.
- Chlorinated hydrocarbons from the use of refrigeration and compression techniques to liquefy chlorine.
- $SF_6$ that is used in the casting operation to protect the molten magnesium from re-oxidation.
- PCDD/F generated by the chlorination step in the electrolytic production of primary magnesium.

***Solid residues, wastes and by-products***

- Dust, fume and sludge
- Calcium and strontium aluminate.

***Waste water emissions***

- Overflow water from wet scrubbing systems.
- PCDD/F, because the production of magnesium in an electrolytic process generates PCDD/F from the chlorination step. This should be removed from the scrubbing water.
- Blow down from cooling water cycles.

### 10.2.1 Consumption of raw material and energy

The required amount of energy for the production of calcium metal using the metallothermic process is about 20 - 25 kWh/kg of produced metal. To this direct energy must be added to the energy employed to produce the calcined CaO and electrolytically-produced aluminium. The production of calcium metal by electrolysis, which is not used in Europe, requires about 33 - 55 kWh/kg of calcium metal for a current efficiency of about 60 %.

The consumption of electrical energy in the electrolysis of magnesium is in the range of 13 - 14 kWh/kg Mg. The energy required for the production of magnesium chloride from the various raw materials must be added.

### 10.2.2 Emissions to air

The available data of the emissions to air for the production of alkali and alkaline earth metals are presented in terms of the emission to air from the production of sodium and lithium metal in Table 10.2, Table 10.3 and Table 10.4. Specific emission factors are also given in this table.

| Pollutant | Sodium metal | | Lithium metal | |
|---|---|---|---|---|
| | (mg/Nm$^3$) | (g/t) | (mg/Nm$^3$) | (g/t) |
| Chlorine | 0.1 - 1 | 0.05 | 1 - 16 | 18.2 |
| HCl | NA | NA | 1 - 2 | 103 |
| Refrigerant R 22 (¹) | | 200 | NA | NA |
| Dust | 4 - 6 | 120 | NA | NA |

(¹) R 22 is an Ozone Depleting Substance and targeted for phase-out.
NA = data not available

**Table 10.2: Emission to air from the production of sodium and lithium metal**

The main environmental input to the atmosphere by producing calcium and strontium metal are dust emissions. Dust may be generated by unloading and crushing the calcined lime, by mixing and compacting lime and aluminium and by grinding and screening the produced metal. Due to the baking operation that is necessary to produce strontium oxide for the production of strontium metal, about 420 kg of $CO_2$ is generated to the atmosphere for each tonne of strontium oxide produced.

The production of magnesium metal is related to the emissions of dust, $SO_2$, $NO_X$, $Cl_2$, HCl, PCDD/F and, in several cases, the emission of sulphur hexafluoride ($SF_6$). Dust is mainly emitted from the calcination of dolime. PCDD/F is generated from the chlorination furnace where magnesium oxide is converted into magnesium chloride. The emission of sulphur hexafluoride ($SF_6$) is due to the need to prevent re-oxidation of the magnesium metal. It should be noted that $SF_6$ has a very high global warming potential (23900 times the effect of $CO_2$) and is therefore a controlled substance under the Kyoto protocol.

Regulation (EC) No 842/2006 on certain fluorinated greenhouse gases (F-Gas Regulation) prohibits the use of F-Gases in applications (Art. 8) where containment was not feasible or where alternatives were readily available. The use of $SF_6$ in magnesium die casting is one of those use prohibitions and applies as of 1 January 2008, except where the quantity involved is below 850kg per year (Article 8(¹)).

| Pollutant | Source and concentration (mg/Nm$^3$) | Unit mass/t of magnesium metal |
|---|---|---|
| Dust | From dolomite calcination 100(¹)<br>From MgO calcination 16<br>From pellet drying 40<br>From chlorination off-gas treatment 3<br>From chlorination (ventilation gas) 16 | 4 kg/t<br>(representing the whole process) |
| $SO_2$ | From dolomite calcination 30<br>From MgO calcination 80<br>From pellet drying 30<br>From chlorination off-gas treatment 200<br>From chlorination (ventillation gas) 50 | 7 kg/t<br>(representing the whole process) |
| $NO_X$ | From dolomite calcination 80<br>From MgO calcination 110<br>From pellet drying 50 | 3 kg/t<br>(representing the whole process) |
| $Cl_2$ and HCl | From chlorination off-gas treatment 70<br>From chlorination (ventillation gas) 50<br>From electrolysis 3 | 4 kg/t<br>(representing the whole process) |
| PCDD/F | From chlorination off-gas treatment 0.8 ng ITEQ/Nm$^3$<br>From chlorination (ventillation gas) 0.8 ng ITEQ/Nm$^3$ | 12 µg/t ITEQ<br>28 µg/t ITEQ<br>13 µg/t ITEQ |
| $CO_2$ | Emission from the whole process | 6.3 t/t |
| $SF_6$ | From the cast-house | 0.45 kg/t of cast magnesium |

(¹) The off-gas from the gas suspension calciner that is used for the dolomite calcination is cleaned by using an ESP

**Table 10.3: Emissions to air from the production magnesium metal by the electrolytic process**

| Pollutant | Source | $mg/Nm^3$ | Unit mass/t of magnesium metal |
|---|---|---|---|
| Dust | Dolomite calcining | <100 | 3.5 kg/t. |
| $CO_2$ |  | 130 - 180 $g/Nm^3$ | 4.5 - 6 t/t |
| $SO_2$ |  | 0.5 | 0.016 kg/t |
| $NO_X$ |  | 90 | 3.1 kg/t |
| $N_2O$ |  | 4 | 0.13 kg/t |
| Dust | Reduction in vacuum | NM | 0.5 kg/t (1) |
| Argon |  | NM | 4.3 $Nm^3/t$ |
| Hydrogen |  | NM | 0.7 $Nm^3/t$ |
| PCDD/F | Reduction, refining and melting | 0.08 ng ITEQ/$Nm^3$ | 3 µg/t ITEQ |
| $SF_6$ | Refining and casting | NM | 0.5 - 1 kg/t |
| (1) Using a wet scrubber<br>NM = not measured |  |  |  |

**Table 10.4: Emission to air from the production of magnesium metal using thermal reduction**

## 10.2.3 Emissions to water

For the production of alkali and alkaline metals, the emissions to water are very dependent on the process used, for instance the abatement system and the type of waste water treatment. A variety of different water collection and waste water treatments exist. The main water pollutants are suspended solids, metal compounds and, in the case of magnesium electrolysis, chlorinated hydrocarbons and PCDD/F. The production of calcium and strontium metal is not related to the generation of process-specific waste waters. Available information about emissions to water is presented in Table 10.5 and Table 10.6.

| Component | Sodium metal | Lithium metal (mg/l) |
|---|---|---|
| Chlorine total | Effluent re-used | NA |
| Suspended solids | Effluent re-used | 20 - 40 |

**Table 10.5: Emissions to water by producing sodium and lithium metal**
[ 103, Farrell, F. 1998 ]

| Pollutant | Source | Emissions | Unit mass/t |
|---|---|---|---|
| Magnesium hydroxide | Dolime slaking |  | 21 kg/t MgO |
| Calcium hydroxide | Dolime slaking |  | 100 kg/t MgO |
| Coke | Pelletisation |  | 1.6 kg/t Mg metal |
| Chlorinated Hydrocarbons(1) | Water treatment | 0.15 $mg/m^3$of water | 0.017 g/t Mg metal (Total 0.053) |
| PCDD/F | Water treatment | 100 ng ITEQ/$m^3$ | 13 µg/t Mg metal Total 33 µg/t Mg metal (ITEQ) |
| (1) Sum of hexachlorobenzene, pentachlorbenzene and octochlorostyrene |  |  |  |

**Table 10.6: Emission to water by producing magnesium metal using the electrolytic process**

The production of secondary magnesium generates dross and crucible residues, which cannot be recycled and therefore should be digested in water to give an inert magnesium hydroxide, with alloying elements, in the form of a hydrated sludge. About 0.5 tonnes of sludge is generated per tonne of metal and contains approximately 50 % water.

### 10.2.4 By-products, process residues and waste

The production of alkali and alkaline metals is related to the generation of several by-products, residues and wastes, which are also listed in the European Waste Catalogue (Council Decision 94/3/EEC). *This has been replaced by a new directive 75/442/EEC (see Section 5.2.4)* The most important process-specific residues from the production of alkali and alkaline metals are listed below in Table 10.7.

| Metal produced | Residue | Source | Amount |
|---|---|---|---|
| Sodium | Filter cake | Sodium cleaning stage | NA |
| | Sediment | Storage tanks(1) | NA |
| | Chlorine | Produced as a by-product | 1.6 t Cl/t metal |
| Lithium | Mother liquor | Crystallisation | NA |
| | Used anodes | Electrolytic cell | NA |
| Calcium | Calcium aluminate | Vacuum furnace | NA |
| | Used furnace linings | Vacuum furnace | NA |
| Strontium | Strontium aluminate | Vacuum furnace | NA |
| | Used furnace linings | Vacuum furnace | NA |
| Magnesium (electrolytic process) | Sludge and gravel | Dolime slaking | 0.05 t/t MgO |
| | Slag | Chlorination furnace | 0.14 t/t metal |
| | Sludge that contains PCDD/F | Water treatment | 0.01 t/t metal |
| | Sludge that contains metals | Electrolysis and cast-house | 0.04 t/t metal |
| | Dolime dust | By-product from dolomite calcination | 0.28 t/t MgO |
| | Excess electrolyte | By-product from electrolysis | 0.18 t/t metal |
| Magnesium (thermal process) | Dolomite and filter dust | Dolomite and limestone screening | 1 t/t metal |
| | Granulated slag | Reduction vacuum furnace | 2.5 - 3 t/t metal |
| | Fine dry slag | | 0.5 - 0.7 t/t metal |
| | Wet slag | | 0.3 - 0.5 t/t metal |
| | Slag | Refining stage | 0.3 t/t metal |

(1) Sediment from storage tanks are burnt on an open hearth and fumes are collected and scrubbed in a two-stage water scrubber discharged into a third stage using HCl, which treats also fumes from washing the filter cake
NA = data not available

**Table 10.7: Residues from the production of alkali and alkaline metals**

## 10.3 Techniques to consider in the determination of BAT

The sections of this document entitled 'Techniques to consider in the determination of BAT' set out techniques considered generally to have potential for achieving a high level of environmental protection in the industries within the scope of the document. The background to the way the techniques are described is given in Section 2.1.2 and Table 2.2.

This section presents a number of techniques for the prevention or reduction of emissions and residues as well as techniques reducing the overall energy consumption. They are all commercially available. Examples are given in order to demonstrate techniques which illustrate a high environmental performance. The techniques that are given as examples depend on information provided by the industry, European Member States and the evaluation of the European IPPC Bureau. The general techniques described in Chapter 2 as 'common processes' apply to a large extent, to the processes in this sector and influence the manner in which the main and associated processes are controlled and operated.

The raw material handling and pretreatment processes and the process control and abatement systems are particularly relevant. The control of electrolytic cells and furnace operating parameters and the prevention of diffuse emissions from electrolytic cells, furnaces, tapping and pouring processes are also important. Techniques used by other sectors are also applicable particularly those relating to the collection, handling and scrubbing of chlorine gas and the production of sodium hypochlorite using two scrubbers in series. These techniques are covered in the BAT Reference Document for the Chlor-Alkali Industry, which should also be referred to.

### 10.3.1 Materials, storage and handling

**Description**
The raw materials used for the production of alkali and alkaline metals are sodium chloride, lithium and strontium carbonate, etc. limestone, dolomite magnesite and reducing agents, e.g. aluminium powder. The main environmental impact from the storage and handling of these materials are dust emissions, which sometimes arise as diffuse dust emissions [ 196, Finkeldei, L. 1999 ].

The raw materials are preferably stored and handled inside where closed drums, silos, bins and hoppers are used to prevent diffuse emissions to the environment as well as to the workspace. Limestone and dolomite may also be stored in stockpiles where the appropriate measures against the generation of dust should be taken.

Closed conveyors and transfer systems are used for the handling of dusty fine materials, where extraction and filtration equipment is used for dusting delivery points. The dust laden air from the silos, closed conveyors and charging systems are cleaned by using fabric filters, which may be monitored by measuring the pressure drop to control the cleaning mechanism. Some plants use crushers or agglomeration and pelletisation equipment to obtain the desired size of charging material. Fabric filters clean the suction air of crushers and agglomeration equipment.

**Achieved environmental benefits**
Prevention and capture of dust a d reduction of emissions.

**Cross-media effects**
No data was reported.

**Operational data**
Given in the descriptions of the process above.

**Applicability**
These techniques are applicable to most installations.

**Economics**
No data was reported.

**Driving force for implementation**
Environmental impact and energy costs due to lost material.

**Example plants**
UK, FR, DE.

**Reference literature**
[ 196, Finkeldei, L. 1999 ], [ 290, EC 2006 ].

## 10.3.2 Pretreatment techniques

The production of magnesium metal is partly based on calcined dolomite and magnesite as a raw material. The calcination may be made in rotary or vertical furnaces. Different fuels, for instance natural gas, can heat the furnaces. A new technology used for calcining dolomite is the gas suspension calcining process which is presented in the following example.

### 10.3.2.1 Gas suspension calcining process for dolomite and magnesite

**Description**
The gas suspension calcining process consists of several process stages. The first stage is drying the dolomite in a flash dryer using the hot off-gases from the plant. The dry material is then crushed in a special cone crusher. The pulverised feed is injected into the riser between the second and the first preheater cyclone. Upon entering the riser duct, the material initially falls countercurrently to the hot gas stream. After being preheated in the fourth cyclone, the material has reached calcining temperature and is directed to the calciner where complete calcination takes place. The calciner is basically a vertical cylinder where air, fuel and material enter at the bottom and exhaust gases carrying calcined material leave at the top. The calcined particles are carried by the gas stream to a disengaging cyclone from which the hot gases pass to the preheater while the product is discharged by the force of gravity to the cooler. The process is controlled by a high standard computerised instrumentation and control system [ 196, Finkeldei, L. 1999 ]. See Figure 10.8.

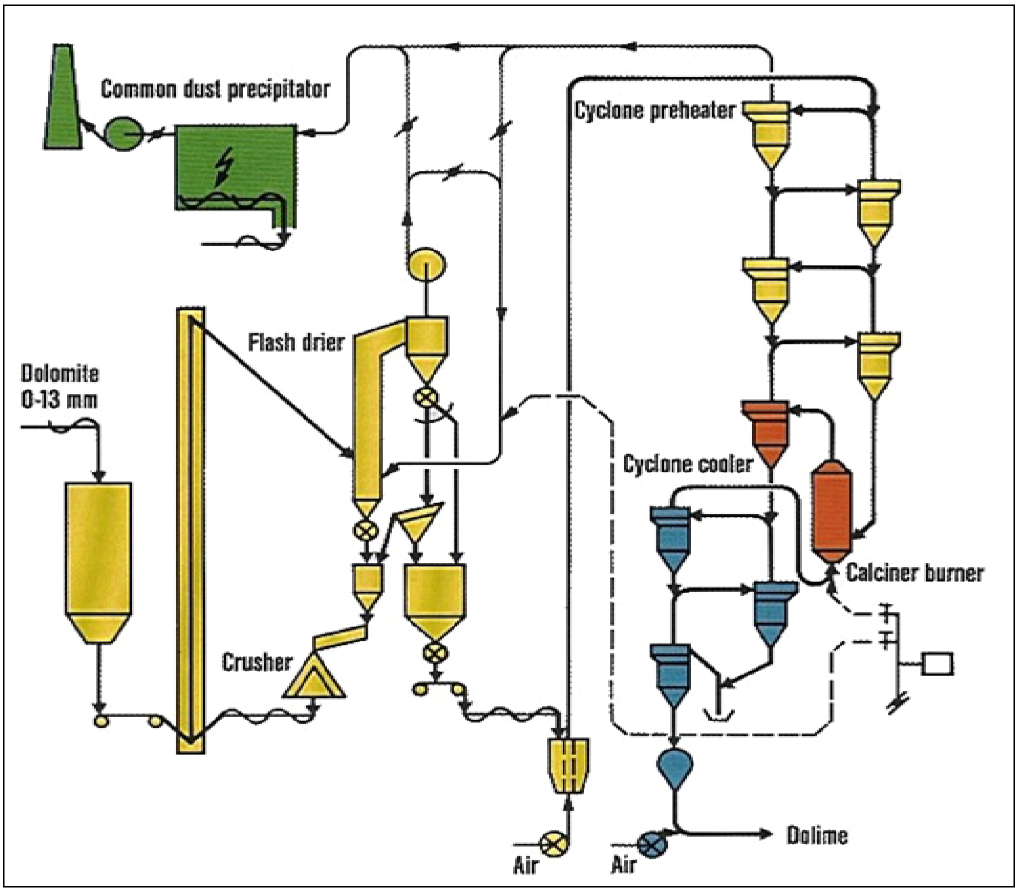


**Figure 10.8: Gas Suspension calciner**

**Achieved environmental benefits**
Reduction of fuel consumption compared to other systems, due to the intensive use of product and off-gas heat energy.

**Cross-media effects**
No data was reported.

**Operational data**

| | |
|---|---|
| Fuel consumption | 1145 kcal//kg |
| Power consumption | 33 kWh/t product |

The emission level of dust using an ESP is less then 30mg/Nm$^3$.

**Applicability**
This technique is applicable to new and existing plants (also of other production processes where calcination takes place, e.g. in the lime production).

**Economics**
The process has lower operating costs than other systems.

**Driving force for implementation**
Reduction in energy consumption.
**Example plants**
DE.

**Reference literature**

[ 147, FL Smidth (DK) 1992 ].

## 10.3.3 Core processes

The most important part of the alkali and alkaline earth metal production is the electrolytic cell for the electrolytic production process and the vacuum furnace used for the thermal reduction process. According to the small number of producers and subsequently the small number of operational plants in the EU and worldwide, the techniques presented as applied techniques are also techniques considered in the determination of BAT.

All electrolytic magnesium is produced by electrolysis of magnesium chloride, in most cases water-free (anhydrous) chloride. Thus, there are two core steps in the process:

- the production of anhydrous magnesium chloride from raw materials, and
- the electrolysis of the magnesium chloride.

There are a number of processes for the preparation of anhydrous chloride. The following example gives the description of a dehydration process that has been successfully implemented.

### 10.3.3.1 Primary magnesium production using the dehydration process

**Description**
The $MgCl_2$ brine dehydration process developed by Norsk Hydro has been implemented in the Norsk Hydro Canada plant which started up in 1989. The process is described below and is illustrated in Figure 10.9 [ 200, Amundsen 1999 ].

***The $MgCl_2$ brine dehydration plant*:**
The plant produces $MgC1_2$ brine by dissolving magnesite rock in hydrochloric acid (HCl). After purification to remove dissolved impurities such as iron and aluminium, the brine is subjected to evaporation and particulation to create a granular material ("prills") suitable for fluidised bed drying techniques. The prills are subsequently dried in two-stages, first by hot air and then by HCl gas, to produce an essentially anhydrous $MgCl_2$ product.

***Electrolysis and HCl synthesis:***
The high-amperage electrolysis cells of are operated at around 400 kA. They are fed on a continuous basis with anhydrous $MgCl_2$ prills from the dehydration plant. Liquid magnesium metal is withdrawn from the cells intermittently and transported in closed vessels to the casthouse.

The chlorine gas formed in the electrolysis process is recycled by reaction with hydrogen to produce the hydrochloric acid used in the magnesite-dissolving stage. Energy is recovered from this HCl synthesis stage in the form of steam generated.

***Refining, alloying and casting*:**
In the casthouse, the magnesium metal is refined, alloyed and cast into ingot products.

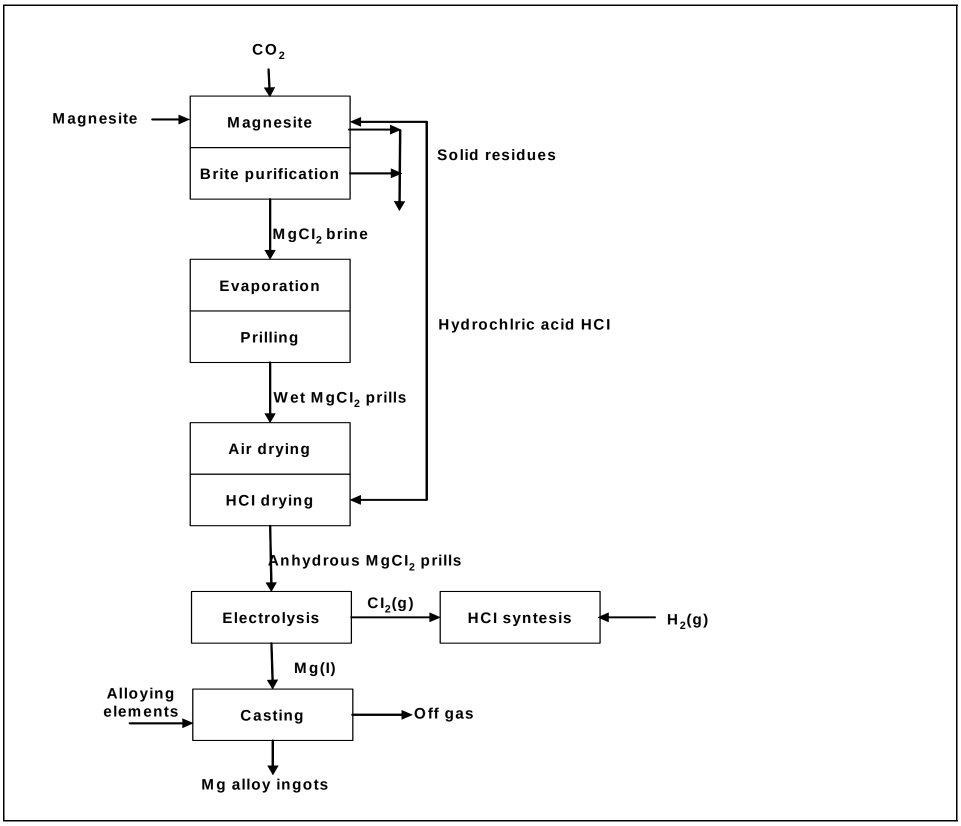


**Figure 10.9:** **Block diagram for the dehydration process for primary magnesium production**

## Achieved environmental benefits

The following typical environmental performance data have been achieved [ 200, Amundsen 1999 ]:

### *Air emissions:*

| | | |
|---|---|---|
| Dust | 0.4 | kg/t Mg |
| $SO_2$ | <0.2 | kg/t Mg |
| $NO_X$ | 2 | kg/t Mg |
| $Cl_2$ + HCl | <1.0 | kg/t Mg |
| $SF_6$ | 0.5 | kg/t Mg |
| PCDD/F(1) | <1.0 | µg/t Mg |

### *Water emissions:*

Chlorinated Hydrocarbons: <0.01 g/t Mg as the sum of hexa- and penta-chlorobenzene and octachlorostyrene

PCDD/F: <0.1 µg/t Mg as the sum of PCDDs and PCDFs expressed as ITEQ

## Cross-media effects

No data has been reported.

## Operational data

Given above in the description.

## Applicability

This technique is applicable to new plants.

## Economics

No data has been reported.

## Driving force for implementation

Reduction in emissions.

**Example plants**
Canada.

**Reference literature**
[ 200, Amundsen 1999 ].

## 10.3.4 Gas collection and abatement

The techniques for fume collection and abatement discussed in Chapter 2 of this document are techniques to consider for the production of alkali and alkaline metals. Fabric filter and wet scrubbers and also multi-stage scrubbers are normally used for off-gas-cleaning . The ventilation air from a cell-room where sodium metal is produced can be extracted by using a two-stage venture scrubber and a packed tower using caustic soda to remove chlorine.

As can be shown in the next section, the off-gas from the chlorination furnace in a magnesium production is cleaned in a series of wet scrubbers and wet electrostatic precipitators before being finally subjected to incineration in an afterburner. The chlorine gas formed by the magnesium electrolysis is cleaned in a fabric filter in order to remove entrained salts before being recycled back to the chlorination stage.

### 10.3.4.1 Treatment of off-gases that contain PCDD/F and chlorinated hydrocarbons

**Description**
Off-gases from the chlorination furnaces in the magnesium plant contain $Cl_2$ and HCl, PCDD/F and chlorinated hydrocarbons. The off-gases are treated in a series of wet scrubbers to remove the $Cl_2$ and HCl, and then wet electrostatic precipitators to remove aerosols from the gas, before finally being subjected to incineration. $SO_2$ gas is added to the off-gases between scrubbing stages to convert $Cl_2$ to HCl and so enhance the efficiency of the scrubbing. Water from the off-gas treatment is transferred to a waste water treatment plant [ 200, Amundsen 1999 ].

***The incineration plant*:**
**A**fter scrubbing, the off-gases still contain unacceptable amounts of PCDD/F and CHCs. They are therefore subjected to a final incineration treatment, where volatile organic compounds including PCDD/F and chlorinated hydrocarbons are destroyed.

The incineration plant has five vertical chambers filled with ceramic stoneware for heat exchange, and are switched by flow control valves to achieve effective heat recuperation. Incoming gas is led through chambers in the hottest chamber and heated to reaction temperature before entering the horizontal combustion chamber on top of the chambers. In the combustion chamber the CO content of the gas (approximately 1 - 2 %) is burned together with fuel gas supplied through three gas burners to keep the temperature in the combustion chamber above 800 ºC.

The treated gas is then led through the cool chambers to recover its heat content for heating in-coming gas after the switching of chambers. Treated gas is then vented to the stack [ 200, Amundsen 1999 ].

**Achieved environmental benefits**
Significant reduction of chlorinated hydrocarbons and PCDD/F and the recovery of the heat energy that is generated in the combustion chamber of the incineration plant [ 200, Amundsen 1999 ].

Destruction efficiencies achieved:

| | |
|---|---|
| Chlorinated hydrocarbons | 99.9 % (total efficiency) |
| PCDD/F | 99.9 % (total efficiency) |
| CO | 100 % |

Outlet concentrations:

| | |
|---|---|
| Chlorinated hydrocarbons | 0.01 mg/Nm$^3$ as the sum of hexa- and penta-chlorobenzene and octachlorostyrene. |
| PCDD/F | 0.8 ng I-TEQ/Nm$^3$ as the sum of PCDDs and PCDFs. |

**Cross-media effects**
In the scrubbers the PCDD/F and chlorinated hydrocarbons are transferred from the air to the water side, therefore an additional waste water treatment is needed.

**Operational data**

| | |
|---|---|
| Volumetric capacity: | 70000 Nm$^3$/h |
| Combustion chamber temperature: | Above 800 ºC |
| Residence time in combustion chamber: | Minimum 2 seconds |

Energy

| | |
|---|---|
| Fuel gas | 30000 GJ/yr |

**Economics**
No data has been reported.

**Applicability**
This technique is applicable to all new and existing plants.

**Driving force for implementation**
Reduction of PCDD/F emissions.

**Example plants**
Canada.

**Reference literature**
[ 200, Amundsen 1999 ].

## 10.3.5 Process control

The principles of process control discussed in Section 2.5 are applicable to the production processes used in this group. Computerised control techniques can be used for most of the process stages and different production routes.

## 10.3.6 Post-furnace operations

Alkali and alkaline metals are often sold in ingots, which is the case for magnesium, or in shaped pieces of different sizes. Metal ingots are made by casting the liquid metal into moulds where the metal need to be prevented from re-oxidation. Alkali metals such as sodium is also pressed into metal billets.

### 10.3.6.1 Extrusion plant for the production of alkali metal billets

**Description**

The metal is fed into a twin screw extruder, which is cooled in a way that the temperature falls slightly below the melting point just before the extrusion die. The sodium metal billets produced can be cut by an automatic cutting device under a protective gas. The process is shown in Figure 10.10

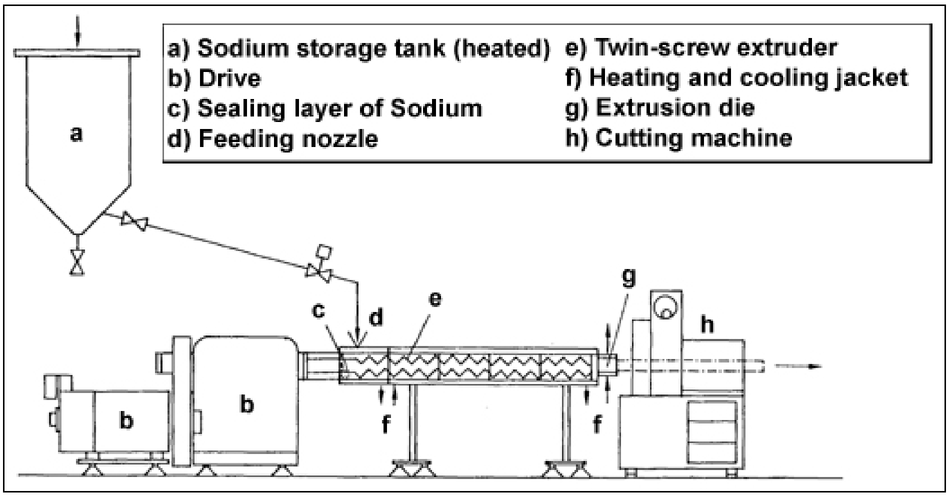


**Figure 10.10: Schematic of an extrusion plant for the production of alkali metal billets**

**Achieved environmental benefits**
The formation of impurities by reaction with air and atmospheric moisture is avoided.

**Cross-media effects**
No data has been reported.

**Operational data**
No data has been reported.

**Applicability**
This technique is applicable to all new and existing plants

**Economics**
No data has been reported.

**Driving force for implementation**
Reduction in emissions

**Example plants**
UK.

**Reference literature**
[ 104, Ullmann's Encyclopedia 1996 ].

## 10.3.7 Waste water

This is a site-specific issue, existing treatment systems are reported to be of a high standard. The techniques listed in Section 2.12.2 are the techniques to consider. In a number of installations cooling water and treated waste water including rainwater is re-used or recycled within the processes.

All waste water should be treated to remove dissolved metals and solids as well as PCDD/F and chlorinated hydrocarbons. The removal of PCDD/F and chlorinated hydrocarbons from the scrubbing water is necessary. An example of a waste water treatment plant that reduces PCDD/F and chlorinated hydrocarbons from scrubbing water is given in Section 10.3.7.1.

#### 10.3.7.1 Treatment of waste water that contains PCDD/F and chlorinated hydrocarbons

**Description**

Contaminated waste water streams from various parts of the magnesium plant, including water from the chlorination off-gas treatment, are treated in a waste water treatment plant to reduce the contents of PCDD/F and chlorinated hydrocarbons by more than 99 %.

**The water treatment plant**

The waste water treatment plant that is shown in Figure 10.11 is based on three different unit operations [ 200, Amundsen 1999 ].

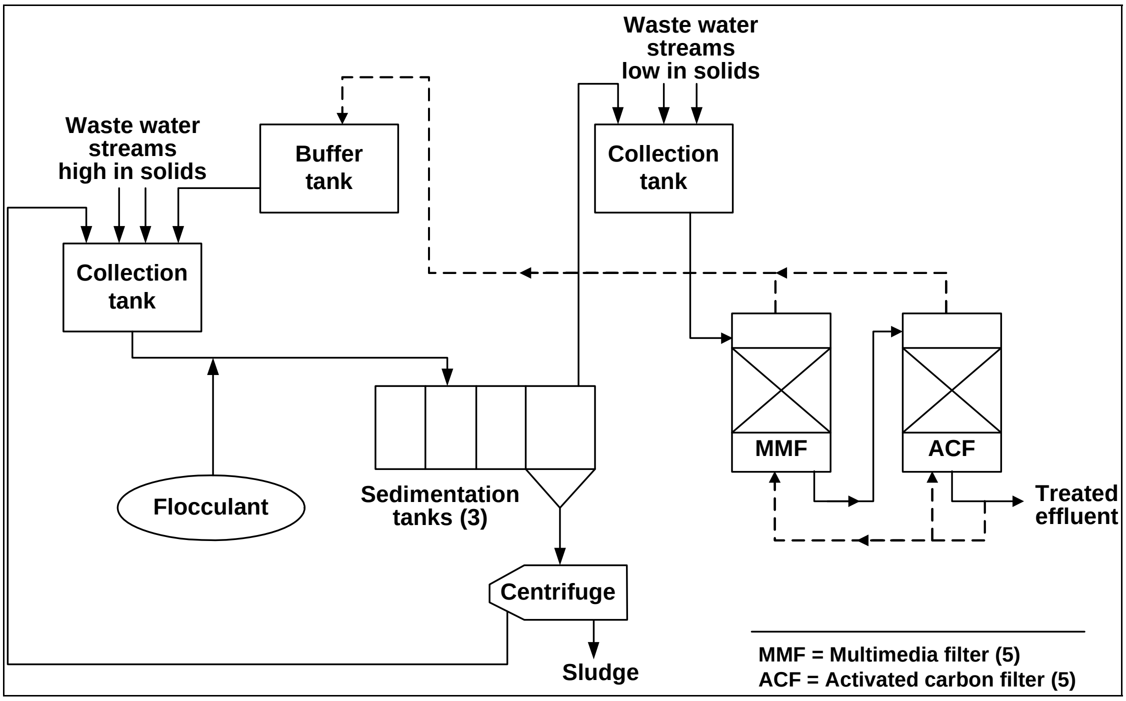


**Figure 10.11: Treatment plant for cleaning waste water contaminated by PCDD/F and chlorinated hydrocarbons**

Waste water streams with high concentrations of solid particles are collected and the solids separated by use of flocculation and sedimentation. The sludge from the sedimentation units is dewatered in a centrifuge to a water content of approximately 50 %. The solids from the water treatment that contain PCDD/F and chlorinated hydrocarbons, are incinerated off site.

The larger volume of waste water streams with low solid particle concentrations are treated in multimedia filters (sand filters), removing particles down to 1 µm. Solids are periodically washed back to the sedimentation units.

The last step in the treatment process is polishing on activated carbon. Small particles and the water-soluble part of PCDD/F and chlorinated hydrocarbons are adsorbed on activated carbon. The carbon is replaced periodically, and the used carbon is incinerated off site.

The waste water treatment plant is an integrated part of the chlorination plant. The plant is operated from a central control room with no extra operators needed. Periodical work is related to sludge handling, maintenance and replacement of the activated carbon.

**Achieved environmental benefits**

Efficiencies achieved: *THESE SHOULD BE UNDER OPERATIONAL DATA ??*

| | |
|---|---|
| Chlorinated hydrocarbons | 99.5 % or better |
| PCDD/F | 99.5 % or better |

Water outlet concentrations:

| | |
|---|---|
| Chlorinated hydrocarbons | 0.15 mg/Nm$^3$ of water as the sum of hexa- and penta-chlorobenzene and octachlorostyrene. |
| PCDD/F | 100 ng I-TEQ/m$^3$ of water as the sum of PCDDs and PCDFs. |

**Cross-media effects**
The sludge from the waste water treatment plant should be incinerated, which again produce emissions to air and soil.

**Operational data**

For the water treatment plant
Volumetric capacity: 600 m$^3$/h
Materials of construction allow acidic waste water to be treated at a pH as low as 1.5
Sludge generated: Approximately 350 t/yr (50 % water)

**Applicability**
This technique is applicable to all new and existing plants.

**Economics**
No data has been reported.

**Driving force for implementation**
Reduction of emissions of PCDD/F and chlorinated hydrocarbons.

**Example plants**
NO.

**Reference literature**
[ 200, Amundsen 1999 ].

### 10.3.8 By-products, process residues and waste

The processes that were discussed earlier as applied techniques in Sections 10.1 and 10.2 of present emission and consumption levels are all techniques to consider in the determination of BAT. The most important factor to reduce the environmental impact of discharging residues as waste are process-integrated measures that result in the generation of fewer residues. If the amount of process residues is minimised by using primary measures, the extended amount should be recycled or re-used as much as possible. The specific feed materials will influence the final process choice. The techniques discussed in Section 2.13.3 should also be considered in conjunction with these processes.

## 10.4 Best Available Techniques

In understanding this section and its contents, the attention of the reader is drawn back to the Preface of this document and in particular the fifth section of the Preface: ‘How to understand and use this document’. The techniques and associated emission and/or consumption levels, or ranges of levels, presented in this section have been assessed through an iterative process involving the following steps:

- identification of the key environmental issues for the sector which for the production of alkali and alkaline earth metals are: chlorine, HCl, PCDD/F, $SF_6$, dust fume, $CO_2$, $SO_2$, waste water, residues such as sludge, aluminate, filter dust and slag;
- examination of the techniques most relevant to address these key issues;
- identification of the best environmental performance levels, on the basis of the available data in the European Union and worldwide;
- examination of the conditions under which these performance levels were achieved; such as costs, cross-media effects, and the main driving forces involved in the implementation of the techniques;
- selection of the best available techniques (BAT) and the associated emission and/or consumption levels for this sector in a general sense, all according to Article 2(12) and Annex IV to the Directive.

Expert judgement by the European IPPC Bureau and the relevant Technical Working Group (TWG) has played a key role in each of these steps and in the way in which the information is presented here.

On the basis of this assessment, best available techniques, and as far as possible emission and consumption levels associated with their use, are presented in this section that are considered to be appropriate to the sector as a whole and in many cases reflect the current performance of some installations within the sector. Where emission and consumption levels 'associated with best available techniques' are presented, this is to be understood as meaning that those levels represent the environmental performance that could be anticipated as a result of the application, in this sector, of the techniques described, bearing in mind the balance of costs and advantages inherent within the definition of BAT. However, they are neither emission nor consumption limit values and should not be understood as such. In some cases, it may be technically possible to achieve better emission or consumption levels but due to the costs involved or cross-media considerations, they are not considered to be appropriate as BAT for the sector as a whole. However, such levels may be considered to be justified in more specific cases where there are special driving forces.

The emission and consumption levels associated with the use of BAT have to be seen together with any specified reference conditions (e.g. averaging periods).

The concept of ‘levels associated with BAT’ described above is to be distinguished from the term ‘achievable level’ used elsewhere in this document. Where a level is described as ‘achievable’ using a particular technique or combination of techniques, this should be understood to mean that the level may be expected to be achieved over a substantial period of time in a well maintained and operated installation or process using those techniques.

Where available, data concerning costs have been given together with the description of the techniques presented in the previous sections. These give a rough indication about the magnitude of the costs involved. However, the actual cost of applying a technique will depend strongly on the specific situation regarding, for example, taxes, fees, subsidies, and the technical characteristics of the installation concerned. It is not possible to evaluate such site-specific factors fully in this document. In the absence of data concerning costs, conclusions on economic viability of techniques are drawn from observations on existing installations.

The BAT (including the associated emission and consumption levels) given in this section are 'BAT in a general sense' (i.e. considered to be appropriate to the sector as a whole). It is intended that they are a reference point against which to judge the current performance of an existing installation or to judge a proposal for a new installation. In this way, they will assist in the determination of appropriate 'BAT-based' conditions for the installation or in the establishment of general binding rules under Article 9([8]) of the IPPC Directive. It is foreseen that new installations can be designed to perform at or even better than the BAT levels presented in this section. It is also considered that existing installations could move towards the BAT levels presented in this section or do better, subject to the technical and economic applicability of the techniques in each case.

While the BAT reference documents do not set legally binding standards, they are meant to give information for the guidance of industry, Member States and the public on achievable emission and consumption levels when using specified techniques. The appropriate permit conditions for any specific case will need to be determined taking into account the objectives of the IPPC Directive and the local considerations.

**Recommendation to help users/readers of this document:**

It is strongly recommended that this section on BAT be read in conjunction with the sections of this document that describe the techniques to consider in the determination of BAT. The applicability of the techniques and measures are reported in these sections and should be taken into account at a local level. To help the reader, references to the appropriate sections are included in the description of BAT.

If not otherwise mentioned, BAT associated emission and consumption levels given in this section are expressed as follows:

- for pollutants emitted to air (except dioxins): expressed on a daily average basis with standard conditions of 273 K, 101.3 kPa, measured oxygen content and dry gas with the plant operating normally under steady-state conditions and no dilution of the gases;
- for dioxins: expressed as the average over the sampling period which should preferably be a minimum of 6 hours;
- for waste water: based on qualified random samples or twenty four hour flow proportional composite samples.

As described in the Preface, this document does not propose emission limit values. The best available techniques and the ranges of emission or consumption levels associated with best available techniques (BAT-AEL ranges) are related to installations with different sizes, different kinds of operation and different raw materials. In this document, special local considerations cannot be taken fully into account. The determination of appropriate permit conditions will involve taking account of local, site-specific factors such as the technical characteristics of the installation concerned, its geographical location and the local environmental conditions. In the case of existing installations, the economic and technical viability of upgrading them also should be taken into account. Even the single objective of ensuring a high level of protection for the environment as a whole will often involve making trade-off judgements between different types of environmental impact, and these judgements will often be influenced by local considerations.

Although an attempt is made to address some of these issues, it is not possible for them to be considered fully in this document. The techniques and emission and consumption levels presented here will therefore not necessarily be appropriate for all installations. On the other hand, the obligation to ensure a high level of environmental protection including the minimisation of long-distance or transboundary pollution implies that permit conditions cannot be set on the basis of purely local considerations. It is therefore of the utmost importance that the information contained in this document be fully taken into account.

Section 2.20 to this document reports BAT for the following common processes and the following sections should be referred to for those techniques that are BAT:

- environmental management systems (EMS) (Section 2.20.1)
- material handling and storage (Section 2.20.2)
- process control (Section 2.20.3)
- fume and gas collection (Section 2.20.4)
- the prevention and the destruction of PCDD/F (Section2.20.5)
- sulphur dioxide removal (Section 2.20.6)
- the removal of mercury (Section 2.20.7)
- effluent treatment and water re-use (Section 2.20.8)
- energy efficiency (Section 2.20.9)
- intermediate products, process residues and wastes (Section 2.20.10)
- emission monitoring (Section 2.20.11)
- prevention of the formation of $NO_X$ (Section 2.20.12)
- removal of dust and particles (Section 2.20.13)

BAT for the production of alkali and alkaline metals is the combination of the generally applicable techniques reported in Section 2.20 and the specific techniques indicated in this section.

## 10.4.1 Prevention and control of emissions to air

### 10.4.1.1 Core processes

**a) BAT is to prevent diffuse emissions and optimise the use of energy by using one of the metallurgical processes given in Table 10.8 (See Section 10.1).**

| Produced metal | Process | Production unit | Abatement technique | Comments |
|---|---|---|---|---|
| Sodium | Electrolysis of fused sodium chloride | Electrolytic cell (Downs cell) | Wet scrubber for cleaning the cell room air during special operations such as changing diaphragms | The possible associated level of chlorine in the ventilation air is <1mg/Nm$^3$.<br>Chlorine alarms should be deployed in the cell room and in the chlorine processing plant |
| Lithium | Electrolysis of lithium and potassium chloride | Electrolytic cell (Downs cell) | Wet scrubber for cleaning the cell room air | The possible associated level of chlorine in the ventilation air is < 1 mg/Nm$^3$<br>Chlorine produced by the cell room is collected by partial vacuum and then absorbed in caustic soda to produce sodium hypochlorite.<br>Chlorine alarms should be deployed in the cell room |
| Potassium | Reduction of potassium chloride with sodium metal | Reaction column | Wet scrubber | There is no information about a plant producing potassium metal in the EU available |
| Calcium | Thermal reduction of calcium oxide with aluminium | Electrically-heated vacuum furnace | | The metal is condensed in the cooled part of the furnace.<br>There are no significant emissions from the furnace operation |
| Strontium | Thermal reduction of strontium oxide with aluminium | Electrically-heated vacuum furnace | | The metal is condensed in the cooled part of the furnace.<br>There are no significant emissions from the furnace operation |
| Magnesium | MgCl$_2$ brine dehydration | Evaporation/prilling | | PCDD/F emissions are <10 µg/t ITEQ. The process of chlorination can no longer be regarded as BAT for new plants producing magnesium by electrolysis |
| | Electrolysis of magnesium chloride (1) | High-amperage electrolysis cell | Fabric filter to clean the chlorine gas formed by the electrolysis, which is then recycled to the chlorination stage | The cell is operated in the rang of 300 - 400 kA.<br>The cell is fed with liquid magnesium chloride on an intermittent basis or with solid magnesium chloride on a continuous basis.<br>Liquid magnesium metal is withdrawn from the cell intermittently.<br>The amount of SF$_6$ used in the cast-house should be reduced as much as possible, and replaced by a less harmful substance as soon as possible(1) |
| | Thermal reduction of magnesium oxide by silicon | Electrically-heated vacuum furnace | ESP and (wet) fabric filter | The amount of SF$_6$ used in the cast-house should be reduced as much as possible, and replaced by a less harmful substance when it is possible(1) |

(1) Due to the extremely high global warming potential of SF$_6$, its use in the cast-house should be reduced as much as possible, and it should be replaced by other substances with lower global warming potential as soon as possible. It has been reported that SO$_2$ might be an alternative.

**Table 10.8: Production units considered as BAT for the production of alkali and alkaline metals**

### 10.4.1.2 Post furnace operations

**a) BAT is to prevent diffuse emissions and to optimise the use of energy by using one of the techniques given in Section 10.3 and listed below where they are applicable to the metal produced.**

- Crushing, grinding and screening materials in enclosures under reduced pressure and the use of cyclones and fabric filters to collect the ultrafines.
- Treatment of the ultrafines of calcium and strontium metal with water to avoid fire hazards.
- Separating the grinding and screening steps.
- Storing calcium in enclosures that are fire safe.
- Using nitrogen or other inert quenching in case of fires.

**b) BAT is to replace $SF_6$ with other substances with lower global warming potential as soon as possible. It has been reported that $SO_2$ might be an alternative.**

The F-Gas Regulation entered into force on 4th of July 2007 and prohibits the use of $SF_6$ in magnesium die casting as of 1 January 2008, except where the quantity involved is below 850 kg per year (Art 8([1])).

### 10.4.1.3 Fume and gas collection and abatement

**a) BAT is to prevent and control emissions to air from the production of alkali and alkaline metals using the techniques given in Table 10.8 and Table 10.9 or a combination of them (See Sections 2.4.5 and 2.9).**

**The emission levels given in Table 10.9 are the BAT-AELs.**

| Pollutant | Techniques | BAT-AELs | Comments |
|---|---|---|---|
| Dust | Fabric filter | <1 - 5 mg/$Nm^3$ | A bag burst detection system is needed (See Sections 2.9.2.2.4 and 2.20.13) |
| | ESP | 5 – 20 mg/$Nm^3$ | Cleaning the off-gas from a dolomite calciner used in the production of magnesium metal (See Section 2.9.2.2.1) |
| Cl | Multi-stage venturi scrubbers with a subsequently packed tower using caustic soda | <1 mg/$Nm^3$ | For cleaning the cell-room air during special operations such as changing diaphragms (See Sections 10.1.1, 10.2.2 and 11.3.3.4) |
| PCDD/F from the chlorination in Mg production | Multi-stage scrubbers connected with a wet ESP and an afterburner | <0.1 ng I-TEQ/$Nm^3$ | (See Sections 2.10.2.1, 2.20.5 and 10.3.4.1) |
| Chlorinated hydrocarbons | Multi-stage scrubbers connected with a wet ESP and an afterburner | 0.01 mg/$Nm^3$ | (from the chlorination stage in Mg production See Section 10.3.4.1) |
| NB: Collected emissions only. BAT-AELs are given as daily averages based on steady-state operation or, in cases where continuous monitoring is not practicable, as the average over the sampling period. For PCDD/F, the BAT-AEL is the average over the sampling period which should preferably be a minimum of six hours. | | | |

**Table 10.9: BAT and BAT-AELs to prevent and control emissions to air from the production of alkali and alkaline earth metals**

### 10.4.2 Effluent treatment and water re-use

**a) BAT is to prevent and control emissions of metals and acids to water by using the following techniques:**

- Treating the scrubbing of effluent from the chlorination stage of magnesium production in order to minimise the emissions of PCDD/F and chlorinated hydrocarbons to water. The treatment method is flocculation and solids separation followed by a second treatment stage using activated carbon.
- Using closed water cycles for wet scrubbers, cooling systems and granulation presses.
- Treatment of the bleed from closed water cycles to remove solid matter and metal compounds from the water.
- Treatment of waste waster to allow recycling and re-use as far as possible.
- Treatment of scrubbing liquids and analysing them before discharge.
- Containment of plant drainage systems and treatment of effluents according to their content with analysis before discharge.

**The emission levels given in Table 10.10 for a magnesium plant, including water from the chlorination off-gas treatment, are the BAT-AELs (see Section 10.3.7.1).**

| **Component** | **BAT-AEL** |
|---|---|
| Chlorinated hydrocarbons | 0.15 mg/Nm$^3$ |
| PCDD/F | 100 ng I-TEQ/m$^3$ |
| NB: Chlorinated hydrocarbons are expressed as the sum of hexa- and penta-chlorobenzene and octachlorostyrene and PCDD/F are expressed as the sum of PCDDs and PCDFs expressed as TCDD equivalents. BAT-AELs are based on qualified random samples or twenty four hour flow proportional composite samples. | |

**Table 10.10: BAT-AELs for emissions to water from magnesium production**

By-products, process residues and wastes??

## 10.5 Emerging techniques

The processes for the production of alkali and alkaline metals are sometimes developed directly by the company who uses the processes, therefore information on emerging techniques are very limited. Research has been done in order to build large electrolytic cells for the production of lithium and sodium metal as well as the process control systems, which should reduce the high labour costs and increase the productivity.

# 11 PROCESSES TO PRODUCE NICKEL AND COBALT

## 11.1 Applied processes and techniques

Nickel is produced from oxidic (laterite and saprolite) or sulphidic ore, about 60 % of the nickel comes from sulphide deposits and 40 % from oxide deposits. There are several variations in the processes used to produce nickel from these ores and these variations are dependent on the grade of the concentrate and also on the other metals that are present in the material [ 92, Laine, L. 1998 ].

Cobalt is usually present in nickel and copper ores and is recovered during their production. Refining of the recovered by-product that contains cobalt is performed by a combination of processes governed by the composition of the concentrate and the physical and chemical characteristics of the final product. Cobalt arsenide ores are also sources of cobalt. These ores are roasted to remove the majority of arsenic as arsenic oxide [ 104, Ullmann's Encyclopedia 1996 ]. The process however is not used in the EU.

Table 11.1 shows the composition of some ores.

| Source of ore | Type | Ni (%) | Cu (%) | Co (%) |
|---|---|---|---|---|
| Murrin Murrin (Australia) | Laterite | 1.07 | | 0.08 |
| Cerro Matoso (Colombia) | Laterite | 2.16 | | |
| Selebi-Phikwe (Botswana) | Sulphide | 0.77 | | |
| Sudbury area (Canada) | Sulphide | 1.18 | 1.73 | |
| Raglan (Canada) | Sulphide | 2.56 | 0.71 | |
| Vale INCO, Copper Cliff | Sulphide | 1.55 | 2 | 0.04 |
| Cosmos (Australia) | Sulphide | 5.7 | 0.2 | 0.1 |
| Mount Keith (Australia) | Sulphide | 0.6 | 0 | |

**Table 11.1: Composition of some ores**

Secondary nickel and cobalt are consumed directly in the form of remelted scrap and other recycled products generally in the production of ferro-nickel and stainless steel [ 92, Laine, L. 1998 ]. Other secondary materials such as catalysts and precipitator dusts are recovered in the primary smelting processes, usually in the slag furnace.

Because these metals are so closely associated, their production processes are dealt with together as far as possible [ 92, Laine, L. 1998 ].

### 11.1.1 Oxidic ores

In laterite ores, nickel and cobalt are bound with iron and manganese oxides or silica compounds and are difficult to upgrade to a concentrate. Smelting of these ores with a source of carbon in an electric furnace can be used. Ferro-nickel is produced or a nickel matte can be made after the addition of sulphur. The generic flow sheet is shown in Figure 11.1.

Prior to smelting, the ore is usually preheated or calcined in a rotary kiln [ 106, Raffinot, P. 1993 ]. An electric furnace is then usually used for smelting.

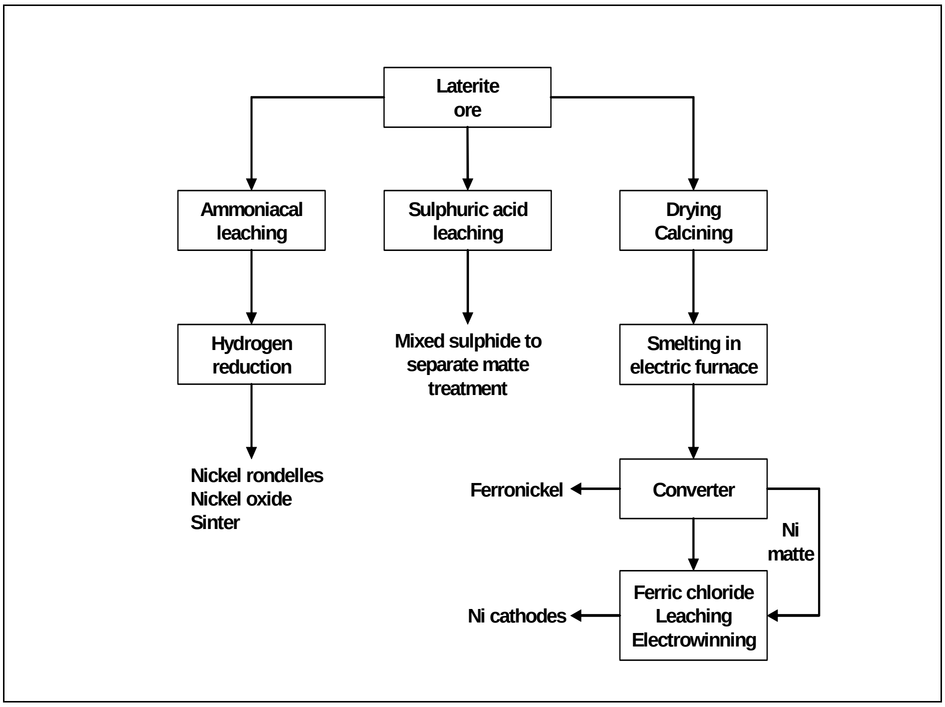


**Figure 11.1: Generic flow sheet for nickel production from laterite ores**

Saprolite ores can be smelted with sulphur so that the nickel oxide is converted to a nickel sulphide matte and iron is removed as a slag [ 106, Raffinot, P. 1993 ]. The matte is treated in the same manner as matte produced from sulphide ores.

Smelting to ferro-nickel accounts for a large proportion of nickel production from laterite ores. These processes are discussed under ferro-alloys in Section 9.1.4. Leaching of laterite with ammonia is also used to extract nickel [ 19, HMIP (UK) 1994 ], [ 56, Knuutila, K. 1997 ], [ 94, Laine, L. 1998 ] and this process is becoming more important. Although conversion of nickel oxide to impure nickel and then to nickel carbonyl, which is volatile, is used to produce refined nickel, the nickel oxide is produced from the smelting of a sulphidic ore. The laterite ores generally have a maximum nickel content of 3 % and are therefore not used directly in this process.

The pressure leaching of laterites with sulphuric acid is principally a simple and straightforward process. The temperature, pressure and other parameters may vary from case to case to achieve the best possible metallurgical conditions depending on the ore and products in question and other objectives. The temperature of the leaching autoclaves is usually between 230 and 260 °C and pressures up to 43 bar are used. Oxygen can also be used in the process.

The resultant solution is purified either by modern solvent extraction methods or by traditional precipitation methods. For example hydrogen sulphide is used to selectively precipitate nickel and cobalt sulphides which are sent for further metal recovery. The solution can be neutralised so that iron precipitates. Nickel and cobalt will be precipitated and re-leached with ammonia.

Solvent extraction is used to separate nickel and cobalt chlorides or sulphates. Metallic nickel can be produced by electrowinning and cobalt can be precipitated as cobalt sulphide. Alternatively nickel and cobalt can be recovered as metal powders using hydrogen reduction.

Table 11.2 shows the processes used in the EU-27.

| Company Name | Location | Industry sector | Process description |
|---|---|---|---|
| Eramet | Sandouville, | Nickel metal | Nickel refinery by a hydrometallurgical |

| | | | |
|---|---|---|---|
| | France | producer, Nickel salts producer (Ni chloride, Ni hydroxycarbonate) | process, receiving imported nickel matte which is ground, dissolved with chlorine, purified and refined by electrowinning ($NiCl_2$ salt and Ni metal production) |
| Xstrata Nickel | Kristiansand, Norway | Nickel metal producer | Metal refinery by a hydrometallurgical process, receiving matte which is grained, dissolved with chlorine, purified and refined by electrowinning (Ni metal production) |
| Norilsk Nickel | Harjavalta, Finland | Nickel metal producer, Ni sulphate producer, Ni hydroxycarbonate producer | Ni refining and Ni salts production. Refining (electrowinning and hydrogen reduction) |
| Boliden | Harjavalta, Finland | Nickel Smelting | Sulphidic ore concentrates brought to the plant. Direct Outotec Nickel flash smelting (DON process®). Producing nickel matte from sulphide concentrates. Boliden also operates a copper flash smelter in the same site producing copper anodes from sulphide concentrates. The emissions of nickel smelter and copper smelter are inseparable and thus emissions reported in this exercise originate from both smelters. The dust emissions are monitored in three stacks, ventilation gases, Ni drying plant and Cu drying plant |
| Inco Europe Ltd | Clydach Swansea, UK | Ni metal producer, Ni sulphate producer (in China, not in Clydach), Ni chloride producer (in China, not in Clydach) | Imported nickel oxide. Refining of nickel using the carbonyl process |

**Table 11.2: Processes used in EU-27**

*Crosscheck this table with the information in Section 1.10. and deside whether this table shold be relocated to this section.*

### 11.1.2 Sulphidic ores

Nickel-bearing sulphide ores can be concentrated, e.g. by flotation to upgrade the nickel content. Nickel concentrates that generally contain 7 - 25 % Ni are produced which makes further processing easier. The nickel concentrates are usually smelted under oxidising conditions to remove iron sulphide and other gangue materials from the concentrate to produce a nickel matte. The Outotec flash furnace is used in Europe; the Outotec and INCO flash furnaces and electric or shaft furnaces are used elsewhere in the world.

The nickel is recovered into a sulphide matte that contains 35 - 70 % Ni, Co and Cu. The matte can be treated in a Peirce-Smith converter or alternatively it can be granulated or cooled slowly before a hydrometallurgical recovery stage [ 139, Riekkola-Vanhanen, M. 1999 ]. The converter stage is not used in Europe.

Important components of the nickel mattes are cobalt, copper and precious metals. The slag produced during smelting also contains recoverable metal and is treated in an electric furnace to produce more nickel matte. This can be granulated and treated separately [ 92, Laine, L. 1998 ], [ 94, Laine, L. 1998 ]. Secondary materials are sometimes recovered in the electric furnace. Figure 11.2. gives an overview of the process options.

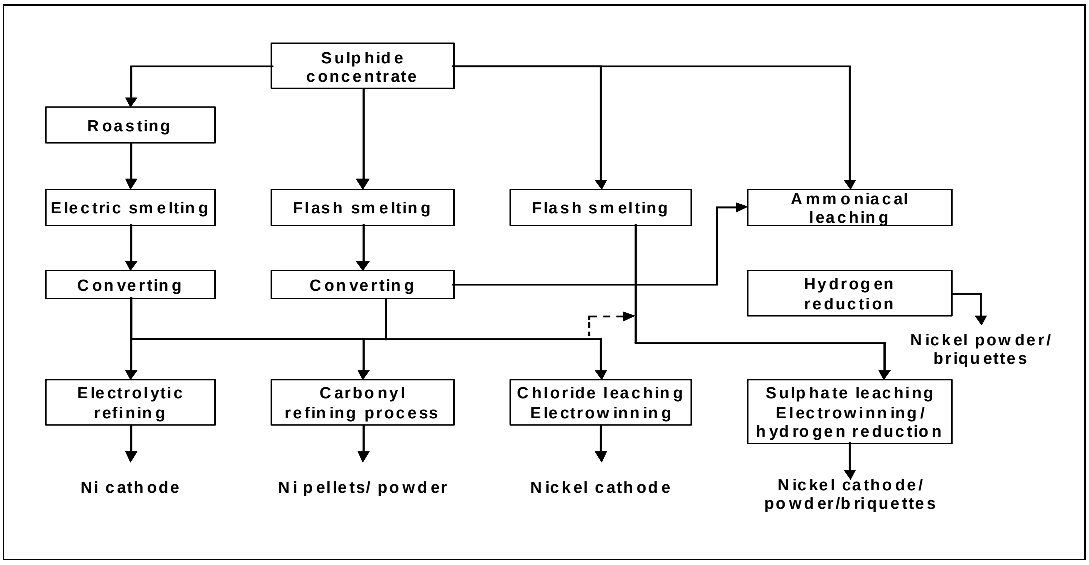


**Figure 11.2: Generic flow sheet for the production of nickel from sulphide concentrates**

### 11.1.2.1 Conventional flash smelting process

Conventional smelting processes are used to remove iron and other gangue materials from sulphide concentrates to produce nickel matte. Worldwide there are five other smelters, which use this process. Two of these use a flash smelting furnace designed by BHP Billiton (formerly Western Mining Corporation), where the smelting and slag cleaning furnaces have been built together to form one larger unit.

There are differences in operations between the smelters. The most visible difference is the matte grade but variations in the raw material composition also cause some differences. The generic flow sheet is shown below in Figure 11.3.

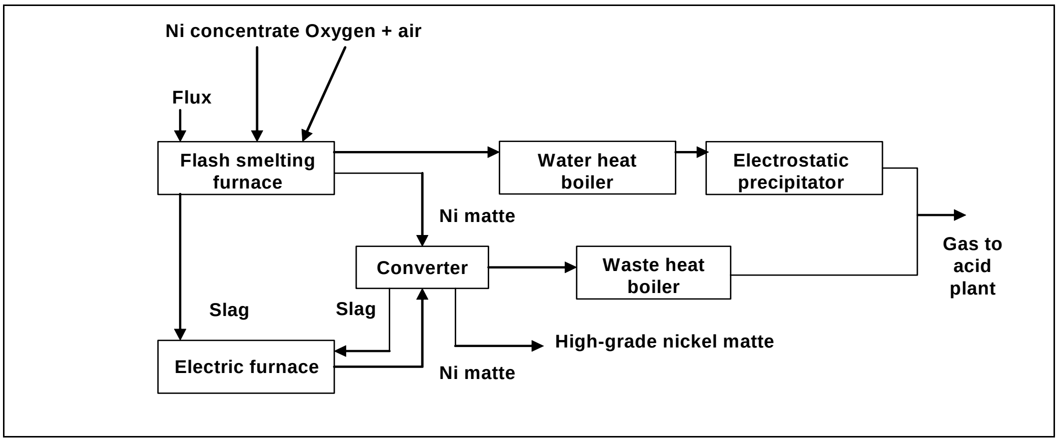


**Figure 11.3: Conventional flash smelting**

### 11.1.2.2 Direct Outotec Nickel (DON) process

In Europe only the Direct Outotec Nickel (DON) process is used. The DON process combines both smelting and converting to produce a high grade matte which is further treated hydrometallurgically. [ 310, DIRECT OUTOKUMPU NICKEL TECHNOLOGY 2006 ].

The slag passes by launder to an electric slag-cleaning furnace where it is treated with coke and a sulphidising agent to produce more nickel matte and a cleaned slag for disposal. The two mattes have different compositions and are treated separately. The process is shown in

Figure 11.4. The converter stage is not used in the EU but the DON process combines both smelting and converting stages to produce a high grade matte which is further treated hydrometallurgically. The matte is granulated and ground before passing to the leaching stage.

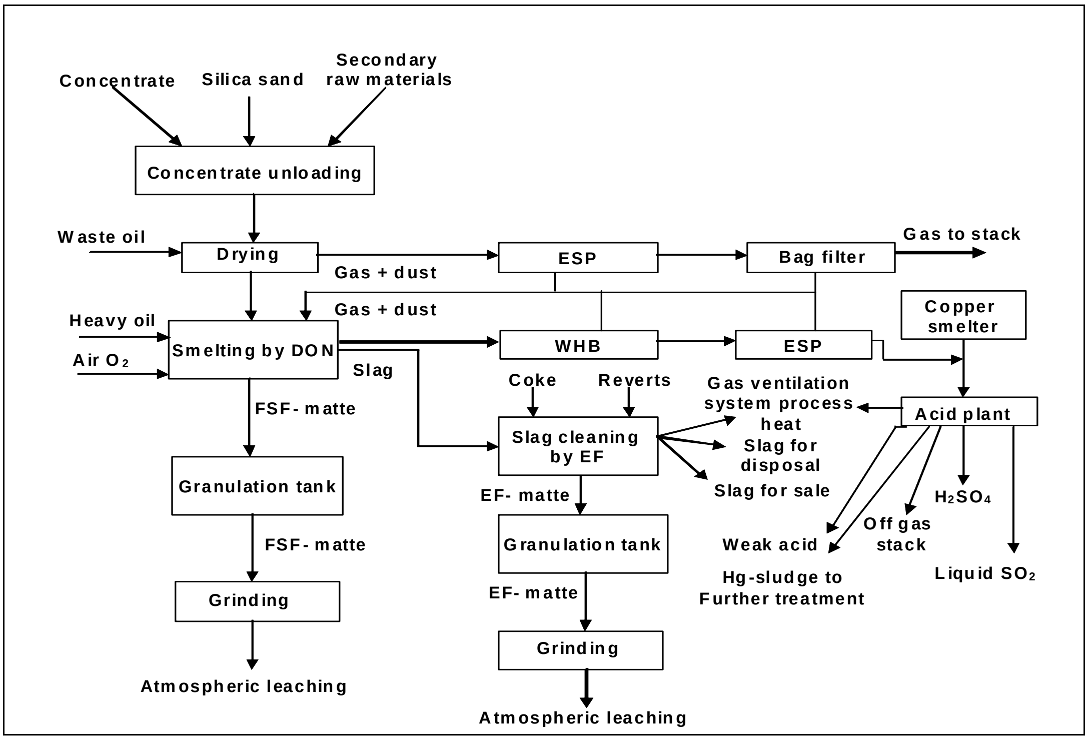


**Figure 11.4: The DON process**

### 11.1.2.3 Heap leaching

Open heap leaching is usually carried out at the mine. Material is crushed and ground to allow intimate particle/acid contact and then formed into natural heaps on an impervious liner. Acid is sprayed onto the heaps and percolates through the mass. It is collected on the liner and is recirculated to allow the metal content to buildup . Bacteria are used to enhance the leaching process and improve efficiency and this technique is used for some nickel ores where zinc, cobalt and copper are leached simultaneously and then separated prior to metal recovery [ 284, Talvivaara June 2008 ].

## 11.1.3 Matte refining processes

The mattes produced by the smelting processes must be treated further in order to recover and refine the metal content. Nickel matte must go through a multistage refining process to reject iron and recover copper, cobalt and precious metals. Matte can be treated pyrometallurgically but hydrometallurgical processes are more commonly used. A variety of electrorefining, leaching, reduction and precipitation processes are carried out. Nickel is recovered from purified solutions by electrowinning or by hydrogen reduction.

Figure 11.5 shows the generic processing routes.

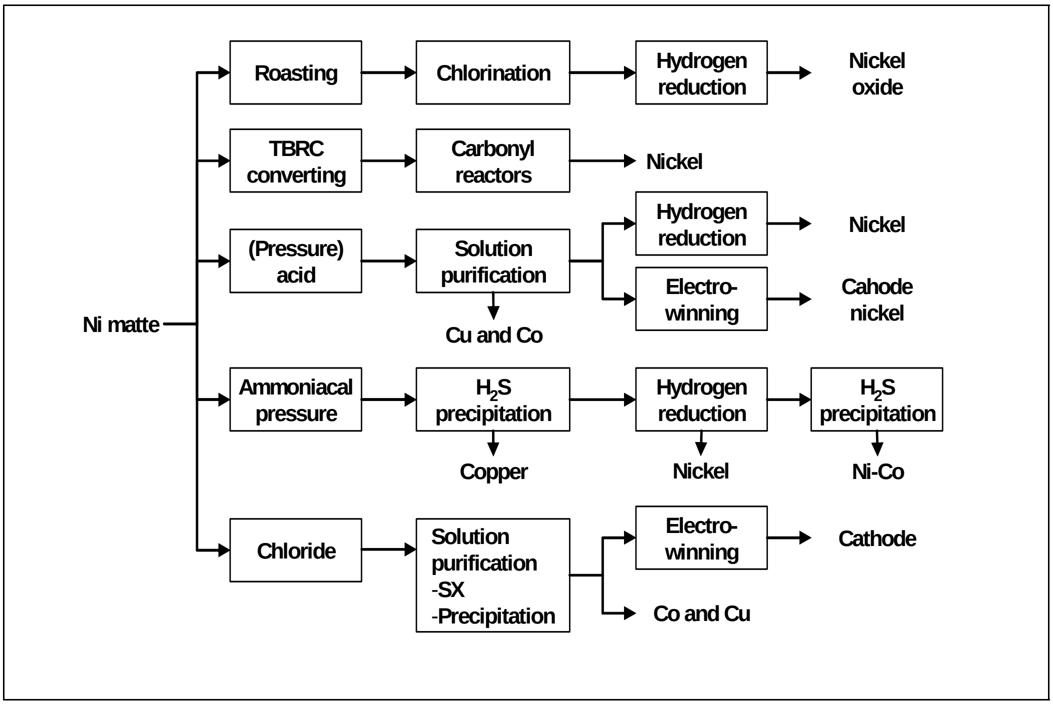


**Figure 11.5: Generic flow sheet for nickel matte refining processes**

### 11.1.3.1 Chloride leaching of matte followed by electrowinning

Matte is leached in a chloride solution in several stages at a high temperature and pressure using chlorine gas as an oxidant. The chlorine gas is generated in the electrowinning cells and is returned to the leaching circuit. Copper is precipitated as the sulphide and then iron and arsenic are precipitated as hydroxides and arsenates to purify the leachate. Copper sulphide is roasted in a fluidised bed furnace and the resulting calcine is leached with spent copper electrolyte. Copper is then electrowon.

Cobalt is removed by solvent extraction of the chloride solution using an organic solvent and is electrowon. The nickel solution is then purified further using chlorine to remove lead and manganese and is then electrowon in diaphragm cells using titanium anodes. The cells are sealed to recover the chlorine that is formed at the anode.

This is known as the Falconbridge process and is shown in Figure 11.6.

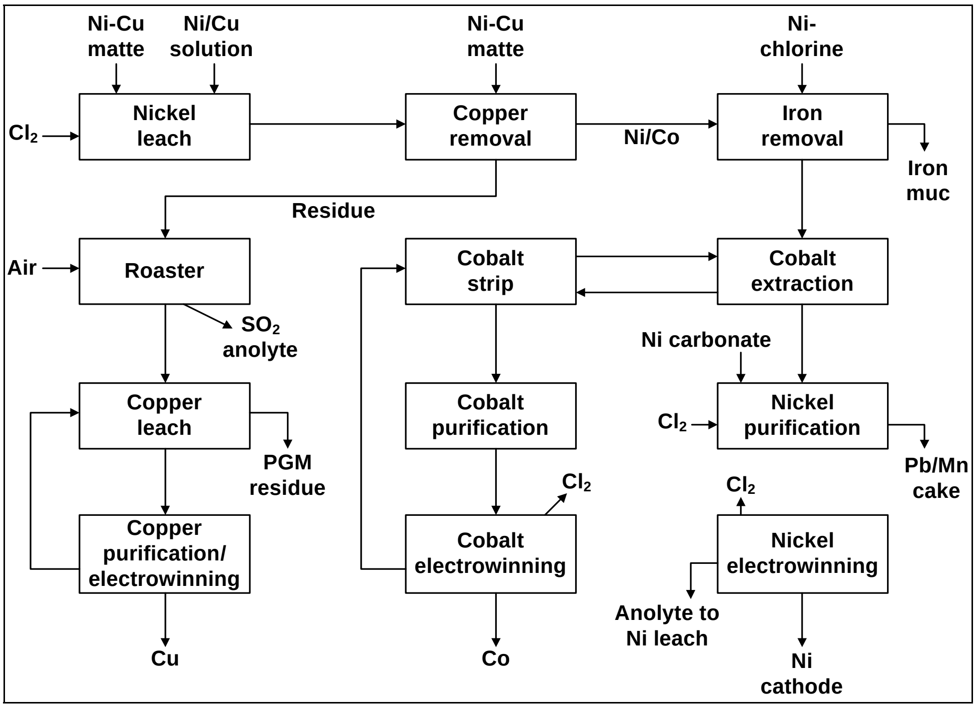


Figure 11.6: Falconbridge process

### 11.1.3.2 Sulphate-based atmospheric pressure leaching followed by electrowinning/hydrogen reduction

Matte is leached in a sulphate-based anolyte recycled from nickel electrowinning[ 57, Knuutila, K. et al. 1996 ], [ 58, Kojo, I.V. et al. 1997 ]. Nickel sulphide matte is leached in an atmospheric leaching stage using oxygen or air-sparged leach vessels with the aid of copper ions. Dissolved iron is oxidised to form iron oxide which precipitates (see Figure 11.7).

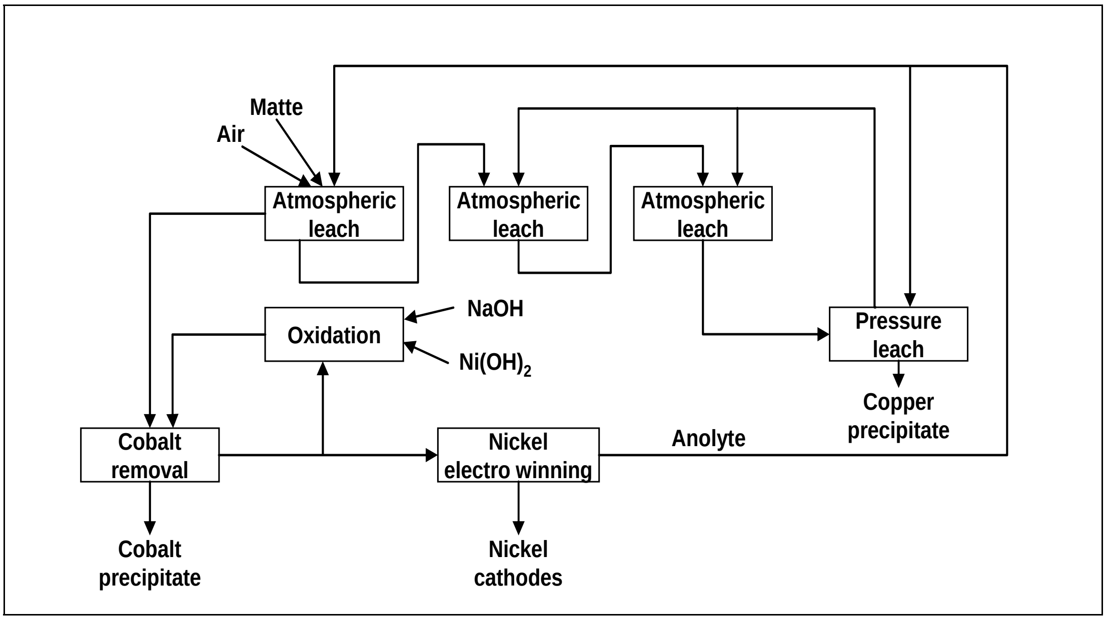


Figure 11.7: Sulphate-based leaching process

The residue from atmospheric leaching is passed to the pressure leaching stage where the nickel content is dissolved and copper is precipitated as copper sulphide, which is returned to the copper smelter. The iron oxide precipitate is returned to the nickel smelter. Alternatively the iron residue is disposed of. The nickel solution from the atmospheric leach is purified by solvent extraction to remove cobalt and impurities. Cobalt can be electrowon or reduced to cobalt powder using hydrogen. Nickel can be electrowon from the purified sulphate solution to produce cathodes [ 310, DIRECT OUTOKUMPU NICKEL TECHNOLOGY 2006 ].

Nickel powder can be produced by adding ammonia and ammonium sulphate to the solution. The mixture is then reduced in an autoclave using a hydrogen atmosphere. The powder is sold or can be sintered into briquettes. The sulphuric acid present is neutralised by ammonia. The ammonium sulphate is recovered for sale or re-use in the process.

This process has been developed into a two-stream process to allow separate treatment of the mattes produced from the smelter and the slag cleaning furnaces. The flowsheet of the DON refinery process shown in Figure 11.8.

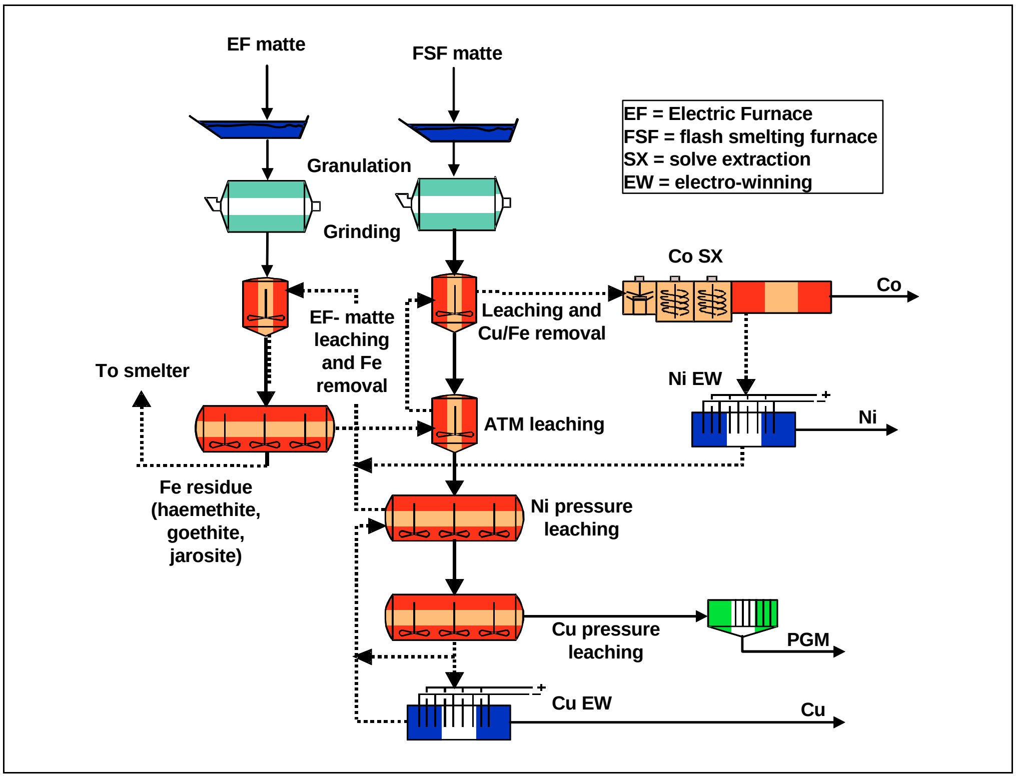


**Figure 11.8: Flow sheet of the DON refinery process**

### 11.1.3.3 Ammonia pressure leach and hydrogen reduction

Matte is leached into ammoniacal ammonium sulphate solution in pressure autoclaves using air as an oxidant. After the precipitation of copper sulphide, nickel solution is reduced with hydrogen in the autoclaves to produce metallic nickel powder. The ammonium sulphate formed in the hydrogen reduction stage is recovered by crystallisation and drying. After the hydrogen reduction, the rest of the dissolved nickel and all the cobalt are precipitated with hydrogen sulphide for further treatment [ 92, Laine, L. 1998 ] [ 94, Laine, L. 1998 ]. This is known as the Sherritt process and is shown in Figure 11.9.

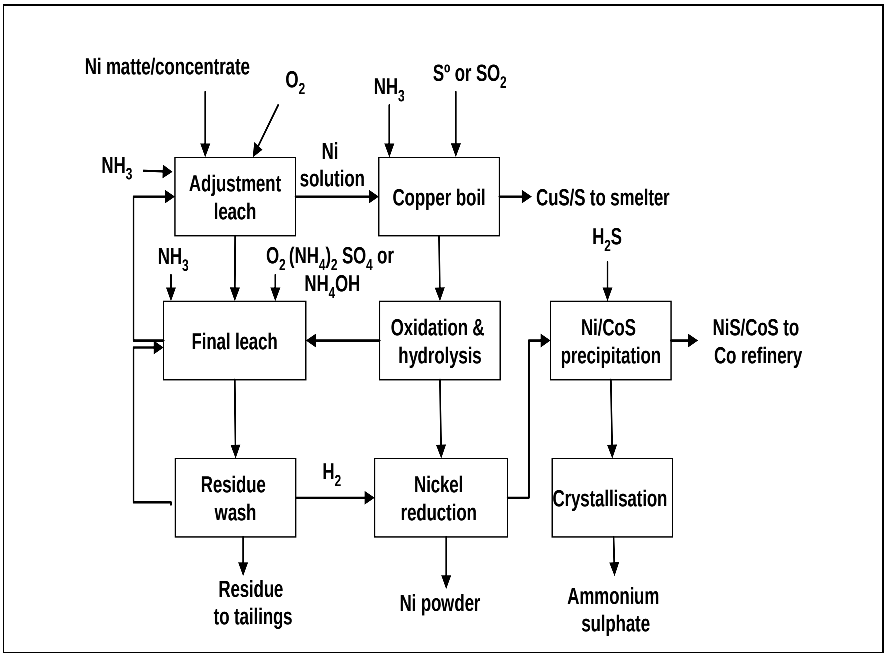


**Figure 11.9:** **Sherritt ammoniacal leaching**

### 11.1.3.4 Ferric chloride leaching

Matte is leached in several stages using recycled ferric chloride in the presence of chlorine (which is generated from the electrowinning cells) near to boiling point. Sulphur remains in the elemental state and is filtered from the final solution. Iron is then removed by solvent extraction using tributyl phosphate allowing ferric chloride to be recovered. Cobalt is removed in a further solvent extraction stage using tri-iso-octylamine. Cobalt chloride solution is sold [ 92, Laine, L. 1998 ], [ 94, Laine, L. 1998 ].

Other minor impurities such as Cr, Al, Pb are removed using a combination of electrolysis, ion exchange and active carbon. Nickel is then electrowon from the purified solution in diaphragm cells using titanium anodes and nickel cathodes. Chlorine is collected and returned to the leach circuit.

### 11.1.3.5 Carbonyl process

The low pressure carbonyl process uses an impure oxide produced by smelting sulphide ore as the raw material to refine the nickel. This oxide is reduced to an impure metal using hydrogen and the metal is then activated. Nickel carbonyl is then formed by the reaction of the metal with carbon monoxide at low temperature and pressure. Nickel carbonyl is volatile and is refined by separation from the solid impurities. The solid residue is returned for further processing to the primary smelter to recover other metals that are present [ 19, HMIP (UK) 1994 ], [ 25, OSPARCOM 1996 ].

Nickel carbonyl gas passes from the reactor and is then decomposed using heat to form powders and pellets. It can also be decomposed onto other substrates such as carbon fibres to produce nickel-coated materials. During decomposition, carbon monoxide is released and is recovered and re-used to produce more nickel carbonyl. Pure nickel salts are produced by the reaction of nickel pellets with acids. Any off-gases from the process are incinerated to destroy any nickel carbonyl and carbon monoxide. Dust from the afterburner is removed.

### 11.1.3.6 Matte electrorefining

Nickel matte can be cast into anodes. These are dissolved in a diaphragm electrolysis cell using a chloride/sulphate electrolyte. The electrolyte from the anode compartment is purified and circulated through the cathode bag. The anodes are also bagged to collect the slime that contains sulphur. Elemental sulphur and precious metals are recovered from the slime. This process is limited to mattes that have a low copper content [ 94, Laine, L. 1998 ].

### 11.1.3.7 Solvent extraction

Most of the processes described above use a solvent extraction stage to remove iron and to separate nickel and cobalt prior to electrowinning or transformation. Metal ion complexes are formed using chelating agents so that the desired metal ions can be extracted into an organic phase. The desired ions are then back extracted into a second aqueous phase by altering the conditions of a second aqueous phase.

The choice of solvent and chelating (complexing) agent allows specific metal ions to be removed from aqueous solution and to be concentrated. The solvent/chelating mixture is recycled between the extraction and winning baths. The baths comprise a mixer/settler to allow solvent/water contact and then phase separation. Sealed or covered systems are used to prevent the emission of solvent fumes. Figure 11.10 shows a generic process outline [ 239, ENIA 2008 ].

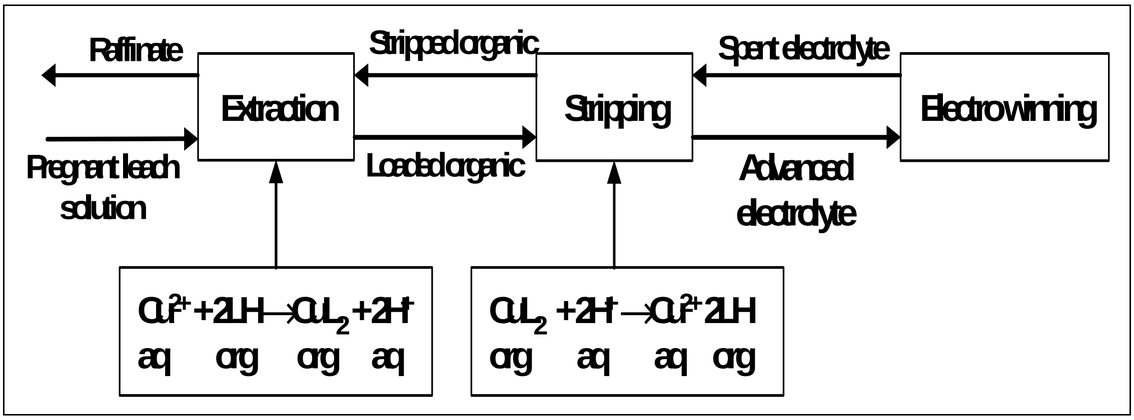


**Figure 11.10: Solvent extraction (SX) process outline**

Overwork

### 11.1.3.8 Nickel matte refining process

Eramet has developed a refining process that originated in the nineteen seventies which can: (See Figure 11.11) [ 239, ENIA 2008 ].

- obtain very high purity nickel metal
- recover all of the by-products
- minimise the solid residue production.

Pyrometallurgical nickel matte is leached by chlorine in a chloride medium. The major constituent of the leaching residue is elemental sulphur. This by-product, after roasting, allows the production of sulphuric acid.

The major constituents of the leaching solution are nickel, cobalt and iron chlorides. Impurities like aluminium, chromium, manganese and lead are also present.

After complementary oxidation of the solution, the iron is first extracted by solvent extraction using tributylphosphate (TBP) as an extractant. The stripping is performed with water. The iron chloride solution is sold, after concentrations up to 40 wt – % ~~w/w~~ $FeCl_3$. It is used in water treatment processes.

The cobalt is extracted from the iron-depleted solution by solvent extraction using tri-iso-octylamine as extractant. The stripping is performed with water. The cobalt chloride is sold, after complementary purification and concentrations up to 27 wt- % ~~w/w~~ $CoCl_2$, as raw material for chemical specialties production.

In order to obtain a totally pure nickel chloride solution, hydroxides are precipitated to allow the elimination all the main impurities such as Al, Cr, etc. This is followed by lead removal using an electrolytic process.

The pure nickel chloride solution is used as raw material to produce high quality nickel salts, such as nickel chloride solution or crystals, or nickel hydroxycarbonate and high purity nickel metal (Ni ≥99.99 %) obtained by electrolysis in the chloride medium. Chlorine evolves at the anode, made of titanium alloy and is collected and directly recycled to the matte leaching step.

The energy used for the nickel production is in the range of 20 GJ per tonne of nickel which is in accordance with the energy use of the refining stages.

Emissions to air
The process has the following emissions to air:

| | |
|---|---|
| Ni | 0.025 kg/t Ni |
| $Cl_2$ | 0.010 kg/t Ni |
| VOC | 3.6 kg/t Ni |
| $SO_2$ | 3.7 kg/t Ni |
| $CO_2$ | 600 kg/t Ni |

Emissions to water
The process has the following emissions to water:

| | |
|---|---|
| Ni | 0.017 kg/t Ni |
| suspended Solids | 0.18 kg/t Ni |
| COD | 2.0 kg/t Ni |

Residues and Waste production
The Eramet nickel refinery using the process described here over does not produce any solid residue for disposal.

The waste production is 22 kg/t Ni. This data does not include wastes that are not linked to the production process itself.

Flow sheet of the Eramet refining process is shown in Figure 11.11.

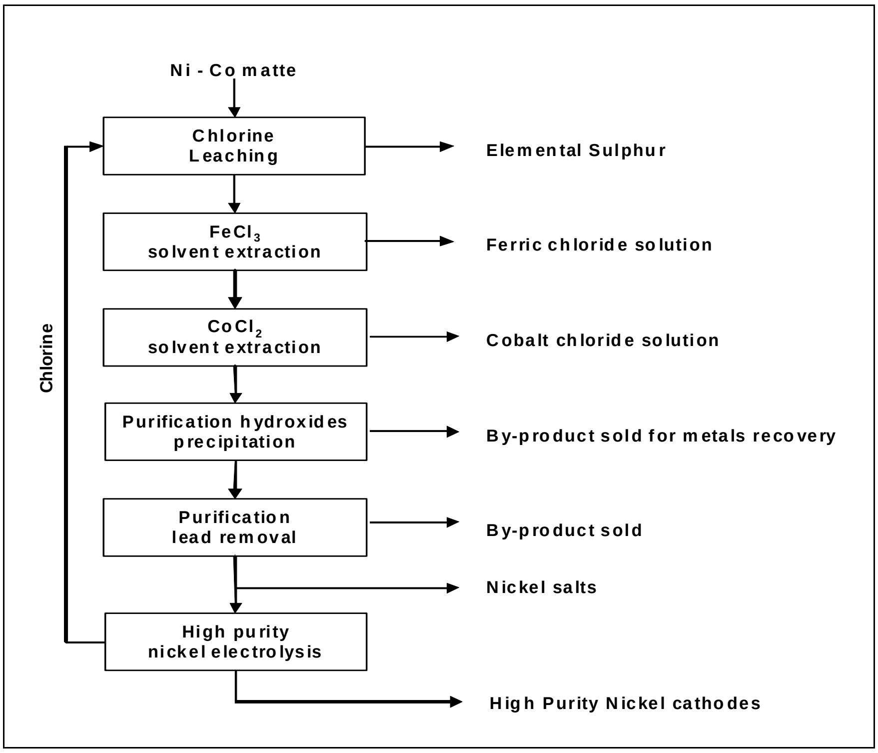


Figure 11.11: Flow sheet of the Eramet refining process

### 11.1.4 Nickel alloy production from secondary materials

The process includes raw materials preparation, melting (including tapping and casting), ingot stripping and dressing, scrap recycling and "electroslag refining" with a throughput about 7000 t/year.

Raw materials for the process consist of recycled scrap, purchased scrap and virgin material. Scrap in the form of turnings, swarf off-cuts, etc. is treated to remove oil by centrifuging and/or degreasing. Raw materials are weighed into charging vessels to the desired alloy composition. The charging vessels are then transported to the relevant furnace.

Melting is carried out in an induction furnace, with fumes captured by one of two extraction systems fitted with fabric filters. Some of the metal is further refined in vacuum refining furnaces. Vacuum induction melting is carried out in a 7.5 tonnes capacity furnace. Casting from the furnace is carried out either under vacuum or argon. Vacuum arc refining is carried out producing solid ingots under vacuum. Vacuum is provided by steam ejectors and gases from the ejectors are cooled using spray condensers. Slag is refined in an electric furnace.

Three casting techniques are used: top casting, uphill casting and durville casting. Casting fluxes and anti-piping compounds are used during casting. Ladles used for casting are preheated by gas-fired burners.

The ingots from casting are stripped of any residual refractory material, etc. Solid waste from the casting processes, casting/ladle refractories, slags, etc. are collected for the recovery of residual metal. The stripped ingots may then be subjected to various processes: machining, sawing, grinding and shot blasting. The scrap from these processes in the form of dust, swarf and turnings is collected for reprocessing or sale.

### 11.1.5 Cobalt production

Cobalt is produced during the recovery of nickel after separation by solvent extraction (SX) and is described above in Section 11.1.3.7. Cobalt can be electrowon from the solution to produce saleable cathodes using diaphragm cells in the same manner as nickel [ 233, Farrell Nordic Mission 2008 ].

Cobalt can also be recovered from the solution as a powder by hydrogen reduction. Alternatively, the solution can be treated to precipitate an impure cobalt by-product for further refining or may be sold.

Further refining of these and other by-products that contain cobalt, intermediates and recycled materials is performed using atmospheric and oxygen pressure leaching in a sulphuric or hydrochloric acid medium. Separation using hydroxides, carbonates and amine or ammonium complexes is also used [ 104, Ullmann's Encyclopedia 1996 ].

Precipitation, solvent extraction and ion exchange techniques are used to purify the solutions. Cobalt is then recovered as metal powder, metal oxide or salts. The products are made with a wide variety of very specific physical and chemical characteristics. Pyrolysis of carboxylates, high temperature reduction of oxides, precipitation and crystallisation techniques are used depending on the particle size or other characteristics that are required [ 104, Ullmann's Encyclopedia 1996 ].

These processes are commercially confidential and very site-specific in nature. A generic flow sheet is shown in Figure 11.12 and a more specific process is shown in Figure 11.13.

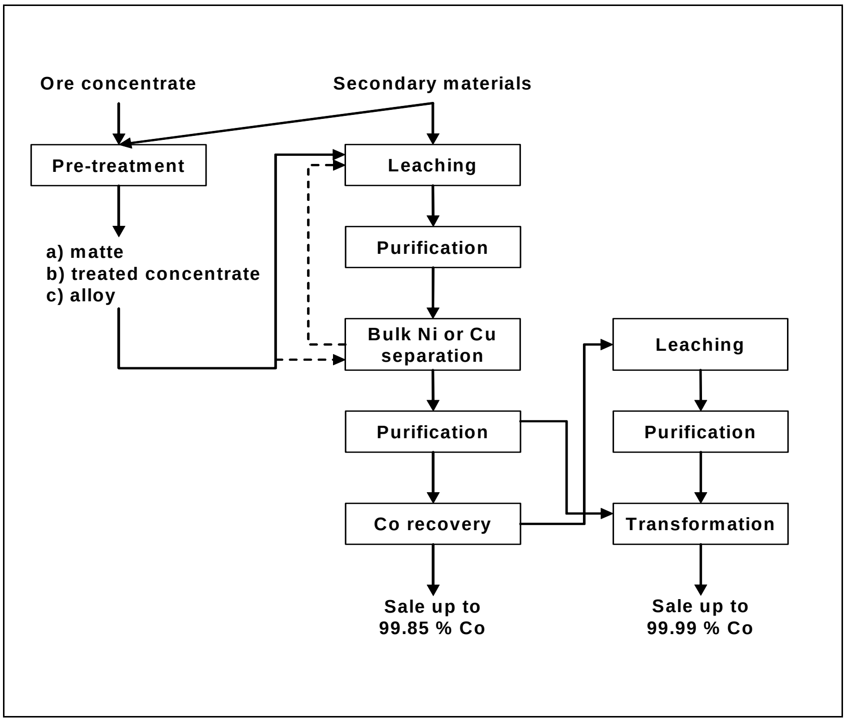


**Figure 11.12: Generic flow sheet for cobalt production**

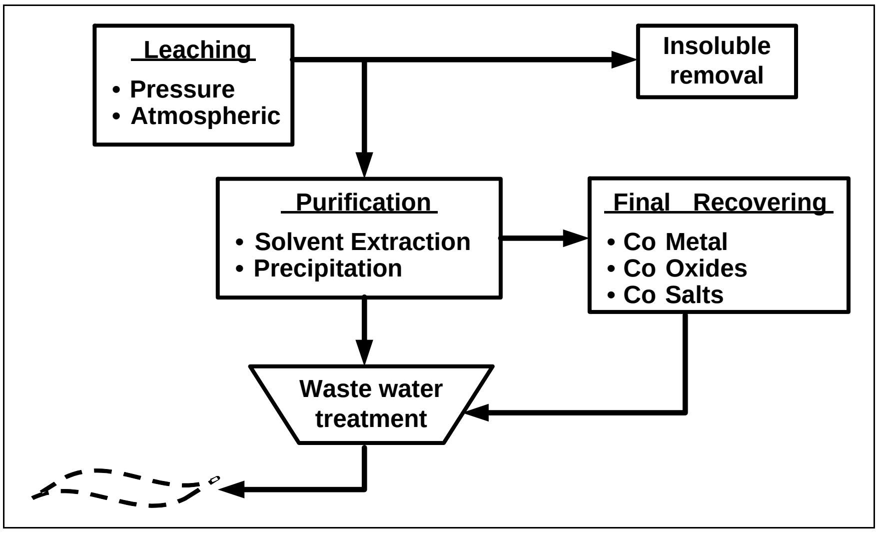


**Figure 11.13: A practical cobalt flow sheet**
[ 233, Farrell Nordic Mission 2008 ]

# 11.2 Current emission and consumption levels

## 11.2.1 Energy consumption

The energy consumed for the production of matte from sulphidic concentrates is reported to be in the range 25 to 65 GJ per tonne of nickel for concentrates that contain 4 to 15 % Ni. The energy consumed in the various refining stages is reported to be 17 to 20 GJ per tonne of nickel.

## 11.2.2 Emissions to air

The potential emissions of concern to air from nickel and cobalt production are:

- sulphur dioxide ($SO_2$) and other acid gases
- oxides of nitrogen ($NO_X$) and other nitrogen compounds
- metals and their compounds including As
- dust
- chlorine
- VOCs and odours
- CO and carbonyls (alarm levels set at 80 parts per billion).

The relevance of the potential substances emitted from the major sources is given in Table 11.3 and are discussed later in this section.

| **Component** | **Roasting or smelting** | **Leaching and purification** | **Electrolysis** | **Solvent Extraction** | **Sulphuric acid plant** | **Final recovery and transformation** |
|---|---|---|---|---|---|---|
| Sulphur dioxide and trioxide (1) HCl | •••(1) | • | • | • | ••• | |
| VOC (including CO and odours) | • | • | | •• | | |
| Chlorine | | •• | •• | | | |
| Nitrogen oxides | •(1) | | | | • | |
| Dust and metals | •••(1) | • | • | | | •• |

(1) The direct emissions from the roasting or smelting stages of sulphidic ores are treated and/or converted in the gas-cleaning steps and sulphuric acid plant; the remaining emissions of sulphur dioxide and nitrogen oxides of the sulphuric acid plant are still relevant. Diffuse or non-captured emissions are also relevant from these sources.
••• More significant – • less significant

**Table 11.3: Significance of potential emissions to air from cobalt and nickel production**

The sources of emissions from the process are:

- roasting
- other pretreatment
- smelting, converting and slag treatment
- leaching and purification
- solvent extraction
- electrolysis
- final recovery or transformation stage
- sulphuric acid plant.

### 11.2.2.1 Sulphur dioxide and other acid gases

The major sources of sulphur dioxide emissions are diffuse emissions from the roaster or smelter. Uncaptured emissions from the ladle transfer and blowing stages of the converter and direct emissions from the sulphuric acid plant are also significant. Good extraction and sealing of the furnaces prevents diffuse emissions and the collected gases are passed to a gas-cleaning plant and then to the sulphuric acid plant. The gas collection from the converter stages is a significant source of emissions and this aspect is discussed in Chapter 3.3.5.

After cleaning, the sulphur dioxide in the gas from the roasting stages is converted to sulphuric acid. Sections 2.11.3.4 and 2.20.6 provide more information about the techniques and emissions from sulphuric acid plants in this sector.

During startup and shutdown there may be occasions when weak gases are emitted without conversion. These events need to be identified for individual installations and many companies have made significant improvements to process control to prevent or reduce these emissions. Sulphur dioxide emissions from some processes are shown in Table 11.4.

| Process | Product | Metal production (tonnes per year) | Sulphur dioxide (kg per tonne of metal produced) |
|---|---|---|---|
| Grinding/Leaching | Co and Compounds | 5000 | 0.01 |
| Ni Smelter | Ni, Co, Cu | 200000 | 18 |
| NB: The data refers to specific raw materials - grinding of matte produced from sulphidic ore - smelting of Cu/Ni sulphidic concentrates. | | | |

**Table 11.4: Sulphur dioxide production from some nickel and cobalt processes**
[ 239, ENIA 2008 ]

During electrolysis, there are emissions of aerosols (diluted hydrochloric and sulphuric acids and metal salts) to the tank house. These emissions leave the tank house via the (natural) ventilation or from the cooling towers and are classed as diffuse emissions. Cells can be covered by foams or plastic beads to reduce the production of mists. Cell room ventilation air can be demisted and the solution returned to the electrolysis stage.

Chlorine is formed during the electrolysis of chloride solutions. This is collected in the sealed anode compartment and is returned to the leaching stage. Chlorine monitors are used to detect leaks and scrubbers are used to remove traces of chlorine from the ventilation air and other sources.

### 11.2.2.2 VOCs

VOCs can be emitted from the solvent extraction stages. A variety of solvents are used and they contain various complexing agents to form complexes with the desired metal that are soluble in the organic layer. Emissions can be prevented or minimised by using covered or sealed reactors and in this case, emissions in the order of 30 mg/Nm$^3$ have been reported.

The solvents can be aliphatic or aromatic in nature but usually a mixture is used. VOCs can be classified according to their toxicity but aromatic and chlorinated VOCs are usually considered to be more harmful and require efficient removal. Solvent vapours are emitted depending on the temperature of the extraction stage and the vapour pressure of the solvent components at that temperature. VOC concentrations of up to 1000 mg/Nm$^3$ (~1 kg/h) have been reported but the operating conditions are not known [ 92, Laine, L. 1998 ]. The nature of the solvents and conditions of use need to be determined so that the hazard can be assessed.

VOCs can be removed using condensers or by cooling the ventilation air and recovering the solvent for further use. Mass emissions of 0.2 kg per tonne of metal produced have been reported following condensation [ 92, Laine, L. 1998 ]. Carbon filters or biofilters can also be used to reduce VOC emissions further but do not allow solvent recovery.

### 11.2.2.3 Dust and metals

Dust carryover from the roasting, smelting and converting processes are potential sources of direct and diffuse emissions of dust and metals. In some processes, the gases are collected and treated scrubbers and fabric filters or in the gas-cleaning processes of a sulphuric acid plant. Dust is removed and returned to the leaching process. Fabric filters and scrubbers are used to remove dust and large particles. Dust and metal emissions from some processes are shown in Table 11.5 and Table 11.6 but it should be noted that different processes and process stages are involved and the data is not comparable [ 260, OutoK etccccc 2000 ].

| Process | Product | Production (tonnes) | Dust (kg per tonne of metal) | Ni (kg per tonne of metal) |
|---|---|---|---|---|
| Matte grinding | Ni | 12000 | 0.02 | 0.005 |
| Refining nickel matte | Ni | | 0.04 | |
| Carbonyl process | Ni | 40000 | 0.01 | 0.005 |
| DON process and copper smelter (1) | Ni, Cu | 240000 | 0.25 | 0.02 |
| (1) The DON process and copper smelter comprises a site that includes drying, smelting (Cu+Ni), Cu converting, slag cleaning (Cu+Ni), all Ni matte refining processes and other abatement processes | | | | |

**Table 11.5: Dust and metal emissions from some European processes**
[ 239, ENIA 2008 ]

| Process | Product | Production (tonnes) | Co (kg per tonne of metal) | Ni (kg per tonne of metal) | VOC (kg per tonne of metal) |
|---|---|---|---|---|---|
| Grinding/leaching | Co | 10000 | 0.1 | | |
| Solvent extraction | Co | 10000 | | | 4.0 |
| Final recovery or transformation | Co | 10000 | 0.8 | 0.1 | |
| **Total** | **Co** | **10000** | **0.9** | **0.1** | **4.0** |

**Table 11.6: Emissions to air from some process stages of Co production**
[ 239, ENIA 2008 ]

### 11.2.2.4 Chlorine

Chlorine is used in some leaching stages and is produced during the subsequent electrolysis of chloride solutions. The leach vessels are sealed and there is the provision of chlorine gas scrubbing to remove uncaptured chlorine.

The anodes in the electrolysis cells are contained in a membrane and enclosed by a collection hood. The chlorine evolved is collected and re-used in the leaching stage. The systems are sealed and diffuse emissions occur only during membrane or pipework failure. Chlorine alarms are used extensively in leach and cell rooms to detect such failures and there are normally no emissions of chlorine [ 233, Farrell Nordic Mission 2008 ].

The presence of chlorine in waste water can lead to the formation of organic chlorine compounds if solvents, etc. are also present in a mixed waste water.

### 11.2.2.5 Hydrogen, carbon monoxide and carbonyls

Carbon monoxide and hydrogen are used in the vapometallurgical refining of nickel to produce crude nickel and then nickel carbonyl. These gases are explosive or very toxic and so sophisticated reactor seals and control equipment is used to prevent emissions. Comprehensive monitoring and alarm systems are used. Hydrogen is also used as a reducing agent in hydrometallurgical or pyrometallurgical recovery or transformation processes. CO is also produced in electric reduction furnaces if afterburning is not used. Robust process design including scaled equipment and appropriate gas exhaust systems are used to avoid explosive gas mixtures.

Carbon monoxide is recovered and waste process gases are finally incinerated to destroy any carbon monoxide or carbonyl that may be present. Nickel carbonyl is converted to nickel oxide which is recovered.

### 11.2.2.6 Nitrogen oxides

The roasting and smelting stages are potential sources of nitrogen oxides ($NO_X$). $NO_X$ may be formed out of nitrogen components that are present in the concentrates or as thermal $NO_X$. The sulphuric acid produced can absorb a large part of the $NO_X$ and this can therefore affect sulphuric acid quality. If high levels of $NO_X$ are present after the roasting stages, treatment of the roasting gases may be necessary for reasons of product quality and environment. Direct smelting uses oxygen enrichment except for slag fuming and can reduce the thermal $NO_X$. Other furnaces that use oxy-fuel burners also show a reduction in $NO_X$ but the reverse may be true at lower levels of oxygen enrichment when the temperature increase and the nitrogen content is significant. The range for all of the processes is 20 to 400 mg/Nm$^3$.

### 11.2.2.7 Diffuse emissions

Besides process emissions, diffuse emissions occur. The major diffuse emission sources are:

- dust from storage and handling of concentrates
- leakage from roasters, smelters and converters
- dust from the exhaust gases of leaching and purification vessels
- exhaust gases (including HCl, $Cl_2$ and VOCs) from the solvent extraction and electrowinning units
- dust from the exhaust gases of casting furnaces
- miscellaneous emissions including building ventilation air.

Although diffuse emissions are difficult to measure and estimate, there are some methods that have been used successfully (see Section 2.4.3). Table 11.7 gives some estimates from a primary smelter where the smelter and converter ventilation gases are collected and treated with the dryer gases.

| Emissions | Primary capture (t/yr) | Secondary capture (t/yr) | Diffuse (t/yr) |
|---|---|---|---|
| Sulphur dioxide (1999) | 523 | 2242 | 147 |
| Sulphur dioxide (2004) | 630 | 1976 | 248 |

**Table 11.7: Significance of secondary fume capture and diffuse emissions**
[ 239, ENIA 2008 ]

Table 11.7 above shows that diffuse emissions can be significant in primary smelting if ventilation gases are not collected and treated. The 2004 data was supplied in the industry response to draft 1 of this document. In this case they would be much higher than abated emissions. Refining processes are reported to have lower diffuse emissions and the carbonyl process is particularly well sealed. Action to reduce diffuse emissions may be needed in many processes.

It is possible to reduce the diffuse emissions arising from granulation fumes by treating the fumes with NaOH solution. Another way to reduce them, is by using covered, ventilated lids on the launders. These launders can be heated by using fuel or preferably by using electrically heated covers, which then allow an efficient collection of diffuse emissions thanks to the small amount of gas released.

Diffuse emissions from molten material transportation are also significant. In DON process as well as in flash smelting - flash converting processes there is no ladle transportation of molten material and thus diffuse emissions are much easier to control.

The collection of diffuse emissions is described in Section 2.3.

## 11.2.3 Emissions to water

Metals and their compounds and materials in suspension are the main pollutants emitted to water. The metals concerned are Cu, Ni, Co, As and Cr. Other significant substances are fluorides, chlorides and sulphates.

Possible sources of waste water are:

- hydrometallurgical purification processes
- matte granulation
- waste water from wet scrubbers
- waste water from wet electrostatic precipitators
- waste water from slag granulation
- anode and cathode washing liquid effluent
- sealing water from pumps
- general operations, including the cleaning of equipment, floors, etc.
- discharge from cooling water circuits
- rainwater run-off from surfaces (in particular storage areas) and roofs
- matte granulation.

Waste water from wet gas-cleaning (if used) of the smelter, converter and fluid bed roasting stages are the most important sources. Other sources are cleaning and miscellaneous sources. The leaching stages are usually operated on a closed circuit and drainage systems are isolated but there are potential problems unless good leak prevention and detection systems are used. Electrolyte bleed liquors are used in the leaching stage.

### 11.2.3.1 Waste waters from abatement plants

If wet scrubbers are used after the leaching and roasting processes, an acidic solution is produced. The scrubber removes fluorides, chlorine, chlorides, most mercury and selenium and some particles that pass the mechanical gas treatment. To avoid the buildup of contaminants, some liquid should be bled continuously from the scrubber and then treated. Dissolved $SO_2$ is removed prior to the discharge. Weak acid can also be treated by concentrating it and feeding it back into the uptake shaft of a flash smelting furnace.

Wet electrostatic filters will also produce an acidic scrubber liquid. This is recycled after filtering or after concentrating it is returned to the uptake shaft of the flash furnace. Some liquid should be bled from this circuit to remove the build-up of contaminants. This bleed liquor is treated and analysed before discharge.

Table 11.8 provides an indication of the composition of the gas-cleaning effluents before treatment.

| Pollutant | Concentration (dissolved) | Composition of suspended solids |
|---|---|---|
| Solids | | 250 - 1500 mg/l |
| Sulphate | 13 - 25 g/l | |
| Chloride | 1.3 - 1.8 g/l | |
| Fluoride | 0.3 - 0.5 g/l | |
| Cobalt | 0.1 - 9 mg/l | 5 - 30 % of suspended solids |
| Nickel | 0.1 - 10 mg/l | 10 - 60 % of suspended solids |
| Copper | 5 - 15 mg/l | <0.05 % of suspended solids |
| Zinc | 0.1 - 2.5g/l | 2 - 6 % of suspended solids |
| Cadmium | 1 - 5 mg/l | |
| Lead | 1 - 3 mg/l | 5 - 50 % of suspended solids |

**Table 11.8: Typical gas-cleaning effluents**

### 11.2.3.2 Miscellaneous sources

*This is an inaapropriate heading*

The electrodes and membrane bags used during electrolysis need to be rinsed periodically to remove deposited material upon the surface. Manganese dioxide can be formed on the surface of the anodes by the reaction of oxygen with dissolved manganese. After rinsing the anodes, the manganese is separated from the rinse water for external re-use. Cathodes are cleaned after removal of the Co or Ni sheets. The anode and cathode washing liquid effluents are acidic and likely to contain copper, nickel, cobalt and suspended solids.

Granulation water from the granulation of matte or slag is usually recirculated in a closed circuit system. There have been reports of the formation of persistent organic chlorine compounds and PCDD/F in some cooling circuits of chlorine leach processes.

Filters and waste water from the hydrometallurgical separation and transformation processes are treated for metal and suspended solid removal. The products of this treatment may be returned to upstream operations, depending on their composition and value. The wet ESP can be used for that purpose. Potential sources of waste waters are reported in Table 11.9.

| Process unit | Operation/source | Use/treatment options |
|---|---|---|
| General | Rainwater from roads, yards, roofs<br>Wet cleaning of roads<br>Cleaning of lorries, etc. | Waste water treatment plant/re-use<br>Waste water treatment plant<br>Recirculation, waste water treatment plant |
| Smelting operation | Cooling water from the furnace, machinery and equipment | Recirculation |
| Matte or slag granulation | Wet ESP effluent (if needed)<br>Granulation water | Recirculation, waste water treatment plant<br>Recirculation |
| Gas cleaning system | Condensate from gas cooling, wet ESP<br>Condensate from mercury removal<br>Leakage | Removal of suspended dusts and re-use as feed, waste water treatment plant<br>After mercury removal to waste water treatment plant<br>Recirculation |
| Sulphuric acid plant | Cooling water equipment<br>Leakage | Recirculation<br>Waste water treatment plant |
| Feed storage | Surface water (rain/wetting) | Waste water treatment plant |

| | | |
|---|---|---|
| Sinter plant | Scrubber (sinter fine cooling) | Waste water treatment plant |
| Roast gas cleaning | Wet gas-cleaning | Waste water treatment plant |
| Roasting/roast gas-cleaning | Wet cleaning of roast gases | Waste water treatment plant |
| Leaching | General operations including wet gas-cleaning | Recovery of metals |
| Purification | General operations<br>Filter cakes | Recovery of metals<br>Countercurrent washing |
| Electrolysis | Cleaning of cells, anodes and cathodes | Recovery of metals |
| All process units | Maintenance | Waste water treatment plant |
| Waste water treatment plant | Effluent treatment | Re-use for certain applications/discharge |

**Table 11.9: Summary table of potential waste water sources and treatment options**

Table 11.10 and Table 11.11 give data for emissions to water and the mass emissions of nickel per tonne produced for some European sites [ 239, ENIA 2008 ].

| Process | Effluent ($m^3/d$) | Flow ($m^3/t$) | Main components (mg/l) | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | Cu | Zn | As | Co | Ni | COD |
| Co | | 200 | <0.1 | <1.5 | <0.1 | <1.5(1) | <1.0 | 25 |
| Cl leach | | 55 | 0.1 | | | 0.2 | 0.7 | |
| Cl leach | | | 1.0 | 1.0 | | 0.25 | 1.0 | |
| Carbonyl | | 450 | 0.4 | | | 0.1 | 1.4 | |
| Smelter + leach (2) | 10900 | | 10 g/t | 4 g/t | 2 g/t | | 10 g/t | |

(1) Co emission is 0.5 kg per tonne of Co produced

(2) The data of Smelter + Leach covers process waters, cooling water, acid plant and rain water from a combined Cu and Ni smelter and nickel leaching.

**Table 11.10: Examples of waste water analyses**
[ 239, ENIA 2008 ]

| Process | Waste water volume ($m^3/d$) | Emission of nickel (g Ni per tonne produced) |
|---|---|---|
| Matte grinding and leaching | 1640 | 15.7 |
| Matte grinding and leaching | 3233 | 16 |
| Nickel smelting and matte refining (1) | 1900 | 29.6 |
| Carbonyl process | 6615 | 30 |

(1) The data of nickel smelter + matte refining covers both Cu and Ni smelter and nickel leaching process.

**Table 11.11: Mass emissions of nickel per tonne produced for European processes**
[ 239, ENIA 2008 ]

### 11.2.4 By-products, process residues and waste

The production of metals is related to the generation of several by-products, residues and wastes, which are also listed in the European Waste Catalogue (Council Decision 94/3/EEC). *This has been replaced by a new directive 75/442/EEC (see Section 5.2.4)* The most important process-specific residues are listed in this section below.

Residues arise as a result of the treatment of liquid effluents. The main residues are gypsum waste ($CaSO_4$) and metal hydroxides that are produced at the waste water neutralisation plant. These wastes are considered to be a cross-media effect of these treatment techniques but many are recycled to the metallurgical process to recover the metals, depending on their value.

Dust or sludge from the treatment of gases are used as raw materials for the production of other metals such as precious metals and Cu, etc. or can be returned to the smelter or into the leach circuit for recovery.

#### 11.2.4.1 Precipitates from purification processes

The production of iron-based solids accounts for a significant volume of waste depending on the process used. The composition is shown in Table 11.12.

| Process | Fe (%) | Zn (%) | Co (%) | Cu (%) | Ni (%) |
|---|---|---|---|---|---|
| Iron hydroxide residues in the chloride leaching process | 40 |  | 0.1 | <0.1 | 1 - 2 |
| Gypsum residues |  | 25 | 2 - 3 |  |  |
| Waste water treatment | <10 | <10 | <0.5 | <1 | <0.05 |

**Table 11.12: Example compositions of different types of residues**

The disposal of these residues can be a considerable cost as specially constructed, lined ponds are used to contain the material. Particular care is taken about leakage and operators of these ponds have to monitor groundwater. There is a significant cross-media effect. One site deposits the waste in underground rock caverns.

#### 11.2.4.2 Pyrometallurgical slags and residues

Slags from smelting processes usually contain very low concentrations of leachable metals after slag cleaning. They are therefore suitable for use in construction, abrasives and other purposes. The slag output is between 4 and 10 times the weight of the metal produced depending on the source of the concentrate. Table 11.13 gives examples of the composition of some nickel slags. The exact composition will also depend on the source of the concentrate [ 139, Riekkola-Vanhanen, M. 1999 ].

| Component | Reverberatory furnace | Electric furnace | Outotec flash(1) |
|---|---|---|---|
| Nickel (%) | 0.2 | 0.17 | 0.1 - 0.3 |
| Cobalt (%) | 0.1 | 0.06 | 0.1 - 0.25 |
| Copper (%) | 0.08 | 0.01 | 0.05 - 0.25 |
| Iron (%) | 38 |  | 35 - 43 |
| Silica (%) | 36 | 35 | 30 - 39 |
| Lime (%) | 2 |  | 0.5 - 7 |
| (1)After cleaning in an electric furnace - |  |  |  |

**Table 11.13: Composition of typical nickel slags**

A number of standard leachability tests are used by Member States and these are specific to the Country in question. Nickel slags are listed in the EU on the amber list of the Transfrontier Shipment of Waste Regulations. The dross and solids, removed during the melting and refining stages, contain metals that are suitable for recovery. Table 11.14 shows some of the treatment or re-use options for solid residues from nickel and cobalt processes.

| Process step | Solid output | Use/treatment options |
|---|---|---|
| Autoclave | Residue | Smelting furnace |
| Iron removal | Precipitate | Smelting furnace or disposal |
| Abatement | Filter dust | Smelting furnace |
| Pressure leaching | Sulphide residue | Cu recovery |
| De-copperising | Cu cement | Cu smelter |

| | | |
|---|---|---|
| Nickel and cobalt regeneration | Impure nickel carbonate | Pure nickel sulphate production |
| Slag treatment | Clean slag | Construction |
| Removal of As, etc. | Gypsum ferri-arsenate | Special disposal or As recovery |
| Effluent treatment | Precipitate | Recovery of other metals or disposal |

**Table 11.14: Some of the treatment or re-use options for solid residues from Ni and Co processes**

#### 11.2.4.3 Other materials

Other residues or sludges arising from the different process stages or from general waste water treatment, depending on their composition and value may be recycled or sent for final disposal.

## 11.3 Techniques to consider in the determination of BAT

The sections of this document entitled 'Techniques to consider in the determination of BAT' set out techniques considered generally to have potential for achieving a high level of environmental protection in the industries within the scope of the document. The background to the way the techniques are described is given in Section 2.1.2 and Table 2.2.

This section presents a number of techniques for the prevention or reduction of emissions and residues as well as techniques reducing the overall energy consumption. They are all commercially available. Examples are given in order to demonstrate techniques which illustrate a high environmental performance. The techniques that are given as examples depend on information provided by the industry, European Member States and the evaluation of the European IPPC Bureau.

The general techniques described in Chapter 2 'common processes' apply in a large extent to the processes in this sector and influence the manner in which the main and associated processes are controlled and operated. Techniques used by other sectors are also applicable particularly those relating to the use of sulphur recovery systems.

The techniques to consider on a site by site basis are strongly influenced by the raw materials that are available to a site, in particular the type and variability of the concentrate, intermediate product (e.g. matte) or secondary raw materials. The other metals that they contain can also be crucial to the choice of process. In a similar manner, the standard of collection and abatement systems used worldwide in the industry reflects local, regional or long-range environmental quality standards and direct comparison of the environmental performance of process combinations is therefore difficult. It is possible however, to judge how a particular process can perform with the appropriate, modern abatement equipment.

The processes described above are applied to a wide range of raw materials of varying quantity and composition and are also representative of those used worldwide. The techniques have been developed by the Companies in this sector to take account of this variation. The choice of pyrometallurgical or hydrometallurgical technique is driven by the raw materials used, their quantity, the impurities present, the product made and the cost of the recycling and purification operation. These factors are therefore site-specific. The basic recovery processes outlined in Section 11.1 on applied techniques therefore constitute techniques to consider for the recovery processes when used with appropriate abatement stages. The techniques to consider for collection and abatement stages and other aspects of process operation and control are covered in Sections 2.8, 2.4.3 and 2.9.

### 11.3.1 Materials storage, handling and pretreatment processes

The raw materials are concentrates, chlorine and other gases, intermediate products, fluxes and fuel, other important materials are products, sulphuric acid, slags and process residues. Important aspects are the prevention of the leakage of dust and wet material, the collection and treatment of dust and liquids and the control of the input and operating parameters of the handling and feeding processes [ 290, EC 2006 ].

**Descriptions**
The materials storage, handling and pretreatment issues specific to this group are given in the list below.

- The potentially dusty nature of concentrates and fluxes means that enclosed storage, handling and treatment systems are techniques to consider in these instances.
- The dust generated by some crushing operations means that collection and abatement may be applicable for this process.

- Concentrates are mixed with fluxes to produce a fairly constant feed, therefore the general practice is sampling and analysis to characterise the concentrates and store individual concentrates separately so that an optimum blend can be prepared for smelting.
- Intermediate products such as matte may also need to be handled in this way depending on the potential to form dust.
- Chlorine, oxygen and other gases will be handled according to specific safety requirements to prevent leaks and contain the gases.
- Process gases such as oxygen, chlorine, hydrogen or carbon monoxide can be stored in approved pressure vessels or can be produced on site. The production of these gases is covered elsewhere. Gases are usually regenerated and recycled during the processes and are returned to the process or storage.
- Acid produced during the process should be stored in double-walled tanks or tanks placed in chemically-resistant bunds. The treatment of acid slimes from the sulphuric acid plant and weak acid from scrubbing systems depends on local processing or disposal requirements unless there is a local use for the material.
- Sludges and other metallic residues that are destined for recovery off site should be stored in drums or other suitable ways depending on the material.
- There are a variety of secondary raw materials used and they range from fine dusts to large single items. The metal content varies for each type of material and so does the content of other metals and contaminants. The techniques used for storage, handling and pretreatment will therefore vary according to the material size and the extent of any contamination.
- The storage of raw materials depends on the nature of the material described above. The storage of fine dusts in enclosed buildings or in sealed packaging is used. Materials that contain water-soluble components are stored under cover. The storage of non-dusty material in open stockpiles and large items individually in the open is used.

**Achieved environmental benefits**
Prevention and capture of dust and other emissions.

**Cross-media effects**
No data was reported.

**Operational data**
Given in the descriptions of the process above.

**Applicability**
These techniques are applicable to most installations.

**Economics**
No data was reported.

**Driving force for implementation**
Environmental impact and energy costs due to lost material.

**Example plants**
UK, ES, DE.

**Reference literature**
[ 290, EC 2006 ].

### 11.3.2 Primary smelting processes

The only smelting process used for the direct production of nickel or cobalt in Europe is the Outotec DON flash smelter using high oxygen enrichment [ 310, Direct Outokumpu Nickel

Technology 2006 ]. This is used to produce a nickel matte and a slag that is treated further in an electric furnace to produce more matte and an inert slag. The mattes are granulated for hydrometallurgical processing and the slag is granulated or cooled and used for civil engineering purposes. The use of the Outotec flash furnace in this manner is characterised by low energy consumption of the overall process (7 MWh per tonne of Ni) and reliable furnace operation. The process features heat recovery in the form of steam and electricity and also the collection and recovery of sulphur dioxide as sulphuric acid. The furnace lining life is reported to be greater than five years. The other processes used worldwide are also techniques to consider.

The Peirce-Smith converter is not used for the production of nickel or cobalt in Europe. The use of this converter would be a technique to consider when used in conjunction with an intelligent secondary fume collection system and furnace blowing control system (see Chapter 3 on Copper).

Cobalt is generally recovered in conjunction with nickel. The process that is used to produce ferro-nickel is covered in Chapter 9, ferro-alloys.

The abatement system used for the primary smelting of sulphide concentrates is the recovery of sulphur dioxide usually by conversion to sulphuric acid in a double contact process with four or more passes. A caesium-doped catalyst is used. Conversion of part of the $SO_2$ into liquid $SO_2$ is also practised with the balance being converted into sulphuric acid. The gases are cooled (with heat/energy recovery) and cleaned before conversion. A combination of coolers and hot electrostatic precipitators or a combination of scrubbers (radial or jet) and wet ESPs are used. Mercury recovery systems are employed using the techniques discussed in Section 2.9.2.8.

**Achieved environmental benefits**
The environmental benefits are the prevention of diffuse emissions of metals, dust and other compounds.

**Cross-media effects**
None are reported.

**Operational data**
None are available.

**Applicability**
The processes and the techniques are suitable for use with new and existing installations.

**Economics**
None was provided but the processes are operating economically.

**Driving force for implementation**
The reduction of emissions and saving raw materials.

**Example plants**
Plants in FI.

**Reference literature**
[ 233, Farrell Nordic Mission 2008 ], [ 310, Direct Outokumpu Nickel Technology 2006 ].

### 11.3.3 Refining and transformation processes

#### 11.3.3.1 Leaching, chemical refining and solvent extraction

The refining processes described in Sections 11.1 and 11.2 are applied to a wide range of raw materials of varying quantity and composition. The techniques have been developed by the companies in this sector to take account of this variation. The choice of a pyrometallurgical or hydrometallurgical technique is driven by the raw materials used, the impurities present and the product made. In particular, the morphology of the final product can be crucial, for example when powders are produced for battery manufacture or when metal coatings are applied to a variety of substrates such as foams [ 139, Riekkola-Vanhanen, M. 1999 ].

The basic refining processes outlined above therefore constitute the techniques to consider for the recovery processes. The application of the reactor sealing, abatement, control and management techniques that are covered in Chapter 2 of this document are techniques to consider.

**Achieved environmental benefits**
The environmental benefits are the prevention of diffuse emissions of metals, dust and other compounds.

**Cross-media effects**
None are reported.

**Operational data**
None are available.

**Applicability**
The processes and the techniques are suitable for use with new and existing installations.

**Economics**
None was provided but the processes are operating economically.

**Driving force for implementation**
The reduction of emissions and saving raw materials.

**Example plants**
Plants in FI.

**Reference literature**
[ 233, Farrell Nordic Mission 2008 ].

#### 11.3.3.2 Minimisation of the emissions of VOCs

**Description**
Use of a low shear mixer for the solvent/aqueous mixture to optimise the droplet size and minimise contact with air reduces the amount of solvent that is evaporated and promote the dissolution of the metal complex. The use of covers for the mixer and separator and settlement stages reduce emissions of VOC to air and carryover in aqueous phase. Use of low shear and variable speed pumping reduces energy consumption of the system.

**Achieved environmental benefits**
Prevention of VOC emissions and reduction of energy use.

**Cross-media effects**
No data was reported.

**Operational data**
Concentration of VOC in occupational air <5 ppm (<30 mg/Nm$^3$) when kerosene was used as solvent.

**Applicability**
This technique is applicable to all solvent extraction processes.

**Economics**
No data has been reported but the process operates viably in several installations.

**Driving force for implementation**
Reduction of emissions

**Example plants**
Finland.

**Reference literature**
[ 92, Laine, L. 1998 ]

### 11.3.3.3 Electrowinning

Electrowinning may produce gases that are evolved at the anode and will produce chlorine or an acid mist. This should be collected and removed, extraction and mist elimination are used and the collected mist returned to the process. Scrubbing the collected gases does not allow re-use of the mist and contributes to waste water.

Cell coverings can be used to reduce the amount of mist formed but are not as effective as demisting. Organic coatings or plastic bead layers can be used. In the case of electrowinning processes based on chloride, the recovery and re-use of chlorine produced from the cells is considered to be part of the process.

There are also dangers of short circuiting in the cells as the cathode increases in thickness. Monitoring cell temperatures using infrared detectors can be used to identify hot spots that indicate short circuiting in the cell.

**Achieved environmental benefits**
The environmental benefits are the prevention of diffuse emissions of metals, dust and other compounds.

**Cross-media effects**
None are reported.

**Operational data**
None are available.

**Applicability**
The processes and the techniques are suitable for use with new and existing installations.

**Economics**
None was provided but the processes are operating economically.

**Driving force for implementation**
The reduction of emissions and saving raw materials.

**Example plants**
Plants in FI.

**Reference literature**
[ 233, Farrell Nordic Mission 2008 ].

### 11.3.3.4 Collection and prevention ~~reduction~~ of chlorine gas emissions

**Description**
Gases produced during the electrowinning and leaching processes are collected. The electrolysis cells are fitted with an integral hood, which collects chlorine gas. Leaching reactors are sealed which allows the gases to be collected. The gas from electrowinning is collected and blown into a central system and returned to the leaching stage. Anodes that comprise a membrane construction with integrated chlorine collection are used to collect the gas.

**Achieved environmental benefits**
This technique reduces the need for an extensive gas scrubbing system by preventing emissions of chlorine. Re-use of chlorine minimises the amount of chlorine purchased. Reduction in the amount of gas scrubbing prevents effluent discharges. Multistage venturi scrubbers can achieve emission levels of < 1 mg/Nm$^3$ of chlorine.
*Unclear: The advantage of the technqies is that scrubbing systems are not needed. How does this info about the venturi scrubber fits than?*

**Cross-media effects**
No data was reported.

**Operational data**
No data has been reported.

**Applicability**
This technique is applicable to all electrowinning processes using chloride based electrolyte. The processes and the techniques for control, mist collection and acid gas recovery and removal are suitable for use with new and existing installations.

**Economics**
No data has been reported. The system is viable in most electrowinning process using chloride solutions.

**Driving force for implementation**
Reduction of emissions.

**Example plants**
NO, FR.

**Reference literature**
[ 92, Laine, L. 1998 ].

### 11.3.3.5 Tank house drainage system

**Description**
Tank house drainage systems are sealed to prevent the direct discharge of any spillages. The collected liquids are returned to the electrolyte or recovered. Electrolyte is bled from the circuit to control the concentrations of other metals. The electrolyte bleed is also recovered and the other metals removed by crystallisation [ 260, OutoK etccccc 2000 ].

**Achieved environmental benefits**

This technique prevents peak discharges to the waste water system that can overload the treatment capacity by preventing emissions that could cause failure of the treatment systems. Recovery of the metal content of electrolyte.

**Cross-media effects**

No data has been reported.

**Operational data**

No data has been reported.

**Applicability**

This technique is applicable to all electrowinning and is suitable for use with new and existing installations.

**Economics**

No data has been reported but the system is viable in most electrowinning.

**Driving force for implementation**

Reduction of emissions and the recovery of other metals.

**Example plants**

NO, FI.

**Reference literature**

[ 92, Laine, L. 1998 ].

#### 11.3.3.6 Hydrometallurgy from sulphidic ores

**Description**

Bioleaching for mixed ores that contain cobalt, zinc and copper using iron and sulphur oxidising bacteria has been developed in Finland and is being commissioned. The naturally occurring bacteria enhances the leaching process by promote the leaching of metals from ore to solution and so improves efficiency. This technique is being used for some nickel ores where zinc, cobalt and copper are leached simultaneously and then separated prior to metal recovery [ 284, Talvivaara June 2008 ], [ 260, OutoK etccccc 2000 ]. Irrigation with the acid-based leaching solution and aeration are the only additional processes. The metals that are leached are recovered in the conventional hydrometallurgical processes that are reported in this section and in Chapters 3 and 5.

**Achieved environmental benefits**

Main environmental impacts relate to the mining activities. Existing, natural leaching of the metals will stop as the metals are removed from the ore body and so emissions to water will be reduced.

**Cross-media effects**

No data has been reported.

**Operational data**

No data has been reported.

**Applicability**

This technique is applicable to the recovery of metals where there is unlimited space, e.g. at the site of the mine.

**Economics**

Confidential.

**Driving force for implementation**
Reduction in emissions and the recovery of other metals.

**Example plants**
FI.

**Reference literature**
[ 233, Farrell Nordic Mission 2008 ], [ 260, OutoK etccccc 2000 ].

### 11.3.3.7 Other metals

Precious metals and copper are often associated with the raw materials and they are either recovered on site or the residues are sent to other refineries. The processes that were discussed earlier in Sections 11.1 and 11.2 are all techniques to consider in the determination of BAT. The specific feed materials will influence the final process choice.

### 11.3.3.8 Production of metal powders, ingots and other products

The specific feed materials and the final products will influence the choice of process and the factors of product size and shape are the main influencing factors.

## 11.3.4 Fume/gas collection and abatement

The techniques discussed in Section 2.4.3 of this document are techniques to be considered for the various process stages involved in the production of cobalt and nickel, etc. The use of containment or secondary hoods is also a technique to be considered. There are several site-specific issues that will apply to the abatement techniques used. This depends on the reagents used in the process and the components present in the off-gas. Some of the techniques are summarised in Table 11.15.

| Reagent used | Components in the off-gas | Treatment method |
|---|---|---|
| Solvents, VOC | VOC, odours | Containment, condensation, activated carbon, biofilter |
| Chlorine, HCl | $Cl_2$ | Collection and re-use, caustic scrubber system |
| Sulphides | Sulphur dioxide | Sulphuric acid plant or scrubber |
| Nitric acid | $NO_X$ | Oxidise and absorb, recycle, scrubber system |
| Ammonia | $NH_3$ | Recovery, scrubber system |
| Hydrogen | $H_2$ | Process control, afterburner |
| Carbon monoxide | CO | Recovery and re-use, afterburner and dust removal. |

**Table 11.15: Chemical treatment methods for some gaseous components**
*Not all of the methods are chemical treatment methods.Rename the table.*

Essentially the process technologies discussed in this section, combined with suitable abatement will meet the demands of stringent environmental protection. An example is given of the collection of chlorine gas that is evolved at the anode during electrowinning and leaching. Other techniques include the containment of solvent vapours using closed solvent extraction reactors and the collection and re-use of solvents and CO. The significance of the components of any VOC depend on the solvent used and these can only be determined locally.

The use of hoods for tapping and casting and the use of secondary fume collection from the smelter and converter stages are also techniques to consider. Tapping fumes will consists of fumes from oxygen lancing, dust from drilling, fumes from the vaporised slugs if a tapping gun is used and fumes from all exposed metal and slag surfaces. These fumes will consist mainly of oxides of the metals that are involved in the smelting process. The design of the hooding system should take account of access for charging and other furnace operations and the way the source of process gases change during the process cycle.

The metal content of the dust varies widely between processes. In addition, for similar furnaces, there are significant variations due to the use of varying raw materials. It is therefore not possible to report specific achievable concentrations for all metals emitted to air in this document.

Low concentrations of metals are associated with the use of high-performance, modern abatement systems such as a membrane fabric filters provided the operating temperature is correct and the characteristics of the gas and dust are taken into account in the design.

### 11.3.5 Process control and management

The principles of process control and management discussed in Sections 2.2 and 2.5 are applicable to the production processes used in this group. Some of the processes are capable of improvement by the adoption of many of these techniques.

### 11.3.6 Waste water

Waste water is a site-specific issue, existing treatment systems are reported to be of a high standard. All waste water should be treated to remove dissolved metals and solids. The techniques listed in Section 2.12.2 are the techniques to consider. In a number of installations, cooling water and treated waste water including rainwater is re-used or recycled within the processes. Similarly, granulation water may require settlement or other treatment prior to discharge to water.

| **Process** | **Effluent ($m^3$/d)** | **Flow ($m^3$/t)** | **Main components (mg/l)** | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | **Cu** | **Zn** | **As** | **Co** | **Ni** | **COD** |
| Co | | 200 | <0.1 | <1.5 | <0.1 | <1.5 | <1.0 | 25 |
| Cl Leach | | 55 | 0.1 | | | 0.2 | 0.7 | |
| Cl Leach | | | 1.0 | 1.0 | | 0.25 | 1.0 | |
| Carbonyl | | 450 | 0.4 | | | 0.1 | 1.4 | |
| Smelter + Leach (1) | 6000 | | 17 g/t | 9 g/t | 2 g/t | | 16.5 g/t | |

(1) The data of Smelter + leach covers both Cu and Ni smelter and nickel leaching.

**Table 11.16: Examples of waste water analyses**

[ 239, ENIA 2008 ]

*This is the same table as in Section 11.2.3.2. Avoid repetition.*

### 11.3.7 By-products, process residues and waste

This is a site and process-specific issue but the minimisation and re-use of residues in other processes and locations, where practicable, should be considered. The techniques to consider in Section 2.13.3 presents techniques to consider in the determination of BAT.

## 11.4 Best Available Techniques

In understanding this section and its contents, the attention of the reader is drawn back to the Preface of this document and in particular the fifth section of the Preface: ‘How to understand and use this document’. The techniques and associated emission and/or consumption levels, or ranges of levels, presented in this section have been assessed through an iterative process involving the following steps:

- identification of the key environmental issues for the sector which for the production of cobalt and nickel are: VOCs, dust, fume, odours, $SO_2$, chlorine CO and other acid gases, waste water, residues such as sludge, filter dust and slag;
- examination of the techniques most relevant to address these key issues;
- identification of the best environmental performance levels, on the basis of the available data in the European Union and worldwide;
- examination of the conditions under which these performance levels were achieved; such as costs, cross-media effects, and the main driving forces involved in the implementation of the techniques;
- selection of the best available techniques (BAT) and the associated emission and/or consumption levels for this sector in a general sense, all according to Article 2(12) and Annex IV to the Directive.

Expert judgement by the European IPPC Bureau and the relevant Technical Working Group (TWG) has played a key role in each of these steps and in the way in which the information is presented here.

On the basis of this assessment, best available techniques, and as far as possible emission and consumption levels associated with their use, are presented in this section that are considered to be appropriate to the sector as a whole and in many cases reflect the current performance of some installations within the sector. Where emission and consumption levels 'associated with best available techniques' are presented, this is to be understood as meaning that those levels represent the environmental performance that could be anticipated as a result of the application, in this sector, of the techniques described, bearing in mind the balance of costs and advantages inherent within the definition of BAT. However, they are neither emission nor consumption limit values and should not be understood as such. In some cases, it may be technically possible to achieve better emission or consumption levels but due to the costs involved or cross-media considerations, they are not considered to be appropriate as BAT for the sector as a whole. However, such levels may be considered to be justified in more specific cases where there are special driving forces.

The emission and consumption levels associated with the use of BAT have to be seen together with any specified reference conditions (e.g. averaging periods).

The concept of ‘levels associated with BAT’ described above is to be distinguished from the term ‘achievable level’ used elsewhere in this document. Where a level is described as ‘achievable’ using a particular technique or combination of techniques, this should be understood to mean that the level may be expected to be achieved over a substantial period of time in a well maintained and operated installation or process using those techniques.

Where available, data concerning costs have been given together with the description of the techniques presented in the previous sections. These give a rough indication about the magnitude of the costs involved. However, the actual cost of applying a technique will depend strongly on the specific situation regarding, for example, taxes, fees, subsidies, and the technical characteristics of the installation concerned. It is not possible to evaluate such site-specific factors fully in this document. In the absence of data concerning costs, conclusions on economic viability of techniques are drawn from observations on existing installations.

The BAT (including the associated emission and consumption levels) given in this section are 'BAT in a general sense' (i.e. considered to be appropriate to the sector as a whole). It is intended that they are a reference point against which to judge the current performance of an existing installation or to judge a proposal for a new installation. In this way, they will assist in the determination of appropriate 'BAT-based' conditions for the installation or in the establishment of general binding rules under Article 9([8]) of the IPPC Directive. It is foreseen that new installations can be designed to perform at or even better than the BAT levels presented in this section. It is also considered that existing installations could move towards the BAT levels presented in this section or do better, subject to the technical and economic applicability of the techniques in each case.

While the BAT reference documents do not set legally binding standards, they are meant to give information for the guidance of industry, Member States and the public on achievable emission and consumption levels when using specified techniques. The appropriate permit conditions for any specific case will need to be determined taking into account the objectives of the IPPC Directive and the local considerations.

**Recommendation to help users/readers of this document:**

It is strongly recommended that this section on BAT be read in conjunction with the sections of this document that describe the techniques to consider in the determination of BAT. The applicability of the techniques and measures are reported in these sections and should be taken into account at a local level. To help the reader, references to the appropriate sections are included in the description of BAT.

If not otherwise mentioned, BAT associated emission and consumption levels given in this section are expressed as follows:

- for pollutants emitted to air (except dioxins): expressed on a daily average basis with standard conditions of 273 K, 101.3 kPa, measured oxygen content and dry gas with the plant operating normally under steady-state conditions and no dilution of the gases;
- for dioxins: expressed as the average over the sampling period which should preferably be a minimum of 6 hours;
- for waste water: based on qualified random samples or 24 hour flow proportional composite samples.

As described in the Preface, this document does not propose emission limit values. The best available techniques and the ranges of emission or consumption levels associated with best available techniques (BAT-AEL ranges) are related to installations with different sizes, different kinds of operation and different raw materials. In this document, special local considerations cannot be taken fully into account. The determination of appropriate permit conditions will involve taking account of local, site-specific factors such as the technical characteristics of the installation concerned, its geographical location and the local environmental conditions. In the case of existing installations, the economic and technical viability of upgrading them also should be taken into account. Even the single objective of ensuring a high level of protection for the environment as a whole will often involve making trade-off judgements between different types of environmental impact, and these judgements will often be influenced by local considerations.

Although an attempt is made to address some of these issues, it is not possible for them to be considered fully in this document. The techniques and emission and consumption levels presented here will therefore not necessarily be appropriate for all installations. On the other hand, the obligation to ensure a high level of environmental protection including the minimisation of long-distance or transboundary pollution implies that permit conditions cannot be set on the basis of purely local considerations. It is therefore of the utmost importance that the information contained in this document be fully taken into account.

Section 2.20 to this document reports BAT for the following common processes and the following sections should be referred to for those techniques that are BAT:

- environmental management systems (EMS) (Section 2.20.1)
- material handling and storage (Section 2.20.2)
- process control (Section 2.20.3)
- fume and gas collection (Section 2.20.4)
- the prevention and the destruction of PCDD/F (Section2.20.5)
- sulphur dioxide removal (Section 2.20.6)
- the removal of mercury (Section 2.20.7)
- effluent treatment and water re-use (Section 2.20.8)
- energy efficiency (Section 2.20.9)
- intermediate products, process residues and wastes (Section 2.20.10)
- emission monitoring (Section 2.20.11)
- prevention of the formation of $NO_X$ (Section 2.20.12)
- removal of dust and particles (Section 2.20.13)

BAT for the production of nickel and cobalt is the combination of the generally applicable techniques reported in Section 2.20 and the specific techniques indicated in this section.

## 11.4.1 Prevention and control of emissions to air

### 11.4.1.1 Pyrometallurgical processes

**a) BAT is to prevent diffuse emissions and optimise the use of energy by using the pyrometallurgical processes that are described as techniques to consider in the determination of BAT in Section 11.3.**
*Inappropriate BAT conclusion.*

### 11.4.1.2 Refining and transformation processes

**b) BAT is to prevent diffuse emissions and optimise the use of energy by using the refining and transformation processes that are described in Section 11.3.3.**
*Inappropriate BAT conclusion.*

### 11.4.1.3 Fume and gas collection and abatement

**a) BAT is to prevent and control emissions of dust, metals and sulphur dioxide from the smelting of sulphide concentrates by using one of the techniques reported in Section 2.11.3.1**.

**b) BAT is to prevent and control emissions of dust, metals, sulphur dioxide, nitrogen oxides, total organic carbon and PCDD/F to air from processes to produce nickel and cobalt by using the techniques given in Table 11.17, Table 11.18 and Table 11.19 or a combination ~~of them~~ (see also Sections 2.9.2.4.1 and 2.9.2.4.2).**
*Inappropriate BAT conclusion. Disaggregate and rewrite.*

| Process stage | Component in off-gas | Techniques |
|---|---|---|
| Material handling and storage | Dust and metals | Correct storage, handling and transfer.<br>Dust collection and fabric filter |
| Grinding, drying | Dust and metals | Process operation. Gas collection and fabric filter |
| Smelting and converting (Sulphidic ore) | Dust, metals and sulphur dioxide | Gas collection, gas-cleaning and sulphuric acid plant |
| Slag treatment | Dust and metals<br>Sulphur dioxide<br>Carbon monoxide | Gas collection, cooling and fabric filter<br>Scrubber<br>Afterburner |
| Leaching and chemical refining | Chlorine | Gas collection and re-use, wet chemical scrubber |
| Carbonyl refining | Carbon monoxide<br>Hydrogen | Sealed process, recovery and re-use.<br>Afterburner and dust removal in fabric filter for tail gas |
| Solvent extraction | VOC (depends on the solvent used and should be determined to assess the possible hazard) | Containment, gas collection, solvent recovery. Carbon adsorption |
| Thermal refining | Dust and metals<br>Sulphur dioxide | Gas collection and fabric filter<br>Scrubber for $SO_2$ |
| Powder production | Ammonia | Gas collection and recovery<br>Acid medium scrubber |
| High temperature reduction | Hydrogen | Sealed process, re-use<br>Afterburner |
| Electrowinning | Chlorine<br>Acid mist | Gas collection and re-use<br>Wet scrubber<br>Demister. |
| Melting and casting | Dust and metals | Gas collection and fabric filter |
| ([1]) Dust arrestment using a fabric filter may require the removal of hot particles to prevent fires. Hot electrostatic precipitators would be used in a gas-cleaning system prior to a sulphuric acid plant. | | |

**Table 11.17: Summary of BAT to prevent and control emissions to air from processes to produce nickel and cobalt**

**The emission values given in Table 11.18 and Table 11.19 are the BAT-AELs.**

| Pollutant | Techniques | BAT-AELs | Comments |
|---|---|---|---|
| Dust | Fabric or ceramic filter | <1 to 5 mg/$Nm^3$ | Bag burst detection should be used *(this is redundant information and not useful for permit writers)*<br>(See Sections 2.9.2.2.4 and 2.20.13) *(there are no data for Ni and Co production in these sections)* |
| Metals | Fabric or ceramic filter | See Sections 11.2.2.3 and *11.3.4 (11.3.4 contains no relevant information)* | The concentration of metals is linked to the concentration of dust and content of the metals in the dust *(this is redundant information and not useful for permit writers)* |

| Pollutant | Techniques | BAT-AELs | Comments |
|---|---|---|---|
| $SO_2$ | Alkali semi-dry scrubber and fabric filter. Wet alkali or double alkali scrubbers using lime, magnesium hydroxide, sodium hydroxide. | <50 to 400 mg/Nm³ | Potential cross-media effects from energy use, waste water and solid residues together with the ability to re-use scrubber products will influence the choice of the technique used (see Section 2.11.3.4) |
| | Fabric filter with dry lime injection into cool gas. | 100 to 500 mg/Nm³ | Part of the reacted lime can be used as a fluxing agent. (see Section 2.11.3.6) |
| *There is no useful information in the document to conclude on BAT-AELs for $SO_2$ for Ni and Co production* | | | |
| $NO_X$ | Low $NO_X$ burner or<br>Oxy-fuel burner | <100 to 300 mg/Nm³ | Higher values are associated with oxygen enrichment to reduce energy use. In these cases, gas volume and mass emission is reduced (see Sections 2.9.2.4.3, 2.20.12 and 11.2.2.6). |
| *There is one range included in Section 11.2.2.6: 20 – 400 mg/Nm³. It is unclear how the BAT-AEL range forNOx has been derived.* | | | |
| Total organic carbon as C | Afterburner<br>Optimised combustion | 1 to 10 mg/Nm³ | REF? (see Section 2.9.2.6) |
| *It is unclear what the origin of organic carbon emissions is. In the list of potential emissions from nickel and cobalt production in table 11.3 organic carbon is not included. Ask TWG.* | | | |
| PCDD/F | High efficiency dust removal system (i.e. fabric filter) or<br>Afterburner followed by quenching or<br>Adsorption by activated carbon or<br>An oxidation catalyst. | <0.1 ng I-TEQ/Nm³ | Treatment of a clean, dedusted gas is required to achieve low levels<br>(See Sections 2.10.2.1 and 2.20.5) |
| *It is unclear what the origin of PCDD/F emissions is. In the list of potential emissions from nickel and cobalt production in table 11.3 PCDD/F is not included. Ask TWG.* | | | |
| NB: Collected emissions only. BAT-AELs are given as daily averages based on steady-state operation or, in cases where continuous monitoring is not practicable as the average over the sampling period. For PCDD/F, the BAT-AEL is the average over the sampling period which should preferably be a minimum of six hours. | | | |

**Table 11.18: BAT and BAT-AELs to prevent and control emissions to air from materials pretreatment, incineration or afterburning, secondary fume collection, smelting, thermal refining, and melting for nickel and cobalt production**

| Pollutant | Techniques | Range associated with the use of BAT | Comments |
|---|---|---|---|
| Acid mists<br>Acid gases<br>Ammonia | Demister<br>Wet alkaline scrubber<br>Acidic scrubber | <10-35 mg/Nm³<br><50 mg/Nm³<br><5 mg/Nm³ | A demister will allow the collected acid to be re-used. (See Section 5.3.5.9) |
| *There is only very general information about* | | | |
| Chlorine | Collection and re-use<br>Alkaline scrubber<br>*There is one technique included in Section 11.3.3.4 the multistage venture scrubber which can achieve <1mg chlorine/Nm3.* | <1 mg/Nm³ | (See Section 11.3.3.4)<br>*Section 11.3.3.4 is about collection and prevention of chlorine emissions by collection and recycling of chlorine. The venture scrubber does not fit in this section.* |
| *11.3.3.4 contains one general value for a venture scrubber which can achieve chlorine concentrations <1mg/Nm3. This is not sufficient to conclude on a BAT-AEL.* | | | |
| CO<br>and carbonyls | Process control and sealed reactor. | 5 mg/Nm³ | For the carbonyl process only (See Section 11.2.2.5). |

| | | | |
|---|---|---|---|
| VOC or solvents as C | Containment, condenser, carbon or biofilter | <5 to 15 mg/Nm$^3$ | (See Section 2.9.2.6) |
| *See Section 11.2.2.2: For sealed or covered reactors emissions of 30 mg VOC can be achieved, without specifying if this refers to C only. In other cases up to 1000 mg/Nm3 are achieved* | | | |
| NB: Collected emissions only. BAT-AELs are given as daily averages based on steady-state operation or, in cases where continuous monitoring is not practicable, as the average over the sampling period. | | | |

**Table 11.19: BAT and BAT-AELs to prevent and control emissions to air from leaching, chemical extraction and refining, electrowinning and solvent extraction for nickel and cobalt production**

## 11.4.2 Effluent treatment and water re-use

**a) BAT is to prevent and control emissions of metals to waste water as described in Section 2.20.8 (also see Section 11.3.6).**

**The emission levels given in Table 11.20 are the BAT-AELs.**

| Component | BAT-AEL (mg/l) |
|---|---|
| Cu | 0.2 to 0.5 |
| Pb | 0.2 to 0.5 |
| Ni | 0.2 to 0.8 |
| Co | 0.2 to 0.5 |
| Zn | 0.2 to 1.0 |
| As | 0.1 to 0.2 |
| Cd | 0.1 to 0.2 |
| Hg | 0.01 to 0.05 |
| NB: BAT-AELs are based on qualified random samples or twenty four hour flow proportional composite samples. | |

**Table 11.20: BAT-AELs for emissions to water from the production of nickel and cobalt**

*The data in Section 11.3.6 (and 11.2.3.2) are not sufficient to conclude on these BAT-AEL. Pb, As, Cd and Hg is not even included in these tables.Try to get better data.*

## 11.4.3 By-products, process residues and waste

**a) BAT is to use or recycle intermediate products and residues (slags, slimes and filter dusts) from the nickel and cobalt processes as far as possible in the process or after leaching tests as construction material using the techniques listed in Table 11.21 (see Section 2.20.10). If recycling or re-use is not economically possible, secure disposal should be used.**

| Process step | Intermediate product or process residue | Use/treatment options |
|---|---|---|
| Autoclave | Residue | Smelting furnace |
| Iron removal | Precipitate | Smelting furnace or disposal |
| Abatement | Filter dust | Smelting furnace |
| Pressure leaching | Sulphide residue | Cu recovery |
| De-copperising | Cu cement | Cu smelter |
| Nickel and cobalt regeneration | Impure nickel carbonate | Pure nickel sulphate production |
| Slag treatment | Clean slag | Construction |
| Removal of As, etc. | Gypsum ferric-arsenate | Special disposal or As recovery |
| Effluent treatment | Precipitate | Recovery of other metals or disposal |

**Table 11.21: BAT for the recycling or re-use of intermediate products or process residues from Ni and Co processes**

*This is the same table as 11.14 inSection 11.2.4.2 but it is not a sufficient description of a BAT which can be used for the permit writing process. Avoid repetition.*

## 11.5 Emerging techniques

Various developments have been reported for the use of low pressure and atmospheric leaching for the production of nickel from sulphidic ores. The main processes are [ 139, Riekkola-Vanhanen, M. 1999 ]:

- activox leaching: fine grinding and leaching at 100 °C, 10 bar
- CESL process: chloride leaching in sulphate solution using ferric chloride.

The processes have been proven at the pilot stage.

- a hydrometallurgical process to produce nickel and cobalt compounds from limonite and low grade saprolite ore. The technology valorises the ore body profile to a much higher extent compared to classical processes. It operates in a sulphuric acid medium at atmospheric pressure using low-risk technologies. The inert solid residue will have to be stockpiled in a waste dump and the waste water will comply with existing regulations and requirements. Energy use is reduced and $CO_2$ emissions are low (~ 10 t/t Ni produced). While demonstrated at pilot scale level, this process is in the final optimization step for the Eramet Weda Bay project in 2009
- three new plants are under construction or are at the commissioning stage for the pressure leaching of laterites using sulphuric acid [ 139, Riekkola-Vanhanen, M. 1999 ]. The processes are similar to the established process used in Cuba but different purification stages are used to remove other metals. An atmospheric chloride leaching process for laterites is also being developed
- a process is being commissioned in Germany to recover nickel and zinc from residues using a oxy fuel furnace and a solvent extraction refining system from sulphate solutions. No data has been reported.

# 12 PROCESSES TO PRODUCE CARBON AND GRAPHITE ELECTRODES, ETC.

## 12.1 Applied processes and techniques

There are a number of processes that are used to produce a wide range of carbon and graphite products. Carbon or graphite anodes and cathodes, electrodes and furnace linings are produced for a variety of ferrous and non-ferrous metal production processes, in particular, primary aluminium smelting, ferro-alloy and steel production.

More than 2000 products of varying sizes, shapes and properties are produced for other applications.

All of the processes use coke or carbon and other raw materials such as pitch to produce pastes, electrodes and shapes. Raw material storage and handling stages use enclosed coke delivery and handling systems and integral dust filters. Coal tar pitch and tar delivery and storage systems use tank back venting and condensers for tank breathing. The main product types and process stages are shown in Table 12.1.

### 12.1.1 Processes to produce electrodes and shapes

Søderberg paste, Søderberg electrodes and graphite electrodes are made either in dedicated installations or in processes associated with primary aluminium smelting., See Table 12.1.

| Input materials | Process | Products |
|---|---|---|
| Anthracite coal | Calcining | Calcined anthracite coal |
| Calcined anthracite<br>Coke<br>Additives (solids) | Storage, handling, grinding, sieving | Coke grain fractions |
| Pitch, additives (liquids) | Storage, handling, | Pitch, additives (liquids) |
| Calcined anthracite<br>Coke<br>Pitch<br>Additives | Mixing | Paste, e.g. tapping pastes |
| Paste | Forming | Green shapes, e.g. Søderberg or green electrodes |
| Green shapes,<br>Impregnated shapes | Baking | Baked shapes, e.g. prebaked anodes |
| Baked shapes<br>Pitch, resins<br>Other additives | Impregnation | Impregnated shapes |
| Impregnated shapes | Re-baking | Rebaked shapes |
| Baked or re-baked shapes | Graphitising | Graphite shapes |
| Baked and graphitised Shapes | Machining | Graphite &carbon components |

**Table 12.1: Overview of process steps for Søderberg paste, Søderberg electrodes and graphite electrodes**
[ 116, VDI (D) 3467 1998 ]

The production of anodes is similar to the production of carbon and graphite electrodes and shapes but there are significant differences in the percentage of coal tar pitch, the recycling of anode butts and also in the baking temperature (see Table 12.2). The production of prebaked anodes and the associated emission data is reported in Section 4.1.1.5.

Gases from all of the processing stages are collected and treated by afterburning, wet scrubbing including the use of seawater, dry scrubbing using coke, wet ESPs or in the case of the production of electrodes at a primary aluminium smelter, by contact with alumina in a scrubber/fabric filter system. Used alumina and coke from dry gas-cleaning is recovered in production processes.

| **Parameter** | **Anode production** | **Carbon electrode first baking stage** |
|---|---|---|
| Baking temperature °C | 900 - 1000 | 800 - 1100 |
| Pitch content % | 14 - 18 | Up to 40 |
| Heating gradient °C/h | 10 - 14 | 1 - 2 |
| Specific gas consumption in $m^3$/h per tonne produced per year | 5000 | 50 – 110 |

**Table 12.2: Comparison of baking processes**
**[ 318, Fume treatment from Baking Furnaces 2007 ]**

Dust from handling and mechanical processes are collected in fabric filters. Solvents from the washing stages of special carbon production are collected and re-used if possible or removed in biofilters.

### 12.1.1.1 Green paste, Søderberg paste, Søderberg electrodes and green shapes

Green paste production is the starting point for the production of all carbon and graphite products. All green pastes are manufactured from a mixture of calcined petroleum coke and up to 28 % coal tar pitch, which acts as a binder. The petroleum cokes are residues from the distillation of crude oils and can therefore be contaminated with substances like metals (e.g. nickel) and sulphur compounds. Highly annealed metallurgical and lignite cokes are used as auxiliaries for packing. Calcined and annealed cokes by themselves are free of hydrocarbons and PAH.

Coke is normally transferred by sealed conveyor or dense phase pneumatic systems and is stored in silos. Pitch is transported in the molten state and is transferred by pumping and is stored in heated tanks. The tank ventilation gases contain hydrocarbon fumes and are usually cleaned. Condensers or oil scrubbers are used [ 75, Nordheim, E. (EEA) 1998 ] and back venting of the tank gases is also used. Petroleum coke is ground and then mixed with pitch in heated mixers. The ratio of coke and pitch is adjusted according to the application and to allow the paste to be handled.

In the case of Søderberg paste, the blend is produced to allow it to be added to the electrode shell. Søderberg paste is normally used for electrodes in the primary aluminium industry but the paste can be made into electrodes by pressing and forming for use in other applications for example in electric furnaces for the production of ferro-alloys.

Søderberg electrodes are also produced from the paste by a forming process. In this case, the green electrodes are formed into the size and shape required and sold [ 75, Nordheim, E. (EEA) 1998 ]. These electrodes are commonly used in submerged arc electric furnaces. A number of variants exist, for example hollow, electrodes can be made to allow furnace feeding through the electrode and composite electrodes can be made to overcome production problems.

### 12.1.1.2 Carbon or graphite electrodes and cathodes and carbon shapes

Carbon or graphite electrodes and cathodes and carbon shapes are made in dedicated production sites which produce a range of electrodes including cathodes and furnace linings.

These electrodes are manufactured from a mixture of petroleum coke and up to 40 % of coal tar pitch but no residual material from old anodes used in the primary aluminium production is used [ 75, Nordheim, E. (EEA) 1998 ], [ 116, VDI (D) 1998 ]. Petroleum coke is calcined at temperatures of up to 2000 – 3000 °C in electrical shaft furnaces. Electrode production involves the crushing, grinding and mixing of the raw materials.

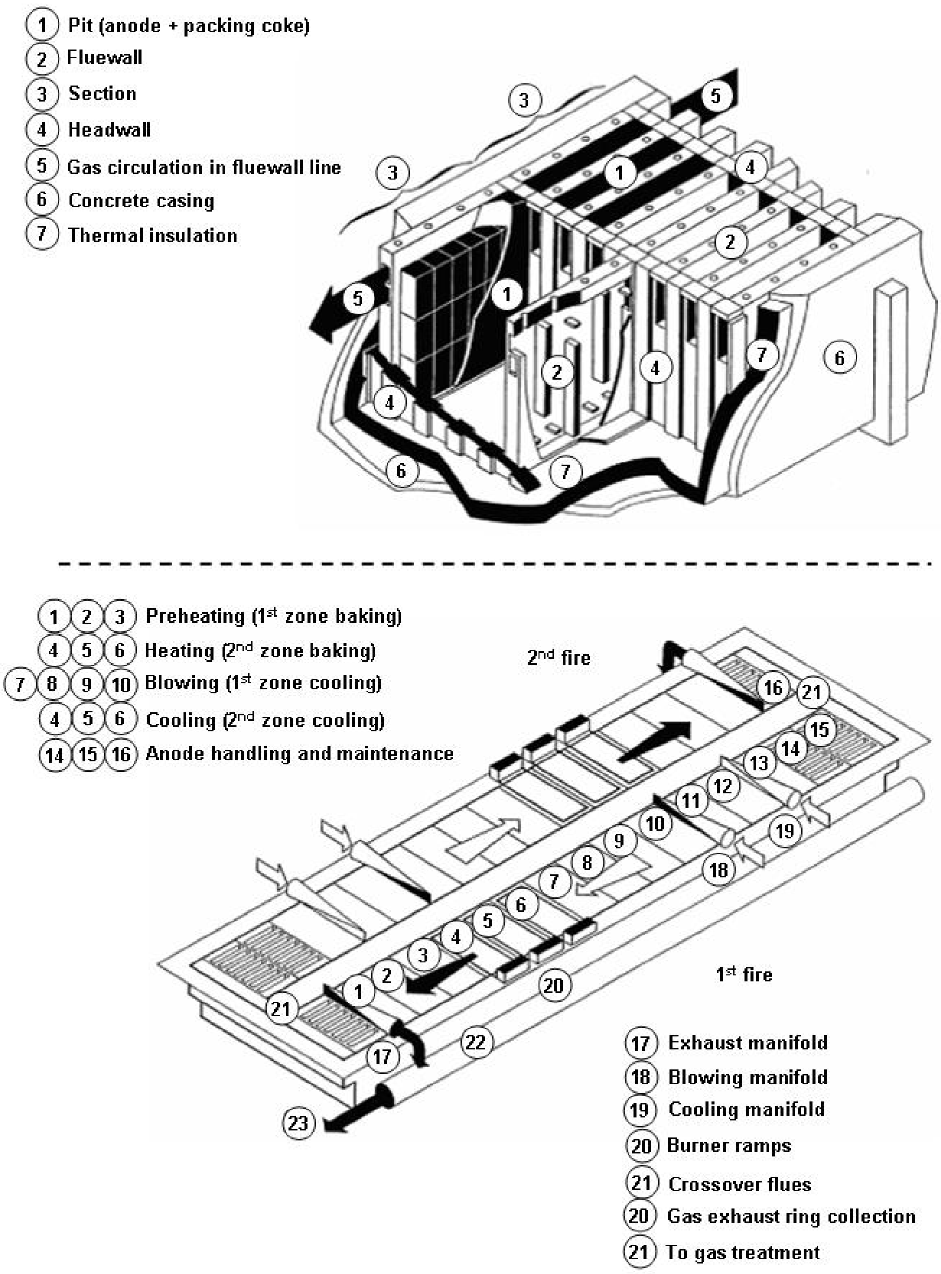


**Figure 12.1: General views of a baking furnace for electrodes and anodes**

The mixed materials are formed into green electrodes. The green electrodes are then baked in ring furnaces comprising a large number of pits, which contain the electrodes. Refractory brick walls separate the pits and ducts are formed for the flue-gases. Green electrodes are stacked in the baking furnace in rows and the heating ducts are formed. Layers of packing coke separate the parts and prevent oxidation. This coke is consumed during the heating and cooling cycle at a rate of up to 40 kg per tonne of electrodes, the remaining coke is re-used. At any one time, pits in separate sections of the furnace are being filled, heated, cooled or emptied [ 91, OSPARCOM 1992 ].

Hot air is passed through the ducts using movable gas-fired burners and the electrodes are baked at 800 to 1100 °C in the absence of air. The ducts are kept under negative pressure to contain the fumes. At the end of the heating cycle, the ducts are connected to blowers to cool the section. Hot air passing from the furnace section being cooled is then recycled through the burners or through other furnace sections to preheat that part of the system. [ 116, VDI (D) 3467 1998 ]

Two main types of furnace are used for baking; open and closed ring furnaces. Open furnaces use a horizontal duct and closed furnaces use a vertical flue. Open furnaces account for 60 % of capacity and a general layout is shown in Figure 12.1. The horizontal ducts of the open furnace are separate and parallel, this allows the heating cycle to be optimised for each duct and so reduces fuel consumption [ 91, OSPARCOM 1992 ]. The use of multiple chambers in the furnace allows heat from one section to be used in other sections as outlined in Figure 12.2. The carbottom furnace is a single chamber furnace and is also used.

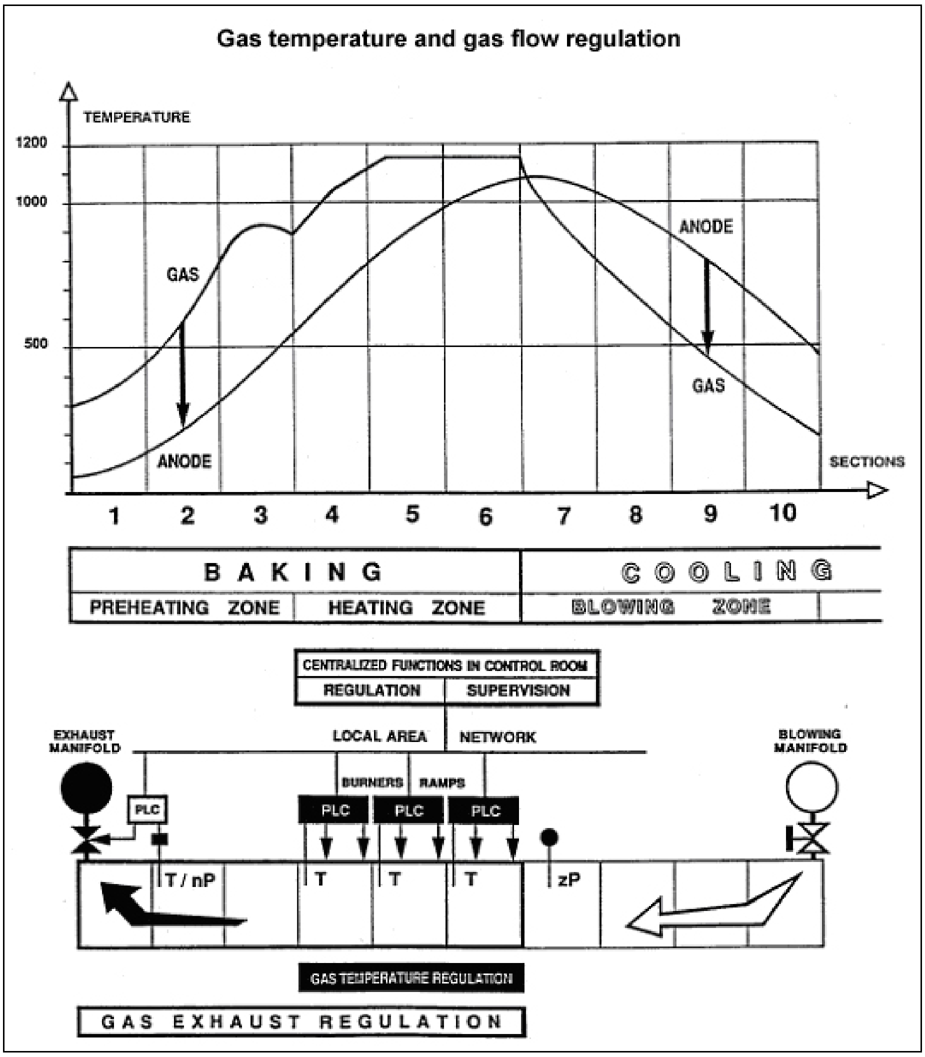


**Figure 12.2: Temperature profile during the baking**

During the baking process the coal tar pitch is converted into coke (carbon) making the material electrically conductive. There is a 5 % loss in weight during baking, for graphite speciality products it can be higher [ 75, Nordheim, E. (EEA) 1998 ]. The baking process takes approximately 18 to 21 days.

### 12.1.1.3 Graphite electrodes

The production process for graphite electrodes is very similar to the production of the prebaked electrodes; normally no residual anode material is used in the blend. Green shapes are first of all baked, the baking temperature used is ~ 1000 °C and the loss in weight during baking may increase up to 15 %.

Single chamber furnaces or pit furnaces as well as closed-ring furnaces are used for the baking stage during graphite electrode production. Tunnel furnaces are used for the small scale production of speciality carbon.

Baked electrode material may then be subjected to impregnation with pitch, re-baking and graphitising. Machining and finishing stages follow to produce graphite electrodes. [ 116, VDI (D) 3467 1998 ]

Graphite is formed when prebaked carbon is heated to approximately 2800 °C. Graphitising of electrodes is usually carried out in Castner or Acheson furnaces as shown in Figure 12.3 and Figure 12.4.

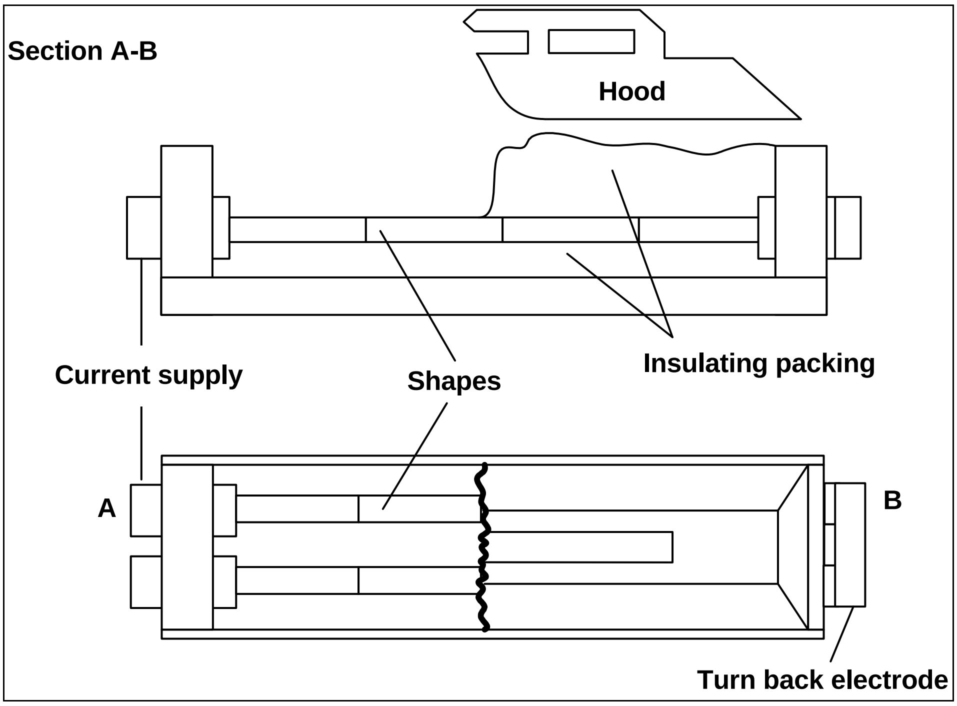


**Figure 12.3: Castner graphitising furnace**

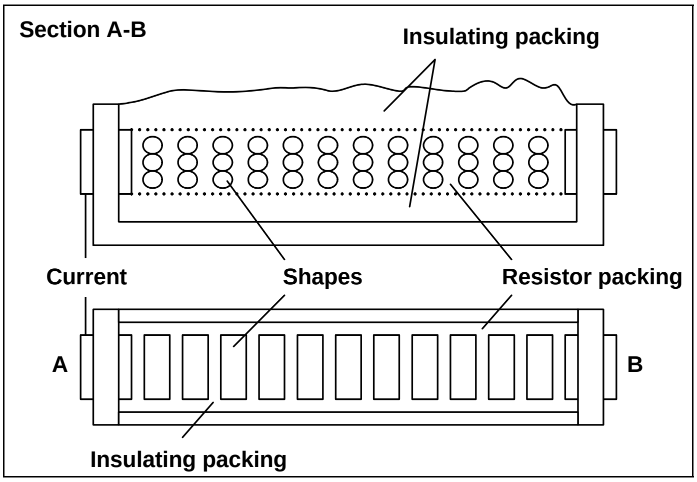


**Figure 12.4:** **Acheson graphitising furnace**

In some cases, no hoods are used where there are only minor diffuse dust emissions and the carbon oxides are well dispersed at the roofline.

The Acheson furnace is used for carbon shapes with irregular dimensions and cross-sections and the Castner furnace is used for shapes with parallel faces and equal cross-sections. Both furnaces are electric resistance furnaces constructed from refractory material. They differ in the way the current is applied to the furnace. In the Acheson furnace, shapes are placed inside the furnace body and the interstices filled with a carbon/graphite mixture (resistor packing), and the current is passed through the resistor packing and the shapes. In the Castner furnace, the shapes form the entire current path and can lead to gains in the current efficiency.

In the Acheson furnace, thermal insulation is provided by a mixture of silicon carbide, coke, sawdust and sand. In the Castner furnace, only coke is used. Heating cycles vary from two to seven days and the cooling cycle takes up to 14 days. At the end of the cycle the insulation and resistor packing are processed and re-used [ 116, VDI (D) 1998 ].

The graphitised shapes are finished by turning, drilling, milling and similar processes to the requirements of the customer. The resultant final shapes are then polished. Dusts produced by these processes are collected and re-used as far as possible. The specific process depends on the final product.

These electrodes are used in electric arc furnaces in a variety of processes. Furnace linings are also produced in the same process and may be used in aluminium cells as cathodes (cathode blocks can be made from prebaked, graphite or mixed prebake/graphite material). Carbon cathodes are also used in electric arc furnaces.

### 12.1.2 Processes to produce other carbon and graphite products

Other graphite products such as seals, brushes, crucibles and similar products are produced in a similar way to graphite electrodes. There are differences in the size and complexity of the products and this affects the processes that are used. Other additives such as sulphur and metals can be added to the blend of raw materials to give the desired physical properties to the product. Sometimes resins are used instead of pitch.

The grinding and mixing stages are important, as there are a wide variety of graphite products and specifications. The characteristics of these products often depend on a particular grain size. The choice of grinding or milling technique is made according to particle size of carbon required for a particular product. Green shapes are formed by moulding and these may be baked, rebaked and graphitised.

Heating the shapes to 2800 °C produces graphite, which is then subjected to a number of finishing process such as machining and polishing [ 116, VDI (D) 1998 ]. Petroleum coke or anthracite is calcined at temperatures of up to 1100 - 1400 °C in rotary kilns or electrical shaft furnaces.

The baked or graphitised components may be impregnated with other materials, e.g. resins or metals. Impregnation is carried out by soaking, sometimes under vacuum and sometimes under pressure, autoclaves are used. Components that have been impregnated or bonded with coal tar pitch are rebaked. If resin bonding has been used, they are cured.

Porous graphite is also produced in the basic process by blending sawdust with the raw materials. During baking, the sawdust is combusted and a porous matrix of carbon or graphite remains.

High purity graphite is produced in a similar way but the graphitising process is used to remove included impurities such as metals. In this case, chlorine or freons are used in the gas stream and they decompose to produce chlorine and fluorine, which react with metallic impurities to form volatile salts therefore removing the metals from the graphite. Current practice includes the use of freons that are recovered from appliances and the process therefore provides a useful method for dealing with these materials. Excess halogens and the metal salts are removed from the off-gas by dry scrubbing. The process stages are described further in the sections below and graphite shape production is shown in Figure 12.5.

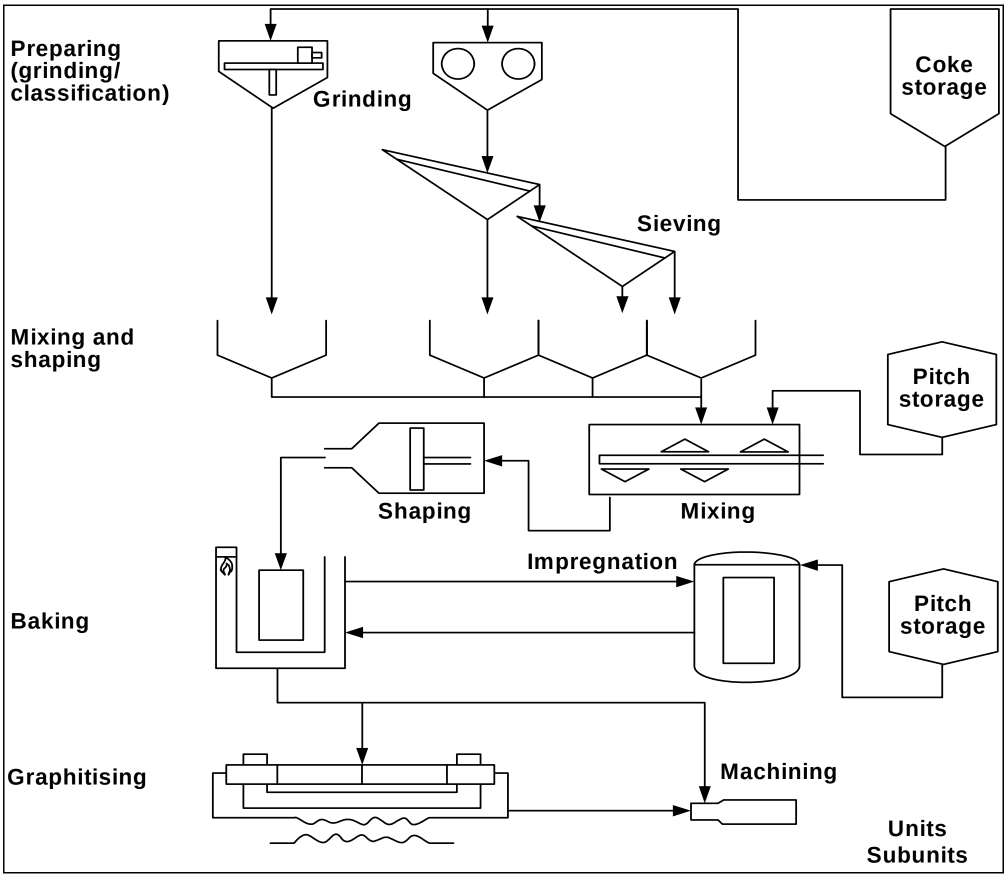


**Figure 12.5: Graphite shape production**

Special products such as carbon fibre reinforced carbon, carbon fibres and carbon fabrics are also made, and an induction or pit furnace is used. The processes used to produce carbon fibres and associated materials can include acrylonitrile as a precursor in the form of polyacrylonitrile cloth (PAN cloth) or as an impregnating agent [ 128, Davies, N. 1998 ]. In these cases, hydrogen and sodium cyanides can be produced during the heating stages in a furnace. Sodium cyanide can be converted at high temperatures in the presence of carbon oxides into sodium carbonate. An afterburner is used to oxidise the gases emitted.

#### 12.1.2.1 Blending and forming

Raw materials are mixed to produce a constant feed and weighing systems are used to prepare a particular recipe depending on the product. A variety of mixers are used depending on the product required, the particle size of the raw material and the throughput required. Heated mixers and screw conveyors (typically at 200 °C) are used to prevent batches from solidifying and to allow efficient discharge of contents. Kneading mixers, paddle mixers and continuous action mixers are used. Continuous or batch operation is practised and can depend on the scale of the operation.

The green mixture is passed to a forming process to produce the shapes required. Die moulding, extrusion and vibrating systems are used. During special carbon production, green shapes may be washed with alcohol to remove excess resin. Large shapes may also be cooled in a closed circuit water bath.

#### 12.1.2.2 Baking and re-baking

Green shapes (or impregnated shapes) are baked at temperatures up to 1300 °C using a variety of furnaces such as tunnel, single chamber, multiple chamber, annular and push rod furnaces depending on the size and complexity of the product. Continuous baking is also carried out. The furnace operations are similar to those used for electrode baking but the furnaces are usually smaller.

The tunnel furnace is fed by preshaped forms that are carried through the fired zone in a metal sagger surrounded by packing material. The furnace is usually gas or oil fired and a recuperator is usually incorporated to preheat fuel or combustion air.

#### 12.1.2.3 Impregnation

Tars, pitches, resins, molten metals can be added to the baked shapes and other reagents are used to fill the voids formed in the carbonised material. Soaking with or without vacuum and autoclaving are used. Various impregnating techniques are used depending on the product but batch or quasi-continuous operations are used. The impregnation cycle usually involves preheating, impregnation and cooling. A hardening reactor may also be used.

Only special carbons are impregnated with various metals.

#### 12.1.2.4 Graphitising

Graphite is formed when prebaked carbon is heated to approximately 2800 °C. Graphitising is carried out in tunnel, Acheson, Castner or induction furnaces depending on the size or shape of the component and the raw material used. Other specialised furnaces are also used, for example, the vacuum graphitising furnace for special products such as carbon composites which are reported in Section 12.1.1.3 [ 116, VDI (D) 1998 ].

#### 12.1.2.5 Product shaping

Sawing, turning, drilling, milling and similar processes are used to process the graphite shapes. The resultant final shapes are then polished. Dusts produced by these processes are collected and re-used as far as possible. The specific process depends on the final product.

#### 12.1.2.6 Special processes

Other processes such as resin or metal impregnation, graphite expansion and carbon fibre formation using controlled heat treatment are also used. A range of tailor-made processes are employed that are not reported here.

## 12.2 Current emission and consumption levels

About 40 % of the coal tar pitch is volatilised during baking and more than 95 % of the volatile hydrocarbons are burnt off at the high temperature in the furnace. Baking therefore results in the residual emission of hydrocarbons and PAH due to their presence in the coal tar pitch. The potential emissions points from the various process stages are shown in Figure 12.6.

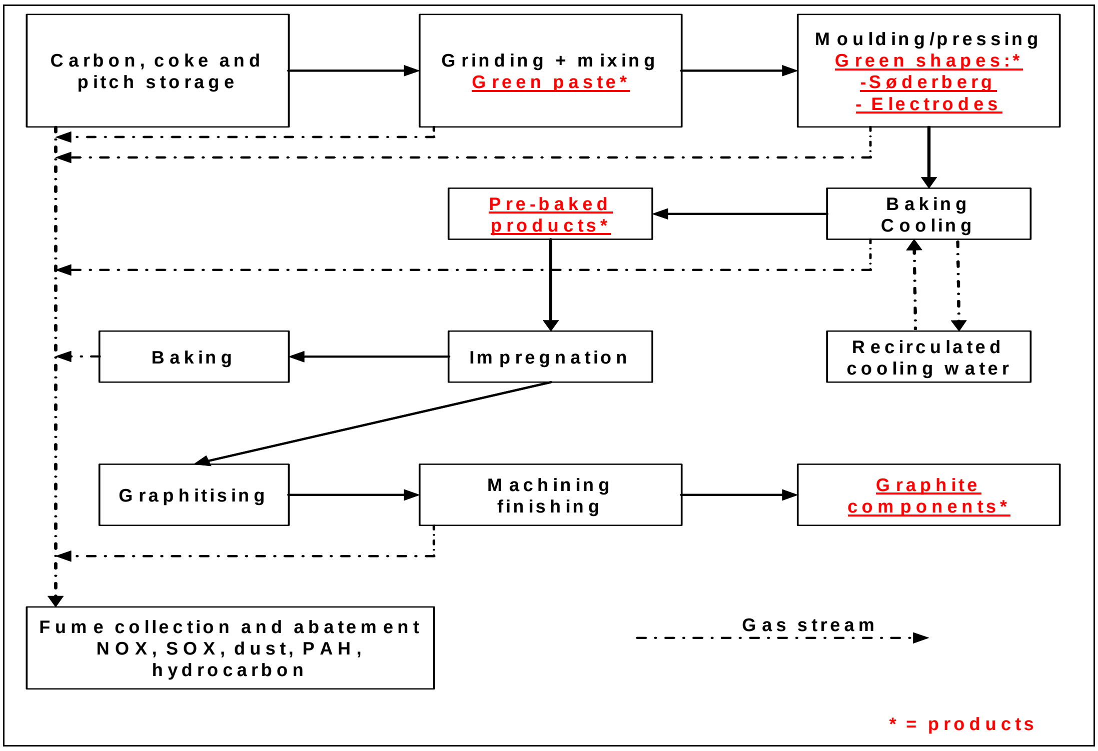


**Figure 12.6: Generic emission diagram of the processes used**

The furnace gases are treated by afterburning, wet scrubbing, dry scrubbing using coke, wet ESPs or, in the case of the production of electrodes at a primary aluminium smelter, by contact with alumina in a scrubber/fabric filter system [ 75, Nordheim, E. (EEA) 1998 ]. Dust from handling and mechanical processes are collected in fabric filters. Solvents from the washing stages of special carbon production are collected and re-used if possible or removed in biofilters.

The removal of PAH by adsorption on alumina or coke is temperature dependent. At higher temperatures, the lighter substances will not adsorb. Modern pre-bake furnaces have a more complete combustion. The old technique of indirect cooling prior to dry scrubbing cannot be used, since the deposit no longer is a free-flowing tar but a sticky powder.

Packing coke is consumed at a rate of ~12 to 18 kg per tonne of electrodes [ 116, VDI (D) 1998 ]. Energy use in graphitising is 9 to 20 GJ/t.

### 12.2.1 Emissions to air

The emissions can escape the process either as stack emissions or as diffuse emissions depending on the age of the plant and the techniques used. Stack emissions are normally monitored continuously or periodically depending on the component measured and reported by on-site staff or off-site consultants to the competent authorities.

There are potential emissions to air of PAH, sulphur dioxide, dust, fluorides (only for anode production if anode butts form a source of carbon), hydrocarbons (from tar or if solvents are used) and cyanide (only for fibre production from acrylonitrile). The formation of $SO_2$ is influenced by the fuel and raw materials used whereas the formation of $NO_X$ is determined by the combustion temperature.

When an anode plant is associated with a primary aluminium smelter, the process gases can be combined with the electrolysis cell gases and reacted with alumina in a dry scrubber. A fabric filter serves the scrubber and the alumina collected is used in the electrolysis cells. The data for combined processes is included with the data reported in Chapter 4.

In standalone processes or other carbon and graphite processes, a combination of techniques such as afterburners, electrostatic filters and fabric filters are used. Coke filters have been recommended [ 28, OSPARCOM 1997 ] but it is concluded that the tar fraction that is emitted by the baking process is the light condensable fraction. This may not be fully carbonised during the subsequent early stages. The fate of the various fractions is shown in Table 12.3.

| Fraction | Fate |
|---|---|
| Gaseous fraction ~30 % | - Burnt off in process |
| Condensable fraction ~25 % | - Collected in abatement |
| Carbonised fraction ~45 % | - Formed into product |

**Table 12.3: Fate of coal tar pitch fractions**

There is therefore a distinct possibility that all of the condensable fraction may not be collected if absorption onto coke only is used for the baking stages. A significant portion of the tars can be recycled from the coke filter material during the temperature gradient of the preheating stage of the baking furnace (see Figure 12.2).

There are also differences in the emission characteristics depending on whether open or closed baking furnaces are used. In open furnaces more volatile hydrocarbons are burnt within the furnace.

#### 12.2.1.1 Polycyclic aromatic hydrocarbons, VOCs and hydrocarbons

Paste, other electrodes and most special carbon products are produced from petroleum coke and coal tar pitch. Emissions of hydrocarbons as tars can occur during delivery, transfer, mixing baking and impregnation. Coal tar pitch also contains PAH, which will also be emitted. PAH are potentially hazardous in the environment as well as inside industrial plants and this is an important issue within the carbon industry. The raw gas characteristics are reported in [ 318, Fume treatment from Baking Furnaces 2007 ].

PAH values are subject to some uncertainty. Several standardised methods exist to measure and report PAH and the following groups have been used for this report: VDI-group I (2), VDI-group II (7), VDI-group I+II (9), OSPAR 11 (11), EPA (16). Current practice for sampling and analysis is to use the VDI method 3874 (2006).

The PAH compounds measured and reported for these conventions are shown in Table 12.4.

| PAH Compounds | PRTR | VDI-I | VDI-II | VDI-I+II | OSPAR 11 | EPA |
|---|---|---|---|---|---|---|
| Naphthalene | X | | | | | X |
| Acenaphthylene | | | | | | X |
| Acenaphthene | | | | | | X |
| Fluorene | | | | | | X |
| Phenanthrene | | | | | X | X |

| | | | | | | |
|---|---|---|---|---|---|---|
| Anthracene | X | | | | X | X |
| Fluoranthene | | | | | X | X |
| Pyrene | | | | | | X |
| Benzo (a) pyrene | X | X | | X | X | X |
| Dibenzo (a,h) anthracene | | X | | X | X | X |
| Benzo (a) anthracene | | | X | X | X | X |
| Benzo (b) fluoranthene | X | | X | X | X | X |
| Benzo (j) fluoranthene | | | X | X | | |
| Benzo (k) fluoranthene | X | | X | X | X | X |
| Chrysene | | | X | X | X | X |
| Indeno (1,2,3,-cd) pyrene | X | | X | X | X | X |
| Benzo (ghi) perylene | | | | | X | X |
| Benzo (b) naptho (2,1-d) thiophene | | | X | X | | |

**Table 12.4: Reporting conventions for PAH**

Low-molecular weight PAH are very sensitive to the sampling and testing conditions and procedures. There is therefore more uncertainty in EPA data due to the possible incompleteness of their collection. Sampling and analysis of PAH in waste gas streams is performed by the validated procedure VDI (Germany) 3874 (2006).

The preferred reporting convention is the EPA 16 as this is compatible with the PRTR reporting requirements [ 299, TWG KOM Report 2007 ].

#### 12.2.1.2 Dust

During production, dust emissions occur during all process stages (calcining, storage, transfer, mixing, grinding, baking, graphitising and shaping). The emissions are mainly caused by dust generated during the grinding, screening and shaping processes and from the carbonisation gases. The mechanical handling and treatment stages are usually enclosed and extracted [ 116, VDI (D) 1998 ]. The source of dust and its characteristics influences the abatement method used to remove it, carbon dust can be very fine and abrasive.

In some cases of manufacturing special carbon and graphite products, absolute filters are used to remove it; the cleaned air is then used in the workplace.

#### 12.2.1.3 Combustion gases

Gases produced from the combustion of gas or fuel oil will be emitted from the process. There are potential emissions of carbon oxides and the oxides of sulphur and nitrogen. Optimisation of combustion conditions and the use of low-$NO_X$ burners is commonly practised and fuel choice is made according to site conditions and availability.

#### 12.2.1.4 Sulphur dioxide

The raw materials from which the products are made contain sulphur and the fuel used for heating can also contain sulphur. This results in the emission of sulphur dioxide during the baking and calcining of coke and coal [ 6, McLellan and Partners Ltd 1993 ]. The emissions of $SO_2$ are in the range 0.5 (gas) to 2 kg (fuel oil) per tonne of aluminium depending on the fuel (based on an anode consumption of 0.4 tonne per tonne aluminium). This is far less than the emissions of sulphur dioxide produced during electrolysis [ 97, Lijftogt, J.A. et al 1998 ]. Sulphur is also added to the blend to produce desired characteristics in special graphite products. This can be a significant source of sulphur dioxide and wet scrubbers are sometimes used to remove this.

### 12.2.1.5 VOCs (from the manufacture of special carbon and graphite products)

VOCs may be emitted from vacuum and other systems used for impregnation. Afterburning or adsorption techniques are used to control these [ 116, VDI (D) 1998 ]. Washing and drying stages in special carbon use solvents such as ethanol. These materials are potential sources of odours and are usually removed at source. Biofilters are used to absorb and decay the organic components and remove odours from the gas stream. The gas is prewetted and usually passes through a number of filters in series. The biofilters operate on a batch basis and the biological substrate (peat, twigs, etc.) is replaced periodically. VOC emissions of less than 20 mg/Nm$^3$ are achieved.

### 12.2.1.6 Cyanides (polyacrylonitrile (PAN) based carbon fibre production)

Cyanides are produced during the decomposition of acrylonitrile (in PAN cloth) used in the production of carbon fibres. HCN concentrations of 55 mg/Nm$^3$ have been reported during periods when abatement has not been available [ 128, Davies, N. 1998 ]. Afterburners are used to decompose hydrogen cyanide.

Sodium cyanide can also be formed if sodium thiocyanate is used as a solvent for acrylonitrile. In this case, the sodium is driven off the carbon fibre during the high temperature treatment stage and sodium cyanide solid is formed during cooling. In the presence of $CO_2$ at high temperatures, it is mainly converted into sodium carbonate. Cyanide emissions of less than 2 to 5 mg/Nm$^3$ are achieved. REF??

### 12.2.1.7 PCDD/F

Test results on emission sources and abatement units in this sector indicate that PCDD/F are not relevant for the conventional carbon and graphite manufacturing processes. This will need to be examined if chlorine compounds or additives are used.

### 12.2.1.8 Summary of the main air pollutants

In the following table the range of emissions for green paste production and baking furnaces without fume treatment are shown.

| Parameter | Units | Open type furnace | Close type furnace | Green paste plant |
|---|---|---|---|---|
| Anode specific flue gas volume | m$^3$/t | 5000 | 3500 | 600 – 1400 |
| CO | mg/Nm$^3$ | <1200 | <1500 | n.n. |
| TOC | mg/Nm$^3$ | 100 – 300 | <1000 | <2000 |
| Tar/condensates | mg/Nm$^3$ | 200 – 400 | 800 – 1200 | 100 – 1000 |
| PAH | mg/Nm$^3$ | 20 – 200 | 40 – 500 | <20 |
| Soot/dust | mg/Nm$^3$ | 100 – 200 | 50 – 100 | <100 |
| $SO_X$ | mg/Nm$^3$ | 100 - 800 | 100 – 800 | <200 |
| HF | mg/Nm$^3$ | 5 – 300 | 5 – 300 | - |

**Table 12.5: Typical emissions during anode baking [528]**

The main air pollutants and emission ranges achieved by various abatement techniques are shown in Table 12.6 and Table 12.7. The emissions depend on the abatement used and this varies depending on whether the carbon and graphite plant is on the same site as a primary aluminium smelter.

| **Product**<br>**Furnace type**<br>**Abatement type** | **Graphite electrode**<br>**Open furnace**<br>**RTO** | **Special graphite**<br>**Open furnace**<br>**ESP + RTO** | **Cathode**<br>**Open furnace**<br>**RTO** | **Graphite electrode**<br>**Close furnace**<br>**RTO** |
|---|---|---|---|---|
| Component | Range mg/Nm$^3$ | Average of 4 measurements in one day mg/Nm$^3$ | Average mg/Nm$^3$ | Range mg/Nm$^3$ |
| PAH - EPA 16 | 2.61 - 19.45 | 0.989 | 1.535 | 2 - 16 |
| BaP | 0.045 - 0.3 | 0.015 | 0.012 | 0.1 - 1.0 |
| Benzene | | | | <1.0 |
| Dust | | | | <20 |

**Table 12.6: Example of emissions from RTOs operating in carbon and graphite baking and rebaking processes REF??**

In the RTO, the different PAH are not destroyed to the same extent; higher molecular PAH are more difficult to remove. The 16 substances normally reported belong to different classes of pollutants in terms of toxicity and it is practice in some countries to report BaP as an indicator of high molecular weight PAH that is more toxic. Table 12.7 shows the rate of destruction of some PAH in an RTO and the effect of pre-treatment.

| **Parameter** | **Unit** | **Upstream of pre-treatment** | **Downstream of pre-treatment** | **Downstream of RTO** |
|---|---|---|---|---|
| Flowrate | m³/h | | | 56150 |
| Temperature | °C | | | 151 |
| $O_2$ | Vol.- % | | | 18.4 |
| Dust | mg/Nm$^3$ | | | 5.6 |
| Benzene | mg/Nm$^3$ | | | <0.03 |
| CO | mg/Nm$^3$ | | | 3.8 |
| $NO_X$ (as $NO_2$) | mg/Nm$^3$ | | | 62.6 |
| TOC | mg/Nm$^3$ | | | 8.9 |
| **PAH** | | | | |
| Naphthalene | mg/Nm$^3$ | 6.1 | 6.0 | 0.021 |
| 2-Methylnaphthalene | mg/Nm$^3$ | 2.8 | 2.8 | 0.012 |
| 1-Methylnaphthalene | mg/Nm$^3$ | 2.0 | 1.9 | 0.012 |
| Acenaphthylene | mg/Nm$^3$ | 2.3 | 2.1 | 0.021 |
| Acenaphthene | mg/Nm$^3$ | 2.9 | 0.5 | 0.026 |
| Fluorene | mg/Nm$^3$ | 2.9 | 2.6 | 0.043 |
| Phenanthrene | mg/Nm$^3$ | 40.9 | 39.5 | 1.104 |
| Anthracene | mg/Nm$^3$ | 6.3 | 5.9 | 0.154 |
| Fluoranthene | mg/Nm$^3$ | 46.3 | 50.3 | 3.445 |
| Pyrene | mg/Nm$^3$ | 30.6 | 32.8 | 2.524 |
| Chrysene | mg/Nm$^3$ | 22.9 | 23.3 | 3.155 |
| Benzo(a)anthracene | mg/Nm$^3$ | 12.3 | 12.3 | 1.314 |
| Benzo(b+k)fluoranthene | mg/Nm$^3$ | 16.3 | 17.1 | 1.739 |
| Benzo(a)pyrene | mg/Nm$^3$ | 3.5 | 4.4 | 0.386 |
| Dibenzo(a,h)anthracene | mg/Nm$^3$ | 0.4 | 0.4 | 0.035 |
| Indeno(c,d)pyrene | mg/Nm$^3$ | 1.8 | 1.8 | 0.149 |
| Benzo(g,h,i)perylene | mg/Nm$^3$ | 1.8 | 1.8 | 0.138 |

**Table 12.7: Rate of destruction of some PAH in an RTO REF??**
*(What is the reference for these data?)*

Emission ranges for some techniques used in the various process stages are shown in Table 12.8 and Table 12.9.

| Source | Abatement type | Pollutant | Concentration range (mg/Nm$^3$) |
|---|---|---|---|
| Material handling and storage. Coke | Cyclone | Dust | 20 - 150 |
| | Fabric filter | Dust | 1 - 90 |
| Material handling and storage. Pitch | Re-venting, condensation | Hydrocarbon | 1 - 75 |
| Grinding, mixing and forming | Fabric filter | Dust | <5 |
| Baking and re-baking | ESP and HF adsorber plus FF | Dust | 2.5 - 90 |
| | | Hydrocarbon | 50 - 250 |
| | | PAH | 0.003 - 6 |
| | | Benzene | 1 - 11 |
| | Afterburner - conventional thermal oxidiser (CTO) *(in section 4.3.3.1 CTO is used for catalytic thermal oxidiser)* | Dust | 1 - 40 |
| | | Hydrocarbon | 2 - 17 |
| | | Benzene | 0.15 - 7.5 |
| | | $SO_2$ | 20 - 100 |
| | | $NO_X$ | 50 - 250 |
| | Afterburner - Regenerative thermal oxidiser (RTO) with or without pre-treatment | Dust | 1 - 60 |
| | | Hydrocarbon | 6 - 100 |
| | | PAH EPA 16 | 2.61 - 19.45 |
| | | Benzene | 0.1 - 3.5 |
| | | $SO_2$ | 2 - 150 |
| | | $NO_X$ | 10 - 40 |
| | | BaP | 0.045 - 0.3 |
| | Dry scrubber. (alumina or carbon/lime) | Dust | <1 - 14 |
| | | Hydrocarbon | 1 - 135 |
| | | PAH | 0.002 - 55 |
| Impregnation or Grinding, mixing and forming *Why is Impregnation mentioned together with grinding, mixing, forming? All the data included are for impregnation only.* | Afterburner - (CTO) With or without pre-treatment *(unclear: where is this statement about pretreatment from?)* | Dust | 1 - 40 |
| | | Hydrocarbon | 3.5 - 7.5 |
| | | PAH | 0.0002 - 0.2 |
| | | Benzene | 0.4 - 7.5 |
| | | $SO_2$ | 100 - 200 |
| | | $NO_X$ | 50 - 250 |
| | Cyclone and/or fabric filter | Dust | 1 - 4 |
| | Cooler | Hydrocarbon | 4 - 40 |
| Graphitising | Fabric filter | Dust | 1 - 20 |
| | | Hydrocarbon | 1 - 25 |
| Machining and shaping | Fabric filter | Dust | 1 - 35 |
| | | Hydrocarbon | 1 - 25 |

**Table 12.8 Examples of emission ranges for a number of carbon and graphite processes to illustrate the different ways of reporting**

REF?? *This table is derived mainly from [345]. What is the sense of the highlighted part of the caption?*

*But for grinding, mixing, forming the figures where not used. Instead impregenation is combined with grind, mixing, forming without taking into account the data for grinding, mixing, forming in [345]. This is unclear.*
*Unclear is also where are the data for BaP from and for PAH EPA 16?*

| Abatement method | PRTR | BaP (µg/Nm$^3$) | VDI-I (µg/Nm$^3$) | VDI-I+II (µg/Nm$^3$) | OSPAR 11 (µg/Nm$^3$) | EPA (µg/Nm$^3$) |
|---|---|---|---|---|---|---|
| CTO | | 0.03 | 0.04 | 3.35(1) | 64.6 | 75.6 |
| CTO | | | <1 | 10 | | 260 - 330 |
| RTO | | | 0.08 - 0.92 | 10 - 20 | | |
| RTO with pre and post treatment(2) | | | | | | 250 – 1250 |
| RTO without pre or post treatment | | 100 – 1000 | | | | 2000 - 19450 |
| Wet scrubber | | 0.15 – 2.5 | 1 - 27 | | | 1670 - 8000 |
| Dry scrubber | | | 1 - 12 | 14 | | |
| Dry scrubber | | | 6.7 - 9.2 | 11 - 1350 | | 2320 - 3754 |
| Dry scrubber | | 1.3 | 1.4 | 153(1) | 46875 | 55383 |
| Dry scrubber | | 0.6 - 2.6 | 0.8 - 2.8 | 150 - 293(1) | 38831 - 46865 | 47794 - 55334 |
| Electrostatic precipitator | | 34 | 43.8 | 471 | 6251 | 8049 |
| Electrostatic precipitator | | 10.6 - 45.3 | 13.7 - 56.5 | 199 - 613 | | |
| Electrostatic precipitator | | 1 - 8 | 1 - 8 | 200 - 800 | | 2650 - 6300 |

(1) VDI -I+II without benzo(b)naphol(2,1-d)thiophene.
(2) Source of raw gas is an anode baking furnace

**Table 12.9: Examples of some ranges of PAH reported using different groups of compounds REF??**

The preferred reporting convention for PAH emissions is the EPA 16.

The relative significance of emissions of $SO_2$, halides, hydrocarbons, cyanide, $NO_X$ and dust from the processes that are used in the production of carbon and graphite is shown in Table 12.10

| Component | Calcining | Storage and handling | Grinding and milling | Mixing and forming | Baking | Impregnation | Graphitising | Machining |
|---|---|---|---|---|---|---|---|---|
| Sulphur dioxide | ••<br>(1,2) | | | | ••<br>(1,2) | | ••<br>(2) | |
| Halides | | •<br>(if anodes reclaimed) | •<br>(if anodes reclaimed) | •<br>(if anodes reclaimed) | •<br>(if anodes reclaimed) | | ••<br>(3) | |
| Hydrocarbons including PAH | • | •••<br>(5)<br>•<br>(6) | • | •• | ••• | ••• | | |
| Cyanide | | | | | ••<br>(4) | | ••<br>(4) | |
| Nitrogen oxides | | | | | ••<br>(2) | | ••<br>(2) | |
| Dust | • | •• | ••• | •• | • | | •• | ••• |

••• More significant – • less significant
(1) With raw materials that contain sulphur.
(2) Combustion gases.
(3) With high purity graphite.
(4) With carbon fibres.
(5) High concentration during loading. Solid pitch.
(6) High concentration during loading. Liquid pitch

**Table 12.10: Relative significance of potential emissions to air from carbon and graphite production REF??**

### 12.2.2 Emissions to water

The production of electrodes and graphite shapes are inherently dry processes. Discharges of process waste water are usually limited to cooling water but most processes use a sealed cooling system. Rainwater run-off from surfaces and roofs may contain carbon dust and associated material. Open storage of raw materials and deposited solid emissions are the source of potential contamination. Typical values for processes associated with primary aluminium production for this contamination are <0.03 kg/tonne for suspended solids and <0.02 kg/tonne for dissolved fluoride [ 97, Lijftogt, J.A. et al 1998 ]. Current practice is to use vacuum systems for material transfer and closed silos for storage. Contamination of run-off is therefore reduced.

Considerable amounts of waste water can be discharged when wet systems are used for air pollution control. The waste water produced by wet systems is regarded to be a cross-media effect of the abatement techniques. Wet ESPs are used frequently to remove hydrocarbons from the furnace exhaust and this is a potential source of contaminated waste water. Some biofilters may also produce waste water depending on the biological process that is used.

The processes can account for the production of waste water consisting of cooling water, used to cool the green shapes or from the flue-gas treatment. For the production of green paste products, sedimentation is used to remove PAH. The cooling process can be performed using indirect water systems, resulting in a discharge of clean cooling water. Indirect water systems can also be used to cool the flue-gases, to make them suitable for abatement with regular techniques [ 91, OSPARCOM 1992 ] such as fabric filters and electrostatic precipitators.

### 12.2.3 By-products, process residues and waste

The production of carbon and graphite is related to the generation of several by-products, residues and wastes, which are also listed in the European Waste Catalogue (Council Decision 94/3/EEC). *This has been replaced by a new directive 75/442/EEC (see Section 5.2.4)* The most important process-specific residues are listed below.

Refractory bricks from the baking furnaces can be re-used in other applications after cleaning or can be disposed as waste. Typical furnace lining life for prebaked anodes is about 100 cycles and this represents approximately 10 kilograms of bricks per tonne of anode produced.

Other residues include the material removed during the shaping, cutting and grinding stages together with tar or pitch fractions. Depending on the material, they are usually suitable for recycling within the process as raw materials or in other processes as fuel or carburant. In some cases, carbonised or graphitised material is deliberately produced so that it can be ground and returned as raw material so that the properties of the product can be controlled.

Used biological substrate is also disposed of but has some value as a soil conditioner provided that toxic components have been decayed.

## 12.3 Techniques to consider in the determination of BAT

The sections of this document entitled Techniques to consider in the determination of BAT" set out techniques considered generally to have potential for achieving a high level of environmental protection in the industries within the scope of the document. The background to the way the techniques are described is given in Section 2.1.2 and Table 2.2.

This section presents a number of techniques for the prevention or reduction of emissions and residues as well as techniques reducing the overall energy consumption. They are all commercially available. Examples are given in order to demonstrate techniques, which illustrate a high environmental performance. The Techniques that are given as examples depend on information provided by the industry, European Member States and the valuation of the European IPPC Bureau. The general techniques described in Chapter 2 as 'common processes' apply to a large extent, to the processes in this sector and influence the manner in which the main and associated processes are controlled and operated.

The particular techniques that are pertinent to this group are outlined below. The raw material handling and pretreatment processes and the process control and abatement systems are particularly relevant. The control of furnace operating parameters and the prevention of diffuse emissions from furnaces is also important. Techniques used by other sectors are also applicable particularly those relating to the use of hydrocarbon and PAH removal systems.

The techniques to consider on a site by site basis are strongly influenced by the product specification and this influences some of the raw materials and processes used. The basic processes outlined in Section 12.1 on applied techniques therefore constitute techniques to consider for the production processes when used with appropriate abatement stages. The techniques to consider for collection and abatement stages and other aspects of process operation and control are covered in Sections 2.3 and 2.5

### 12.3.1 Materials storage, handling and pretreatment processes

**Description**

The potentially dusty nature of some raw materials means that enclosed storage, handling and treatment systems are used in these instances. The dust generated by some crushing and grinding operations means that collection and abatement may be applicable for this process.

The storage of raw materials depends on the nature of the material. The storage of fine dusts in enclosed buildings or in sealed packaging is used. The storage of liquid pitch in tanks should use condensers to remove hydrocarbons during breathing. Displaced gases should be vented back to the tanker during delivery. Materials that contain water-soluble components are stored under cover. The storage of non-dusty, non-soluble material in open stockpiles and large items individually in the open.

Table 12.11 summarises the techniques to consider for the material storage, handling and pretreatment stages.

| Material | Storage | Handling | Pretreatment | Comment |
|---|---|---|---|---|
| Carbon or coke | Silos | Pneumatic.<br>Covered conveyors if non-dusty | Grinding or milling<br>sieving<br>blending | |
| Fuel, pitch and other oils<br>solvents or resins | Tanks or drums in bunded areas | Secure pipeline or manual system | | Oil collection.<br>Back venting of tanks, recovery of solvents |

| | | | | |
|---|---|---|---|---|
| Fine carbon and graphite dust and grained material | Enclosed | Enclosed with dust collection<br>Pneumatic | Grinding or milling<br>Sieving<br>Blending | |
| Coarse carbon and graphite grains and lumps | Covered or open bays | Mechanical loader | Grinding or milling<br>Sieving<br>Blending | |
| Petroleum coke | | Unloading by vaccum loader instead of crane | | [529] |
| Products:<br>shapes<br>powders | Covered or open store<br>Drums or bags | | Impregnation | |
| Process residues for recovery | Covered or enclosed depending on dust formation | Depends on conditions | | Appropriate drainage system |
| Wastes for disposal | Covered or enclosed bays or sealed (drums) depending on the material | Depends on conditions | | Appropriate drainage system |

**Table 12.11: Techniques to consider for material storage, handling and pretreatment methods**

**Achieved environmental benefits**
Prevention and capture of dust and VOCs.

**Cross-media effects**
No data has been reported.

**Operational data**
Given in the Table 12.11.
*In Table 12.11 are no operational data.*

**Applicability**
These techniques are applicable to most installations.

**Economics**
No data has been reported.

**Driving force for implementation**
Environmental impact and energy costs due to lost material.

**Example plants**
UK, DE, NL.

**Reference literature**
[ 274, Farrell Mission in DE 2008 ].

### 12.3.2 Other process stages

**Description**
The processes used are strongly influenced by the product and its specification. These factors are therefore site-specific. The blending and forming, baking, impregnation, graphitisation, product shaping and fume collection and abatement systems described as applied techniques are

therefore techniques to consider in the determination of BAT. Essentially the process technologies discussed in this section, combined with suitable abatement discussed in Chapter 2 will meet the demands of stringent environmental protection [ 345, Additional Data from UBA DE 2009 ], [ 203, Fundación Entorno, Empresa y Medio Ambiente 1999 ]. The following are the techniques to consider:

- Enclosed and extracted grinding and blending of raw materials, fabric filters for abatement. *(→ see section 12.3.2)*
- The use of furnaces with adequate extraction of process gases and regenerative systems to recover energy from hot gases. Furnaces operated on planned basis to allow cooling and heating periods to maximise heat recovery from the gases. *(→ see Section 12.3.2.2)*
- Destruction of cyanides, tars and hydrocarbons in an afterburner if they have not been removed by other abatement.
- The use of low-$NO_x$ burners or oxy-fuel firing. Control of the firing of furnaces to optimise the energy use and reduce PAH and $NO_x$ emissions.
- Adequate maintenance of the furnaces to maintain the sealing of off-gas and air ducts.
- Monitoring of the off-gas collection system to identify blockages or potential explosive mixtures caused by condensing hydrocarbons.
- The use of wet or semi-dry scrubbing to remove sulphur dioxide.
- The use of coke bed filters or dry scrubbers plus fabric filters.
- Electrostatic precipitators to remove tars hydrocarbons and PAH emitted from pitch storage, blending, impregnation, forming and baking stages. Use of afterburners to reduce their levels further.*(see Sections 12.3.2.1 and 12.3.2.2)*
- The use of bio filters to remove odorous components (special carbon production).
- The use of sealed or indirect cooling systems.
- The use of sedimentation to remove PAH from waste water where possible.

**Achieved environmental benefits**
The prevention, capture and treatment of a variety of pollutants.

**Cross-media effects**
No data has been reported.

**Operational data**
Given in the Table 12.12 and Figure 12.7.
*What is meant by the first column heading "reagent used"?*

| **Reagent used.** | **Component in off-gas.** | **Treatment method.** |
|---|---|---|
| Solvents, VOCs | VOC | Condensation, activated carbon, biofilter |
| Freons, halides | $Cl_2$, $F_2$, HF, HCl | Collection, caustic scrubber system |
| Nitric acid | $NO_X$ | Oxidise and absorb, recycle, scrubber system |
| Tars, pitches | Hydrocarbons, PAH | Afterburner, RTO? condensation, ESP,<br>carbon filter, alumina scrubber, wet and or dry scrubbers |
| Sulphur | $SO_2$ | Wet or dry scrubber system |
| Polyacrylonitrile (PAN) | HCN | Afterburning |

**Table 12.12: Treatment methods for gaseous components**

| Source | Abatement type | Pollutant | Concentration range (mg/Nm$^3$) | Best performers reported range (mg/Nm$^3$) | Techniques to consider (X) | Comments |
|---|---|---|---|---|---|---|
| Material handling and storage. Coke | Cyclone | Dust | 20 - 150 | | | |
| | Cyclone and/or fabric filter | Dust | 1 - 90 | 1 – 5 | X | Depends on the characteristics of the dust. |
| | Fabric filter (small and silo filters only) | Dust | | <30 | X | |
| Material handling and storage. Pitch | Re-venting and condensation | Hydrocarbons | <25 | | | |
| | | Hydrocarbons (volatile) | | <10 | X | |
| | | Hydrocarbons (condensable) | | <50 | X | |
| | | Hydrocarbons | 1 – 75 | | X | |
| | Adsorber – Dry scrubber + fabric filter | Hydrocarbons (volatile) | | <10 | X | |
| | | Hydrocarbons (condensable) | | <50 | X | |
| Grinding, mixing and shaping | Cyclone and/or fabric filter | Dust | | 1 – 5 | X | Depends on the characteristics of the dust. |
| | | Dust | | <10 | X | Depends on the characteristics of the dust. |
| | Afterburner - CTO | Dust | 1 – 15 | 1 – 5 | | |
| | | Hydrocarbons | 1 – 100 | <5 | X | |
| | | PAH VDI I+II | 0.007 – 8.0 | <0.1 | X | |
| | | Benzene | 0.06 – 0.25 | | | |
| | Afterburner – RTO | Hydrocarbons (total) | | <5 | X | |
| | Adsorber – Dry scrubber + fabric filter | PAH (total) EPA 16 | | <0.2 | X | The preferred reporting convention is the EPA 16. |

| | | | | | | |
|---|---|---|---|---|---|---|
| | | PAH (total) EPA 16 | | <0.5 | X | The preferred reporting convention is the EPA 16. |
| | | $SO_2$ | | <50 – 200 | X | If sulphur is added to the blend or the fuel contains high %S. |
| | | Dust | 1 – 50 | | | |
| | | Hydrocarbons | 19 – 150 | <25 | X | |
| | | PAH VDI I+II | 0.1 – 1.0 | 0.1 | | |
| | | PAH (total) | | <0.5 | | |
| | | PAH | <30 | | | |
| | Alkaline wet scrubber | Dust | 10 – 50 | | | |
| | | Hydrocarbons | 20 – 150 | | | |
| | | PAH (as B(a)P) | <0.1 | | | |
| | | PAH | 0.1 – 1.0 | | | |
| | | | | | | |
| | | $SO_2$ | | <50 – 200 | X | If sulphur is added to the blend or the fuel contains high %S. |
| Baking and re-baking | Cyclone and/or fabric filter | Dust | | 1 – 5 | X | Depends on the characteristics of the dust. |
| | | Dust | | <10 | X | Depends on the characteristics of the dust. |
| | ESP + HF adsorber + fabric filter | Dust | 2.5 – 90 | | | |
| | | Hydrocarbons | 50 – 250 | | | |
| | | B(a)P | <0.1 | | | |
| | | PAH | 0.003 – 6 | | | |
| | | Benzene | 1 – 11 | | | |
| | Afterburner – CTO | Dust | 1 – 40 | | | |
| | | Hydrocarbons | 2 – 17 | <11 – 30 | | |
| | | PAH VDI I+II | 0.003 – 0.2 | | | |
| | | Benzene | 0.15 – 7.5 | | | |

| | | | | | | |
|---|---|---|---|---|---|---|
| | | $SO_2$ | 20 – 100 | | | |
| | | $NO_X$ | 50 – 250 | | | |
| | | Hydrocarbons (volatile) | | <10 – 25 | X | |
| | | Hydrocarbons (condensable) | | <1 – 5 | X | |
| | | PAH (total) EPA 16 | | <0.2 | | The preferred reporting convention is the EPA 16. |
| | Afterburner – RTO | Dust | 1 – 60 | | | |
| | | Hydrocarbons | 6 – 100 | | | |
| | | PAH VDI I+II | 0.01 – 0.5 | | | |
| | Afterburner – RTO + HF adsorber + fabric filter | PAH | 0.05 – 2.5 | | | Open annular baking furnace. |
| | | Benzene | 0.1 – 3.5 | | | Open annular baking furnace. |
| | | $SO_2$ | 2 – 150 | | | Open annular baking furnace. |
| | | $NO_X$ | 10 – 40 | | | Open annular baking furnace. |
| | | HF | <5 | <1 | | Open annular baking furnace. If cleaned anode butts are recycled. |
| | | PAH (EPA 16) | | 0.2 – 0.5 | | Open annular baking furnace. The preferred reporting convention is the EPA 16. |
| | Adsorber HF – Dry scrubber + fabric filter | Dust | <1 – 14 | | | |
| | | Hydrocarbons (volatile) | | <10 – 50 | X | |
| | | Hydrocarbons (condensable) | | <1 – 5 | X | |
| | | Hydrocarbons | 1 – 135 | <11 – 30 | X | |

| | | | | | | |
|---|---|---|---|---|---|---|
| | | PAH (OSPAR 11) | | <0.2 | X | |
| | | PAH (total) EPA 16 | | <0.5 | | The preferred reporting convention is the EPA 16. |
| | | PAH | 0.002 – 55 | | | |
| | | $SO_2$ | | <50 – 200 | X | If sulphur is added to the blend or the fuel contains high %S. If sulphur is added to the blend or the fuel contains high %S. |
| Impregnation | Cyclone and/or fabric filter | Dust | 1 – 4 | | | |
| | Afterburner – CTO | Dust | 1 – 40 | | | |
| | | Hydrocarbons | 3.5 – 7.5 | | | |
| | | PAH | 0.0002 – 0.2 | | | |
| | | Benzene | 0.4 – 7.5 | | | |
| | | $SO_2$ | 20 – 100 | | | |
| | | $NO_X$ | 50 – 250 | | | |
| | Condensation (Cooler) | Hydrocarbons | 4 – 40 | | | |
| | | PAH VDI I+II | 0.001 – 0.1 | | | |
| Graphitising | Cyclone and/or fabric filter | Dust | 1 – 20 | 1 – 5 | X | Storing and handling coke. Depends on the characteristics of the dust. |
| | | Hydrocarbons | 1 – 25 | <10 | X | Graphitising. Only relevant if green material is handled. |
| Machining and finishing | Cyclone and/or fabric filter | Dust | 1 – 35 | 1 – 5 | X | |
| | | Hydrocarbons | 1 – 25 | <10 | X | Only relevant if green material is handled. |
| Special carbon manufacturing techniques | Containment | VOC or solvents as C | | <20 | X | Mixing and impregnation, if solvents are used. |

| | | | | | | |
|---|---|---|---|---|---|---|
| | Afterburner – RTO | Cyanide | | <2 – 5 | X | Only for carbon and graphite fibre production using PAN. |

**Table 12.13: Emissions from best performers from carbon and graphite production**
[ 345, Additional Data from UBA DE 2009 ]

*This is a contribution from Mr Tillmanns but not from UBA!!! Where are these data from. What are the reference plants and the references. Do we have the measurement data and the corresponding information about the measurement conditions??? On how many measurments do these data rely? Most of the data do not look like measured data. The data in the column concentration range should be consistent with the data in table 12.8 in section 12.2.1.8. But they are not. Some of the data have been changed in table 12.8 and some have been deleted. Clarify!*

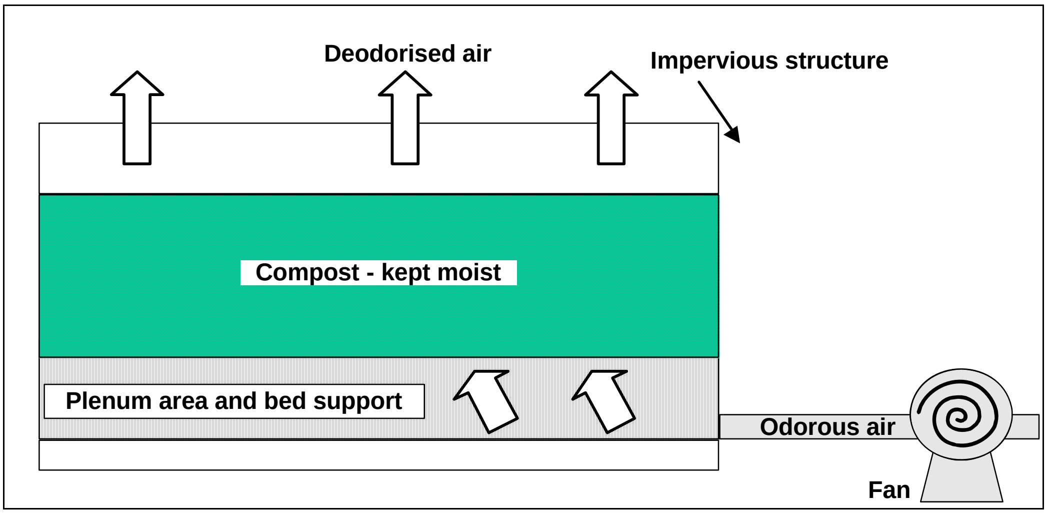


**Figure 12.7: Example of a biofilter**

*The inclution of biofilter is not understandable, because it is the only technique which is not included in the previous table. Without data and real examples this is useless.*

**Applicability**
These techniques are applicable to most installations.

**Economics**
No data has been reported.

**Driving force for implementation**
Reduction of odours and other pollutants.

**Example plants**
UK, DE.

**Reference literature**
[ 274, Farrell Mission in DE 2008 ].

#### 12.3.2.1 Use of condensation and ESPs

**Description**
The volatile hydrocarbons emitted during baking *(volatile hydrocarbons can be emitted from many places in anode production. Condensation is used for more than for the baking stage)* can be condensed and the condensed hydrocarbon particles are removed from the flue-gas. As the PAH tend to adhere to the condensed hydrocarbon particles, the PAH emissions are also reduced. Condensation can be achieved by external and/or internal cooling with air and/or water systems. Condensation is often achieved within conditioning towers ~~[ 345, Additional Data from UBA DE 2009 ]~~.*This is the original text from the existing BREF. No description can be found in [345]*

The condensed hydrocarbon particles can be removed from the flue-gas by regular dust abatement techniques like fabric filters or electrostatic precipitators.

**Achieved environmental benefits**
The removal and recovery of condensable hydrocarbons for use in the process.

**Cross-media effects**
Some energy related emissions due to cooling.

**Operational data**
No data has been reported. [345] contains some data about condensation as an abatement technique for the impregnation stage. Condesation is also mentioned for the pitch storage but not for baking. For baking the ESP is included but only in combination with HF adsorber and FF.

**Applicability**
This technique is applicable to the pretreatment stage for several process abatement stages.

**Economics**
No data has been reported but several installations are operating viably.

**Driving force for implementation**
Reduction of PAH emissions and recovery of tars.

**Example plants**
DE.

**Reference literature**
[ 103, Farrell, F. 1998 ], [ 345, Additional Data from UBA DE 2009 ].

### 12.3.2.2 Use of regenerative afterburner - regenerative thermal oxidiser (RTO)

**Description**
*Liquid pitch storage*
*Paste plant*
*Baking plant*
~~A regenerative afterburner has been used in a number of applications.~~ The process depends on an alternating cycling of gases through a series of support zones where heating, cooling and cleaning cycles take place. The combustible fraction is heated in the heating zone and passes to a common residence chamber where combustion is completed, the hot gases then pass into a cooling section which is heated to become the next heating zone. The zones are changed using a manifold system to allow cleaning and these valves are prone to fouling with carbon and reduce the effectiveness. Pretreatment reduces this fouling and careful design of the valves is also needed [ 318, Fume treatment from Baking Furnaces 2007 ], ~~[ 345, Additional Data from UBA DE 2009 ].~~

In some cases, the gases are pretreated to remove tar and PAH before the RTO so that low PAH values can be achieved and additional energy is therefore needed to maintain temperatures in the combustion zone unless the collected tar is used as a fuel. The operational data is given for a plant that uses pretreatment and post-treatment to achieve very low emissions. The RTO alone has not been shown to achieve these very low emission levels.

**Achieved environmental benefits**
Anode plant emissions consist partially of pitch and tar fumes, composed of polycyclic aromatic hydrocarbons (PAH). These emissions are odourous and potencially carcinogenic. With the RTO process harmful condensed and volatile PAH as well as other organics can be significantly reduced.

With the RTO the sensible heat of the off-gas can be recovered and thus energy consumption can be reduced significantly. The energy content of the organic contaminants (hydrocarbon and PAH) is used to heat the support materials. Depending on the pollutant contents of the fumes, autothermal operation may be possible. ~~Odour reduction is achieved.~~ Energy recovery gives autothermal operation and VOCs are removed without incurring energy related emissions. *Really autothermal?? This is not consistent with the corresponding text in Section 4.3.3.2.*

*Check the highlighted part if the conclusions are correct.*

**Cross-media effects**

No data has been reported.

**Operational data**

The techniques installed comprise four steps and are used in the process that recovers anode butts, [ 242, Nl Anode Input 2008 ]:

1. Removal of coarse tar components and dust: The off-gas from the baking furnace is led through a packed bed of saddle-shaped ceramics. The heavy tar components condense on the bed which are cleaned periodically using the hot gases from the RTO. The off-gases from the cleaning phase pass to the RTO and not the pretreatment stage.
2. Regenerative thermal oxidation (RTO): Ceramic beds are used to preheat the off-gas. By switching the direction of the airflow regularly, these ceramic beds are preheated with the off-gas from the combustion room.
3. The off-gases are lead to the combustion room, where fine tar components and PAHs are destroyed at a temperature of approximately 800 °C.
4. Dry absorption: The off-gases are lead through a moving bed reactor with lime to capture fluorides (and a limited amount of $SO_2$).

*Ad 4.: Fluoride emissions occur when butts are recycled for anode production. Does this always mean that this is an anode plant within a aluminium production plant? If Fluoride adsorption is mentioned here, why is it not an issue for the BAT conclusions? If spent anode butts can be recycled in standalone anode plants Fluorides have to be included in the BAT conclusions.*

Table 12.6 gives some data for a carbon and graphite installation that uses an RTO. The pretreatment does not achieve a significant reduction in this case and the plant is being revised in 2009. *(what means is being revised?)*

Pretreatment of the gases before an RTO will remove some combustible organic carbon however, if an ESP is used for pretreatment, condensed hydrocarbons can partly be utilised in the combustion chamber of the RTO [ 318, Fume treatment from Baking Furnaces 2007 ]. The energy consumption depends on the differential temperature, heat recovery rates of approximately 95 % can be achieved.

**Applicability**

This technique is applicable to a variety of processes. The basic principle is good but the fouling of the change-over valves or change-over to the cleaning phase may cause the emissions of uncombusted material if the design is inadequate or the sealing valves become fouled ~~[ 345, Additional Data from UBA DE 2009 ].~~ Pretreatment of the gases before an RTO will remove some combustible organic carbon, however, if an ESP is used for pretreatment, condensed hydrocarbons can partly be utilised in the combustion chamber of the RTO. Another option currently in an experimental stage are post-treatment measures (e. g. dry scrubber) that might be successful to reduce significantly the relevant emission components behind the RTO.

**Economics**

No data has been reported but several installations are operating viably.

**Driving force for implementation**

Reduction of PAH and benzene emissions and improved energy efficiency.

**Example plants**

DE, UK, NL.

**Reference literature**

[ 103, Farrell, F. 1998 ], [ 242, Nl Anode Input 2008 ], [ 318, Fume treatment from Baking Furnaces 2007 ], [ 345, Additional Data from UBA DE 2009 ].

### 12.3.3 Waste water

All waste water will be treated to remove hydrocarbons and solids. The techniques listed in Section 2.12.2 are the techniques to consider. In a number of installations cooling water and treated waste water including rainwater is re-used or recycled within the processes.

### 12.3.4 By-products, process residues and waste

The principles of the minimisation and re-use of process residues are techniques that form part of BAT. The techniques listed in Section 2.13.3 are the techniques to consider.

## 12.4 Best Available Techniques

In understanding this section and its contents, the attention of the reader is drawn back to the Preface of this document and in particular the fifth section of the Preface: ‘How to understand and use this document’. The techniques and associated emission and/or consumption levels, or ranges of levels, presented in this section have been assessed through an iterative process involving the following steps:

- identification of the key environmental issues for the sector which for the production of carbon and graphite are: PAH, hydrocarbons, dust, fume, odours, $SO_2$, waste water prevention and the re-use of residues such as filter dust;
- examination of the techniques most relevant to address these key issues;
- identification of the best environmental performance levels, on the basis of the available data in the European Union and worldwide;
- examination of the conditions under which these performance levels were achieved; such as costs, cross-media effects, and the main driving forces involved in the implementation of the techniques;
- selection of the best available techniques (BAT) and the associated emission and/or consumption levels for this sector in a general sense, all according to Article 2(12) and Annex IV to the Directive.

Expert judgement by the European IPPC Bureau and the relevant Technical Working Group (TWG) has played a key role in each of these steps and in the way in which the information is presented here.

On the basis of this assessment, best available techniques, and as far as possible emission and consumption levels associated with their use, are presented in this section that are considered to be appropriate to the sector as a whole and in many cases reflect the current performance of some installations within the sector. Where emission and consumption levels 'associated with best available techniques' are presented, this is to be understood as meaning that those levels represent the environmental performance that could be anticipated as a result of the application, in this sector, of the techniques described, bearing in mind the balance of costs and advantages inherent within the definition of BAT. However, they are neither emission nor consumption limit values and should not be understood as such. In some cases, it may be technically possible to achieve better emission or consumption levels but due to the costs involved or cross-media considerations, they are not considered to be appropriate as BAT for the sector as a whole. However, such levels may be considered to be justified in more specific cases where there are special driving forces.

The emission and consumption levels associated with the use of BAT have to be seen together with any specified reference conditions (e.g. averaging periods).

The concept of ‘levels associated with BAT’ described above is to be distinguished from the term ‘achievable level’ used elsewhere in this document. Where a level is described as ‘achievable’ using a particular technique or combination of techniques, this should be understood to mean that the level may be expected to be achieved over a substantial period of time in a well maintained and operated installation or process using those techniques.

Where available, data concerning costs have been given together with the description of the techniques presented in the previous sections. These give a rough indication about the magnitude of the costs involved. However, the actual cost of applying a technique will depend strongly on the specific situation regarding, for example, taxes, fees, subsidies, and the technical characteristics of the installation concerned. It is not possible to evaluate such site-specific factors fully in this document. In the absence of data concerning costs, conclusions on economic viability of techniques are drawn from observations on existing installations.

The BAT (including the associated emission and consumption levels) given in this section are 'BAT in a general sense' (i.e. considered to be appropriate to the sector as a whole). It is intended that they are a reference point against which to judge the current performance of an existing installation or to judge a proposal for a new installation. In this way, they will assist in the determination of appropriate 'BAT-based' conditions for the installation or in the establishment of general binding rules under Article 9([8]) of the IPPC Directive. It is foreseen that new installations can be designed to perform at or even better than the BAT levels presented in this section. It is also considered that existing installations could move towards the BAT levels presented in this section or do better, subject to the technical and economic applicability of the techniques in each case.

While the BAT reference documents do not set legally binding standards, they are meant to give information for the guidance of industry, Member States and the public on achievable emission and consumption levels when using specified techniques. The appropriate permit conditions for any specific case will need to be determined taking into account the objectives of the IPPC Directive and the local considerations.

**Recommendation to help users/readers of this document:**

It is strongly recommended that this section on BAT be read in conjunction with the sections of this document that describe the techniques to consider in the determination of BAT. The applicability of the techniques and measures are reported in these sections and should be taken into account at a local level. To help the reader, references to the appropriate sections are included in the description of BAT.

If not otherwise mentioned, BAT associated emission and consumption levels given in this section are expressed as follows:

- for pollutants emitted to air (except dioxins): expressed on a daily average basis with standard conditions of 273 K, 101.3 kPa, measured oxygen content and dry gas with the plant operating normally under steady-state conditions and no dilution of the gases;
- for dioxins: expressed as the average over the sampling period which should preferably be a minimum of 6 hours;
- for waste water: based on qualified random samples or 24 hour flow proportional composite samples.

As described in the Preface, this document does not propose emission limit values. The best available techniques and the ranges of emission or consumption levels associated with best available techniques (BAT-AEL ranges) are related to installations with different sizes, different kinds of operation and different raw materials. In this document, special local considerations cannot be taken fully into account. The determination of appropriate permit conditions will involve taking account of local, site-specific factors such as the technical characteristics of the installation concerned, its geographical location and the local environmental conditions. In the case of existing installations, the economic and technical viability of upgrading them also should be taken into account. Even the single objective of ensuring a high level of protection for the environment as a whole will often involve making trade-off judgements between different types of environmental impact, and these judgements will often be influenced by local considerations.

Although an attempt is made to address some of these issues, it is not possible for them to be considered fully in this document. The techniques and emission and consumption levels presented here will therefore not necessarily be appropriate for all installations. On the other hand, the obligation to ensure a high level of environmental protection including the minimisation of long-distance or transboundary pollution implies that permit conditions cannot be set on the basis of purely local considerations. It is therefore of the utmost importance that the information contained in this document is fully taken into account.

Section 2.20 to this document reports BAT for the following common processes and the following sections should be referred to for those techniques that are BAT:

- environmental management systems (EMS) (Section 2.20.1)
- material handling and storage (Section 2.20.2)
- process control (Section 2.20.3)
- fume and gas collection (Section 2.20.4)
- the prevention and the destruction of PCDD/F (Section2.20.5)
- sulphur dioxide removal (Section 2.20.6)
- the removal of mercury (Section 2.20.7)
- effluent treatment and water re-use (Section 2.20.8)
- energy efficiency (Section 2.20.9)
- intermediate products, process residues and wastes (Section 2.20.10)
- emission monitoring (Section 2.20.11)
- prevention of the formation of $NO_X$ (Section 2.20.12)
- removal of dust and particles (Section 2.20.13)

BAT for the production of carbon and graphite is the combination of the generally applicable techniques reported in Section 2.20 and the specific techniques indicated in this section.

### 12.4.1 Prevention and control of emissions to air

#### 12.4.1.1 Material handling and storage

**a) BAT is to prevent and control emissions of dust and other components from material handling storage and pretreatment by using the techniques in Table 12.14.**

| Material | Storage | Handling | Pretreatment | Comment |
|---|---|---|---|---|
| Carbon or coke | Silos | Pneumatic.<br>Covered conveyors if non-dusty | Grinding or milling<br>Sieving<br>Blending | |
| Fuel, pitch and other oils<br>Solvents or resins | Tanks or drums in bunded areas | Secure pipeline or manual system | | Oil collection. Back venting of tanks, recovery of solvents |
| Fine carbon and graphite dust and grained material | Enclosed | Enclosed with dust collection<br>Pneumatic | Grinding or milling<br>Sieving<br>Blending | |
| Coarse carbon and graphite grains and lumps | Covered or open bays | Mechanical loader | Grinding or milling<br>Sieving<br>Blending | |
| Products:<br>- shapes<br>- powders | Covered or open storage<br>Drums or bags | | Impregnation | |
| Process residues for recovery | Covered or enclosed depending on dust formation | Depends on conditions | | Appropriate drainage system |
| Wastes for disposal | Covered or enclosed bays or sealed (drums depending on the material | Depends on conditions | | Appropriate drainage system |

**Table 12.14: BAT for the material handling and storage and the pretreatment methods in carbon and graphite production**

### 12.4.1.2 Fume and gas collection and abatement

**a) BAT is to prevent and control emissions to air for the components likely to be present in the off-gases from the carbon and graphite production processes by using the techniques given in Table 12.15, Table 12.16, Table 12.17, Table 12.18, Table 12.19 and Table 12.20 (see Sections 12.3.2) or a combination of them.**

| Source | Techniques | Components in off-gas |
|---|---|---|
| Material handling and storage | Prevention, cooler/condensation, scrubber, afterburner (CTO/RTO),<br>Back venting of tanks | Dust, hydrocarbon and PAH<br>Potentially significant |
| Grinding | Cyclone and/or fabric filter | Dust<br>Handling dried material |
| Mixing and forming | Afterburner (CTO./RTO)<br>Dry scrubber, Coke filter | Dust, hydrocarbon and PAH<br>Handling dried material |
| Baking | Afterburner (CTO/RTO)<br>Cooler, lime/carbon adsorption and fabric filter with a bag burst detection system | Dust, $SO_2$, hydrocarbon and PAH<br>A pre-filter can be used to remove condensable materials |
| Baking or re-baking of other electrodes | Cooler and coated filter<br>Afterburner (CTO/RTO) and fabric filter | Dust, $SO_2$, hydrocarbon and PAH<br>A pre-filter can be used to remove condensable materials |
| Impregnation | Afterburner (CTO/RTO)<br>Gas collection and filter (carbon or biofilter for solvents) | Hydrocarbon and PAH, odours, organic solvents, metal fume |
| Graphitising | Gas collection and fabric filter ($SO_2$ scrubber) | Dust, $SO_2$ |
| Machining and shaping | Cyclone and/or fabric filter | |
| NB: Modern, well-designed electrostatic precipitators may be able to achieve the same performance as a dry scrubber. | | |

**Table 12.15: BAT to prevent and control emissions to air from carbon and graphite production**

**The emission levels given in Table 12.16, Table 12.17, Table 12.18, Table 12.19 and Table 12.20 are the BAT-AELs.**

| Pollutant | Techniques | BAT-AELs | Comments |
|---|---|---|---|
| Carbon dust | Cyclone and/or fabric filter | <1 to 5 mg/Nm$^3$ | Depends on the characteristics of the dust (See Sections 2.9.2.2.3, 2.9.2.2.4 and 2.20.13) |
| | Isolated filter units | <30 mg/Nm$^3$ | for storage silos only (See Section 2.9.2.2.4) |
| Hydrocarbons as C | Condenser, coke or other adsorber.<br>Back venting of gases during delivery | <10 mg/Nm$^3$<br>*This value only applies for volatile hydrocarbons according to table 12.13 in Section 12.3.2* | (See Sections 12.2.1.8 and 12.3.2) |
| NB: Collected emissions only. BAT-AELs are given as daily averages based on steady-state operation or, in cases where continuous monitoring is not practicable as the average over the sampling period. | | | |

**Table 12.16: BAT and BAT-AELs to prevent and control emissions to air from the storage and handling of coke and pitch**

| Pollutant | Techniques | BAT-AELs | Comments |
|---|---|---|---|
| Carbon dust | Cyclone plus fabric filter | <1 to 5 mg/Nm$^3$ | Dust should be monitored continuously<br>(See Sections 2.9.2.2.3, 2.9.2.2.4 and 2.20.13)<br>*See Sections 12.2.1.8 and 12.3.2* |
| PAH (EPA 16) | Pretreatment and Afterburner (CTO/RTO) | <1 mg/Nm$^3$ | Preferred reporting convention<br>(See Sections 12.2.1.8 and 12.3.2) |
| PAH (VDI I) | Afterburner (CTO/RTO) | <10 µg/Nm$^3$ | (See Section 12.2.1.8 and 12.3.2) |
| Hydrocarbons (Total) as C | Afterburner | <5 mg/Nm$^3$ | (See Section 12.2.1.8 and 12.3.2) |
| Hydrocarbons (Total) as C | Adsorber/dry scrubber | <25 mg/Nm$^3$ | (See Section 12.2.1.8 and 12.3.2) |
| NB: Collected emissions only. BAT-AELs are given as daily averages based on steady-state operation or, in cases where continuous monitoring is not practicable, as the average over the sampling period. | | | |

**Table 12.17: BAT and BAT-AELs to prevent and control emissions to air from the grinding and mixing stages**

*What means (CTO/RTO)? Does it mean that one or the other is applied? By the way: In the glossary CTO is defined as conventional thermal oxidising. I believe it should be catalytic thermal oxidising. Otherwise it would not make sense to include in this table 3 types: afterburner, CTO and RTO.*

| Pollutant | Techniques | BAT-AELs | Comments |
|---|---|---|---|
| Dust | Fabric filter | <1 to 5 mg/Nm$^3$ | Depends on characteristics of dust. Dust should be monitored continuously<br>(See Sections 2.9.2.2.4 and 2.20.13) |
| Benzene | Pretreatment and RTO | <1 mg/Nm$^3$ | (See Sections 12.2.1.8 and 12.3.2) |
| PAH (EPA 16) | Pretreatment and RTO | <1 mg/Nm$^3$ | (See Sections 12.2.1.8 and 12.3.2)<br>Preferred reporting convention |
| Hydrocarbons (Total) as C | Afterburner or RTO with pretreatment | <1 to 5 mg/Nm$^3$ | (See Sections 12.2.1.8 and 12.3.2) |
| $SO_2$ | Lime adsorption and fabric filter | <50 to 200 mg/Nm$^3$ | For special products where sulphur is added<br>(See Sections 2.11.3.4 and 12.3.2) |
| NB: Collected emissions only. BAT-AELs are given as daily averages based on steady-state operation or, in cases where continuous monitoring is not practicable, as the average over the sampling period. | | | |

**Table 12.18: BAT and BAT-AELs to prevent and control emissions to air from the baking and rebaking stages**

*Data for impregnation are missing! See table 12.8 in Section 12.2.1.8 and 12.13 in Section 12.3.2. See also existing BREF p.688 table 12.16.*

| Pollutant | Techniques | BAT-AELs | Comments |
|---|---|---|---|
| Dust | Cyclone plus fabric filter | <1 to 5 mg/Nm$^3$ | Depends on characteristics of dust.<br>(See Sections 2.9.2.2.3, 2.9.2.2.4 and 2.20.13) |
| NB: Collected emissions only. BAT-AELs are given as daily averages based on steady-state operation or, in cases where continuous monitoring is not practicable, as the average over the sampling period. | | | |

**Table 12.19: BAT and BAT-AELs for emissions to air from the machining and graphitising stages**

*Table 12.19 contains only cross-references to chapter 2. But the data used for concluding on BAT are taken from section 12.3.2 table 12.13.*

| Pollutant | Techniques | BAT-AELs | Comments |
|---|---|---|---|
| Cyanide | Afterburner | <2 to 5 mg/Nm$^3$ | Only for carbon fibre production using PAN (See Section 12.2.1.6) |
| NB: Collected emissions only. BAT-AELs are given as daily averages based on steady-state operation or, in cases where continuous monitoring is not practicable, as the average over the sampling period. | | | |

**Table 12.20: BAT and BAT-AELs to prevent and control emissions to air from the production of carbon fibres**

### 12.4.2 Effluent treatment and water re-use

**a) BAT is to operate the processes on a closed cycle. No emissions of process water are expected for a new installation (See Section 12.3.3).**

### 12.4.3 By-products, process residues and waste

**a) BAT is to use or recycle carbon and other residues from the production processes within the process or in other processes as far as possible (see also Section 2.20.10). Sludges from sealed circuits and blowdown water are wastes for special disposal. If recycling or re-use is not economically possible, secure disposal should be used.**

## 12.5 Emerging techniques

None reported.

# 13 CONCLUSIONS AND RECOMMENDATIONS

To be written.

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# GLOSSARY

| | | | | | |
|---|---|---|---|---|---|
| µg | Microgram | l | Litre | ppb | Parts per billion |
| EUR | Euro | | | | |
| yr | Year | lb | Pounds weight (avoirdupois) | ppm | Parts per million |
| cm | Centimetre | $m^3$ | Cubic metre | rpm | Revolutions (rotations) per minute |
| Cts (US) | Cents (United States) | mg | Milligram | T | Tonne |
| d | Day | mm | Millimetre | vol-% ~~v/v~~ | Volume % |
| DM | Deutsche Mark | MJ | Megajoule | wt- % ~~w/w~~ | Weight per cent |
| g | Gram | MWh | Megawatt hour | °C | Degree Celsius |
| GJ | Gigajoule | kWh | Kilowatt hour | K | Absolute temperature - Kelvin |
| GW | Gigawatt | $MW_e$ | Megawatt electrical | UKP | United Kingdom Pounds |
| h | Hour | $MW_{th}$ | Megawatt thermal | USD | United States Dollar |
| kg | Kilogram | $Nm^3$ | Normal cubic metre (NTP) 273 K (0 °C) 101.3 kPa (1 atmosphere) | | |
| kWh | Kilowatt hour | ng | Nanogram | | |
| | | | | | |

## Chemical Symbols

| | | | | | |
|---|---|---|---|---|---|
| Ag | Silver | HF | Hydrogen fluoride | PbO | Lead oxide |
| Al | Aluminium | Hf | Hafnium | Re | Rhenium |
| $Al_2O_3$ | Aluminium oxide | Hg | Mercury | Rh | Rhodium |
| As | Arsenic | $H_2SO_4$ | Sulphuric acid | Ru | Ruthenium |
| Au | Gold | In | Indium | S | Sulphur |
| B | Boron | Ir | Iridium | $SO_2$ | Sulphur dioxide |
| Be | Beryllium | K | Potassium | $SO_3$ | Sulphur trioxide |
| Bi | Bismuth | $K_2O$ | Potassium oxide | Se | Selenium |
| C | Carbon | Li | Lithium | Sn | Tin |
| Ca | Calcium | Mg | Magnesium | Sr | Strontium |
| CaO | Calcium oxide, lime | MgO | Magnesium oxide, Magnesia | Sb | Antimony |
| Co | Cobalt | Mn | Manganese | Si | Silicon |
| Cd | Cadmium | MnO | Manganous oxide | $SiO_2$ | Silica, silicon oxide |
| Cl | Chlorine | Mo | Molybdenum | Ta | Tantalum |
| Cr | Chromium | Na | Sodium | Ti | Titanium |
| Cs | Caesium | Nb | Niobium (columbium) | Tl | Tellurium |
| Cu | Copper | $NO_2$ | Nitrogen dioxide | V | Vanadium |
| F | Fluorine | Ni | Nickel | W | Tungsten |
| Fe | Iron | $NO_X$ | Sum of all nitrogen oxides | Zn | Zinc |
| FeO | Iron oxide | Os | Osmium | ZnO | Zinc oxide |
| Ga | Gallium | Pd | Palladium | Zr | Zirconium |
| Ge | Germanium | Pt | Platinum | | |
| HCl | Hydrogen chloride | Pb | Lead | | |

| ENGLISH TERM | MEANING |
|---|---|
| **A** | |
| Accuracy | Associated with measured values. It is an assessment of how close a measurement is to the accepted or true value. Chemical preparations of known purity and/or concentration are used to assess accuracy. These preparations, known as 'standards', are analysed using the same method by which the samples are measured. Accuracy should never be confused with precision: precision measures how closely the analytical results can be duplicated. |
| Achievable level | When using a particular technique or combination of techniques, achievable level means that a certain emission level may be expected to be achieved over a substantial period of time, e.g. a year, in a well designed, well maintained and well operated installation or process using those techniques. |
| Achieved environmental benefits | Main environmental impact(s) to be addressed by the technique (process or abatement), including emission values achieved and efficiency performance. Environmental benefits of the technique in comparison with others. |
| Acid | Proton donor - a substance that, more or less readily, gives off hydrogen ions in a water solution. |
| Acid generation | Production of acidity irrespective of its effect on the adjacent pore water or whether the material is net acid producing or neutralising. |
| Acidification | Adding acid to a substance to achieve acidic properties. |
| Acidity | Measure of the capacity of a solution to neutralise a strong base. |
| Acute effect | An adverse effect on any living organism in which severe symptoms develop rapidly and often subside after the exposure stops. |
| Acute toxicity | An adverse effect that results from a single dose or single exposure of a chemical; any poisonous effect produced within a short period of time, usually less than 96 hours. This term is normally used to describe effects in experimental animals. Acute toxicity is measured by determining the $LD_{50}$ value. |
| Acute pollution | Pollution arising from infrequent events, unplanned events or accidents (see also: chronic pollution). |
| ADEME | Agence de l'Environnement et de la Maitrise l'Energie. |
| ADMS | Atmospheric dispersion modelling system. |
| Adsorption | A surface process. The accumulation of molecules of a gas or liquid to form a thin film on the surface of a solid (surface assimilation). |
| Advantages | See: Benefits. |
| AEL | Associated emission level. |
| Afterburner | A specifically designed additional combustion unit with a burner system (not necessarily used all of the time) that provides time, temperature and turbulence with sufficient oxygen to oxidise organic compounds to carbon dioxide. Units can be designed to use the energy content of the raw gas to provide most of the heat input required and are more energy efficient. |
| Agglomerate | A network of aggregates loosely connected at discrete points. |
| Aggregate | A collection of primary particles that have fused to form a face-to-face sintered structure. |
| Air classifier or ACCU | Machine equipment to separate dust (<0.05 mm) and fine particles from the dry input material (<10 mm) or equipment to remove fine and coarse fractions from an air stream. |
| Alkali | Proton acceptor - a substance that, more or less readily, takes up hydrogen ions in a water solution. |
| Alkalinity | Measure of the capacity of a solution to neutralise a strong acid. |
| Alloy | A metal that is a combination, either in solution or compound, of two or more elements, at least one of which is a metal, and where the resulting material has metallic properties |
| Analysis | Characterisation of the nature of a sample. Analysis versus assessment: a formal, usually quantitative determination of the effects of an action (as in risk analysis and impact analysis). |

| ENGLISH TERM | MEANING |
|---|---|
| Angle of repose | The maximum slope at which a heap of any loose or fragmented solid material will stand without sliding or come to rest when poured or dumped in a pile or on a slope. |
| Anion | A negatively charged ion - an ion that is attracted towards the anode in electrochemical reactions. |
| Annual capital cost | An equal, or uniform, payment made each year over the useful life of the proposed technique. The sum of all the payments has the same 'present value' as the initial investment expenditure. The annual capital cost of an asset reflects the opportunity cost to the investor of owning the asset |
| Annealing | A heat treating process that softens the alloy by slowly cooling the metal through its critical temperature range. |
| Anode | A positive electrode. |
| Anodising | Anodic oxidation - an electrolytic process in which the surface layer of a metal, such as aluminium, magnesium or zinc is converted to a coating, usually an oxide, having protective, decorative or functional properties. |
| APC | Air pollution control - a term applied to the flue-gas treatment (FGT) equipment. Also referred to as flue-gas-cleaning (FGC) |
| APC residues | The residues that arise from air pollution control equipment, including the reacted and unreacted reagents, but excluding the fly ash portion |
| APT | Ammonium para-tungstate |
| Applicability | Consideration of the factors involved in applying and retrofitting the technique, e.g. space availability, process specificities. |
| Approval (of a product, process or service) | Permission for a product, process or service to be marketed or used for stated purposes or under stated conditions. |
| Approval (of a testing laboratory) | Authorisation given by the competent authority to a testing laboratory to perform regulatory measurements, controls or inspection in a specified field. |
| AOD converter | A converter using argon oxygen decarburisation. |
| Assessment | Examination of the level of adequacy between a set of observations and a commensurate set of criteria sufficient for fixed objectives in order to make a decision. Also the combination of analysis with policy related activities such as identification of issues and comparison of risk and benefits (as is risk assessment and impact assessment). |
| Assessment method of emissions | Set of relations between measured data, physical properties, meteorological data, and design data related to equipment or process parameters, and intended to calculate or to assess an emission or an emission factor. |
| Associated emissions to air | In this document are given as daily averages based on continuous monitoring with standard conditions of 273 K, 101.3 kPa, measured oxygen content and dry gas without dilution of the gases with air. In cases where continuous monitoring is not practicable as the average over the sampling period. |
| Associated emissions to water | Are based on a qualified random sample or a 24-hour composite sample. |
| Automatic measuring system | System for measuring the material under investigation, returning an output signal proportional to the physical unit of the parameter to be measured and capable of producing measurement results without human intervention. |
| Ausmelt/ISA Smelt | The Ausmelt/ISA Smelt furnaces and the the KRS furnace are cylindrical bath furnaces that use a steel lance for the injection of natural gas, oil or coal, and oxygen or air into the melt. |
| | |
| **B** | |
| BaP | Benzo(a)pyrene and is used as an indicator of PAH content. |
| BAT | Best available techniques. |
| BAT-AEL | BAT associated emission level. |
| Bath | A solution of chemicals for a specific surface treatment activity, e.g. pickling bath. This also refers to the relevant vat or workstation in a process sequence. |
| BBOC | Bottom blown oxygen cupel. |
| Benefits | Used in this document synonymously with 'advantages' to mean the positive environmental effects considered to be due to the implementation of a technique or other environmental measure. |

| ENGLISH TERM | MEANING |
|---|---|
| Best available techniques | BAT (IPPC Directive) - the most effective and advanced stage in the development of activities and their methods of operation which indicate the practical suitability of particular techniques for providing, in principle, the basis for emission limit values designed to prevent and, where that is not practicable, generally to reduce emission and the impact on the environment as a whole. |
| BF | Blast furnace, a vertical furnace using tuyères to blast heated or cold air into the furnace burden to smelt the contents. (also known as a hearth shaft furnace, a water jacket furnace and a lead shaft furnace). |
| BFG | Blast furnace gas. |
| Bioavailability | Property of a substance which makes it accessible and potentially able to affect an organism's health. Depends on site-specific conditions. |
| Biodiversity | The number and variety of different organisms in the ecological complexes in which they naturally occur. Organisms are organised at many levels, ranging from complete ecosystems to the biochemical structures that are the molecular basis of heredity. Thus, the term encompasses different ecosystems, species and genes that must be present for a healthy environment. A large number of species must characterise the food chain, representing multiple predator-prey relationships. |
| Bioleaching | Process in which minerals are dissolved with the aid of bacteria. |
| | |
| BOD | Biochemical oxygen demand - the quantity of dissolved oxygen required by micro-organisms in order to decompose organic matter. The unit of measurement is mg $O_2$/l. In Europe, BOD is usually measured after three ($BOD_3$), five ($BOD_5$) or seven ($BOD_7$) days. |
| b.p. | Boiling point. |
| BPEO | Best practicable environmental option. |
| Breathing | Gaseous emission due to ambient temperature change, usually daytime heating of contents of storage tanks. Out breathing due to volume increase of gas and evaporation of liquid. Inbreathing due to cooling of contents (night time volume decrease of gas and condensation of vapour) is not considered an emission source. |
| BREF | Best available techniques reference document. |
| Bund | A tank farm bund (or dike) is designed to contain large spills, such as that caused by a shell rupture or a large overfill. The bund consists of a wall around the outside of the tank (or tanks) to contain any product in the unlikely event of a spill. The bund is typically constructed of well compacted earth or reinforced concrete. The volume is normally sized to accommodate the contents of the largest tank within the bund. |
| | |
| **C** | |
| Calibration | Set of operations that establishes, under specific conditions, the systematic difference that may exist between the values of a parameter to be measured and those indicated by a measuring system (with the corresponding values given in reference to a specific 'reference' system, including reference materials and their accepted values).<br>NB: the result of a calibration allows either the assignment of values of the parameters to be measured to the indication or the determination of corrections with respect to indications. |
| Carcinogenic material | A material that is known to cause cancer in man |
| Casting (noun) | General term used for products at or near their finished shape, formed by solidification of a metal or alloy in a mould (ISO 3134-4: 1985). |
| Cathode | A negative electrode. |
| Cation | A positively charged ion - an ion that is attracted towards the cathode in electrochemical reactions. |
| Caustic soda | Sodium hydroxide. |
| CEM | Continuous emission monitoring. |
| CEMS | Continuous emission monitoring system. |
| CEN | Comité Européen de Normalisation (European Committee for standardisation). |
| CFD | Computerised fluid dynamics - a modelling technique used to predict gas flow and temperature in incinerators and other systems. |

| ENGLISH TERM | MEANING |
|---|---|
| COD | Chemical oxygen demand indicating the amount of chemically oxidisable organic matter in waste waters (normally referring to analysis with dichromate oxidation) according to ISO 15705:2002. |
| Combustible material | A material that will continue to show a combustive reaction with air of normal composition and pressure even after the source of ignition is removed. |
| Competent authority (from the IPPC Directive) | The authority or authorities or bodies responsible under the legal provisions of the Member States for carrying out the obligations arising from the Directive. |
| | |
| Compliance assessment | Process to compare actual emissions of pollutants from an installation (manufacturing unit) with the permitted emission limit values within a defined degree of confidence. |
| Component | Substance imbedded in a mixture, e.g. in waste water, waste gas or air. |
| Composite sample | Sample prepared by an operator or by an automatic device and that has been obtained by mixing several spot samples. |
| Concentrate | Marketable product after separation in a mineral processing plant with increased grade of the valuable mineral. |
| Content | Matter contained in a medium. |
| Continuous monitoring | Two types of continuous monitoring techniques are considered:<br>• Fixed *in-situ* (or in-line) continuous reading instruments. The measuring cell is placed in the duct, pipe or stream itself. These instruments do not need to withdraw any sample to analyse it and are usually based on optical properties. Regular maintenance and calibration of these instruments are essential.<br>• Fixed on-line (or extractive) continuous reading instruments. This type of instrumentation extracts a sample of the emission along a sampling line, which is driven to a measurement station, where the sample is then analysed continuously. The measurement station may be remote from the duct, and therefore care must be taken so that the sample integrity is maintained. This type of equipment may allow certain conditioning of the sample. |
| Continuous sampling | Sampling on a continuous basis, and without interruption, of a portion of an effluent, which itself can be continuous or discontinuous. An aliquot of the flow is taken at any time when there is a discharge. Two formats can be identified:<br>• Continuous flow-proportional sampling where a continuous sample is taken from a partial flow ratio of the sample volume to the effluent flowrate.<br>• Continuous sampling at fixed time intervals where equal volumes are taken at fixed time intervals. |
| Control of emission | Techniques used to limit, reduce, minimise, or prevent emissions. |
| Cooling water | Water used for energy transfer (cooling, heating), which is kept in a network separated from industrial water and which can be released back to receiving waters without further treatment. |
| COP | Coefficient of performance. |
| Cross-media conflicts | Resolving issues where there are competing environmental effects, or effects that are difficult to compare, e.g. $NO_X$ reduction versus energy consumption. |
| Cross-media effects | Possible shift of environmental pressure from one environmental compartment to another. Any side-effects and disadvantages caused by the implementation of the technique. |
| Crushing | Comminution process that reduces the particle size of run-of-mine ore to such a level that grinding can be carried out. The is accomplished by the compression of ore against rigid surfaces, or by impact against surfaces in a rigidly constrained motion path. |
| CTO | Conventional thermal oxidiser or afterburner<br>*In Section 4.3.3.1 CTO is used for catalytic thermal oxidiser* |
| CV | Calorific value, e.g. in MJ/kg. |
| CW | Cooling water. |
| CWPB | A centre worked prebaked anode cell. |
| | |
| **D** | |

| ENGLISH TERM | MEANING |
|---|---|
| Daily production capacity | The weight of products (air dry mass) an installation can produce during one day. |
| DC | Direct current (electrical supply). |
| Decommissioning | The shutdown of an installation including decontamination and/or dismantling. |
| DEFRA | Department for Environment, Food and Rural Affairs (for England and Wales). |
| Defrost | The removal of frost from raw materials. |
| Degreasing | Eliminating, as far as possible, oil or grease from a component. |
| D2EHPA | di(2-ethylhexyl) phosphoric acid. |
| Description | Technical description of the technique. |
| De novo synthesis | The mechanism when fine carbon particles which react with inorganic chlorides or organically-bound chlorine in the temperature range of 250 to 500 °C to produce PCDD/F. This process is catalysed by the presence of metals such as copper or iron. |
| $DESO_X$ | A desulphurisation technique. |
| Destruction | E.g. destruction of waste - this refers to the process of chemical conversion of mainly molecular organic species contained in the waste. Carbohydrates, for example, are converted into oxides of carbon and hydrogen. |
| Determinand | Value or parameter that should be determined by measurement or analysis. |
| Dewatering | Process of removing water from an underground min or open pit, or from the surrounding rock or non-lithified area. The term is also commonly used from the reduction of water content in concentrates, tailings and treatment sludges. |
| DG | Directorate General (of the European Commission). |
| Diffuse emission | Emissions arising from direct contact of volatile or light dusty substances with the environment (atmosphere, under normal operating circumstances). These can result from:<br>• inherent design of the equipment (e.g. filters, dryers)<br>• operating conditions (e.g. during transfer of material between containers)<br>• type of operation<br>• a gradual release to other media (e.g. to cooling water or waste water).<br>Fugitive emissions are a subset of diffuse emissions |
| Diffuse emission sources | Sources of similar diffuse or direct emissions which are multiple and distributed inside a defined area; they can be point, linear, surface or volume sources (51, European Commission, 2003). |
| DIN | Deutsches Institut für Normung - the German national organisation for standardisation. |
| Dioxins | Dioxins are referred to in this document as PCDD/PCDF which in turn means polychlorinated di-benzo para dioxin and polychlorinated di-benzo para furans. |
| Discharge | Physical release of a pollutant through a defined outlet, i.e. channelled, system, e.g. sewer, stack, vent, curbing area, outfall. |
| Disposal | Defined by the EC Waste Framework Directive. |
| Dolomite | Type of limestone, the carbonate fraction of which is dominated by the mineral dolomite, calcium magnesium carbonate ($CaMg(CO_3)$). |
| DOC | Dissolved organic carbon. |
| DON process | Direct Outotec Nickel process |
| Drainage | Manner in which the waters of an area exist and move, including surface streams and groundwater pathways. A collective term for all concentrated and diffuse water flows. |
| Driving force for implementation | Reasons for implementation of the technique, e.g. other legislation, improvement in production quality. |
| Dross | The scum or refuse matter which is thrown off, or falls from, metals in smelting the ore, or in the process of melting. In the chapter for aluminium, the term skimmings or dross is used. |
| Drum | A cylindrical closed container rotating on an axis. |
| DSA | Dimensionally stable anodes - metal anodes that are not consumed during use as graphite anodes are, hence dimensionally stable. |
| Dust | A solid, mechanically produced particle with a size ranging from sub microscopic to macroscopic. |

| ENGLISH TERM | MEANING |
|---|---|
| | |
| **E** | |
| E2MS | Energy efficiency management system. |
| EAF | Electric arc furnace. |
| EB | Electron beam. |
| EC | European Commission. |
| Economics | Information on costs (investment and operation) and any possible savings, e.g. reduced raw material consumption, waste charges, also as related to the capacity of the technique. |
| EDTA | Ethylenediaminetetraacetic acid, a complexing agent. |
| EEA | European Environment Agency. |
| Efficiency | A measure of the effectiveness of a technique to achieve a particular result. In some cases, it may be expressed as a ratio of input to output. |
| Effluent | A physical fluid (air or water together with contaminants) forming an emission. |
| EIPPCB | European Integrated Pollution Prevention and Control Bureau. |
| Electrode | A conductor by which an electric current enters or leaves an electrolyte in an electrochemical reaction (or an electric arc or a vacuum tube) (see also: anode and cathode). |
| Electrolysis | A process that decomposes a chemical compound or produces a new compound by the action of an electrical current. The electrical current is passed through an electrolytic cell and oxidation/reduction reactions occur at the electrodes; for example, water can be decomposed into hydrogen and oxygen by electrolysis. |
| Electrolyte | A substance that is capable of conducting an electric current in a solution or fused state. |
| ELV (from the IPPC Directive) | Emission limit value - the mass, expressed in terms of certain specific parameters, concentration and/or level of an emission, which may not be exceeded during one or more periods of time. |
| Electrorefining | An electrolytic refining stage where a metal anode is dissolved and the metal is deposited at the cathode. Impurities called anode sludge are deposited in the cell. |
| Electrowinning<br>EW | An electrolytic production stage where an inert metal anode used and the desired metal in the electrolyte deposited at the cathode. |
| EMAS | European Community Eco-Management and Audit Scheme (Council Regulation 761/2001). |
| Emerging techniques | Techniques with potential for environmental performance improvement but that have not yet been commercially applied or which are still in the research and development phase. Potential future BAT. |
| Emission<br>(from the IPPC Directive) | The direct or indirect release of substances, vibrations, heat or noise from individual or diffuse sources in the installation into the air, water or land as defined in Art. 2($^5$) of the Directive. |
| Emissions | In this document emissions are quoted as the daily average unless stated to the contrary. |
| Emission factor | The estimated average emission rate of a given pollutant for a given source, relative to units of activity. |
| Emission limit value (ELV) (from the IPPC Directive) | The mass, expressed in terms of certain specific parameters, concentration and/or level of an emission, which may not be exceeded during one or more periods of time. |
| Emission pattern | Type of variation of emission over time, for example, emissions can be stable, cyclic, random peaking, random variable, erratic. |
| Emission to air | a) mass of emitted substance related to the volume of waste gas under standard conditions (273 K, 1013 mbar), after deduction of water vapour content, expressed in the units (g/Nm$^3$), (mg/Nm$^3$), (µg/Nm$^3$) or (ng/Nm$^3$).<br>b) mass of emitted substances related to time, expressed in the units (kg/h), (g/h) or (mg/h).<br>c) ratio of mass of emitted substances to the mass of products generated or processed (consumption or emission factors), expressed in the units (kg/t), (g/t) or (mg//t) or (µg/t). |
| Emission to water | Mass of emitted substances related to the volume of waste water, expressed in the units (g/m$^3$), (g/l), (mg/l) or (µg/l). |

| ENGLISH TERM | MEANING |
|---|---|
| EMS | Environmental management system. |
| End-of-pipe technique | A technique that reduces final emissions or consumptions by some additional process but does not change the fundamental operation of the core process. |
| Environment | Interrelated physical, chemical, biological, social, spiritual and cultural components that affect the growth and development of living organisms. |
| Environmental quality standard (from the IPPC Directive) | Set of requirements which must be fulfilled at a given time by a given environment or particular part thereof, as set out in Community legislation. |
| Environmentally harmful material | A material that can cause acute or chronic effects in ecosystems - the classification of environmentally harmful materials takes place in accordance with the agreements included in the 67/548/EEC Directive. |
| EOP | End-of-pipe. |
| EPA | Environmental Protection Agency. |
| EPER | European pollutant emission register defined in Council Decision 2000/479/EC, now replaced by PRTR. |
| EPDM | Ethylene propylene diene M-class rubber |
| EQO | Environmental quality objectives. |
| EQS | Environmental quality standards. |
| Equivalent parameter | Parameter related to an emission, which provides the same (similar) level of information with the same (similar) level of confidence. |
| Erosion | Detachment and subsequent removal of either rock or surface material by wind, rain, wave action, freezing, thawing and other processes. |
| Error | Measurement error - the amount by which an observed or approximate result differs from the true or exact one. These typically result from an inaccuracy or imprecision in the measurement of parameter values. |
| ESP | Electrostatic precipitator. |
| EU | European Union. |
| EU-15 | Member States of the European Union before 1 May 2004. |
| EU-25 | Member States of the European Union from 1 May 2004 until 31 December 2006. |
| EU-27 | Member States of the European Union from 1 January 2007. |
| EUR | Euro - European currency. |
| Evaporation | Physical process by which a liquid is changed into a gas. |
| EWL | European waste list from the European Waste Framework Directive. |
| Example plants | Reference to a plant where the technique is reported to be used. |
| Exhaust air | Air stream (waste gas) from an installation contaminated with gaseous components, normally with low concentrations. |
| Existing installation (from the IPPC Directive) | Installation in operation or existing before the date on which the IPPC Directive came into effect, according to Art.2($^4$) of the Directive. |
| | |
| **F** | |
| FBD | Fluidised bed drier. |
| FBI | Fluidised bed incinerator. |
| FF | Fabric filter. |
| FGC | Flue-gas-cleaning . |
| FGD | Flue-gas desulphurisation. |
| FGT | Flue-gas treatment. |
| FGT residue | Refers to the residues generated when flue-gas treatment is applied to WT installations. Please note that this term is used to differentiate from ‘FGT waste’.<br>Residues arising from flue-gas treatment stages including fly ash and reacted and unreacted reagents. |
| FGT waste | Refers to the waste generated in the flue-gas treatment of combustion processes and it is considered as a ‘waste in’ in this document. Please note that this term is used with a different meaning to ‘FGT residue’. |
| FIBC | Flexible Intermediate Bulk Containers. |
| Fines | Small particle sized material. |
| Flue-gas | Waste gas generated by incineration or combustion processes. |

| ENGLISH TERM | MEANING |
|---|---|
| Flux | A substance that, even in small quantities, lowers the fusion point of material in which it is naturally present, e.g. alkalis in clay, or of material to which it has been added, e.g. borax added to glazes. |
| FSF | Flash Smelting Furnace |
| Fugitive emissions | Emissions caused by non-tight equipment/leak. Emissions into the environment resulting from a gradual loss of tightness from a piece of equipment designed to contain an enclosed fluid (gaseous or liquid). Fundamentally caused by a difference of pressure and a resulting leak. Examples of fugitive emissions are a leak from a flange, a pump, sealed or tightened equipment. |
| Furnace | The part of an installation where combustion commences or is carried out. Section 2.8 of this document reports on the furnaces that are used and gives the definition of abbreviations. |
| Fuzzy logic | A term used to describe a computing network that receives and computes multiple signals by means of a logic system to control operational parameters within predefined set points. |
| | |
| **G** | |
| Galvanising | In UK English: hot dip metal coating. German: Schelztauchüberzug, French: galvanisation à chaud. A term often used to wrongly translate the German: galvanische Metallabscheidung, or similar words from other languages. This term should not be translated into English as 'electroplating'. |
| GHG | Greenhouse gases. |
| Global warming | Greenhouse effect - the shortwave solar radiation passes through the Earth's atmosphere but after being reradiated by its surface as infrared radiation, some of it is absorbed by gases in the atmosphere causing a rise in temperature (known as global warming). It is calculated that 55 % of global warming is caused by absorption of energy by $CO_2$. The remaining 45 % is caused mainly by energy absorption by methane and damage to the ozone layer as a result of the use of various VOX. |
| Good practice | Approach which provides a good framework to the given activity. It does not preclude other approaches which may be more appropriate for a given requirement. |
| Grade | Dimensionless proportion of any constituent in an ore, expressed often as a percentage, grams per tonne (g/t) or parts per million (ppm). |
| Grinding | Comminution process yielding a fine product (<1 mm), where size reduction is accomplished by abrasion and impact and sometimes supported by the free motion of unconnected media such as rods, balls and pebbles. |
| Groundwater | Part of subsurface water in the zone of saturation. Distinct from surface water. |
| GWP | Global warming potential. |
| | |
| **H** | |
| $H_2O_2$ | Hydrogen peroxide. |
| $H_2SO_4$ | Sulphuric acid. |
| H&S | Health and safety programme. |
| HACCP | Hazard analysis critical control points. |
| Harmful material | A material that, by inhalation or entry via the mouth or skin, can cause disorder of a limited nature. |
| Hazardous substances | Substances or groups of substances that have one or several dangerous properties such as toxicity, persistence and bioaccumulability, or are classified as dangerous to humans or the environment according to Directive 67/548 - Dangerous Substances Directive. |
| HAZOP | Hazard and operability study |
| HCl | Hydrochloric acid. |
| Hearth | Part of a furnace. |
| Hearth type furnace | Static furnace with direct heating, also called reverberatory furnace and bale-out furnace. |
| HF | Hydrofluoric acid. |
| HFC | Hydrofluoro carbon. |
| HFO | Heavy fuel oil. |

| ENGLISH TERM | MEANING |
|---|---|
| HMIP | Her Majesty's Inspectorate of Pollution (UK). |
| HNx gas | Nitrogen-hydrogen gas. |
| $HNO_3$ | Nitric acid. |
| Horizontal BREF | BAT reference document prepared to deal with topics common to more than one IPPC industrial sector, namely storage, cooling, waste water and waste gas, and monitoring. |
| HT | High tension electricity. |
| HW or Haz waste | Hazardous waste. |
| | |
| **I** | |
| IBC | Intermediate bulk container. |
| IEF | Information Exchange Forum (informal consultation body in the framework of the IPPC Directive). |
| IF | Induction furnace. |
| Immission | Occurrence and level of polluting substance, odour or noise in the environment. |
| Impact crusher | In impact crushers, material comminution is accomplished primarily through the impact action of beaters, which hit the pieces of rock free-falling through the crusher chamber and throw them against stationary surfaces at high speed. |
| IMPEL | European Union Network for the Implementation and Enforcement of Environmental Law. |
| Independent measurement | Measurement achieved by another control body, using other dedicated equipment, e.g. sampling, measuring, standard material, software. |
| Inert gas | A gas which is not toxic, which does not support human breathing or combustion and which reacts scarcely or not at all with other substances. Inert gases are mainly nitrogen and the rare gases like helium, argon, neon, xenon, krypton. |
| Installation (from the IPPC Directive) | A stationary technical unit where one or more activities listed in Annex I of the IPPC Directive are carried out, and any other directly associated activities which have a technical connection with the activities carried out on that site and which could have an effect on emissions and pollution. |
| IPPC | Integrated pollution prevention and control. |
| IPPC Directive (the) | Council Directive 96/61/EC of 24 September 1996 concerning integrated pollution prevention and control (IPPC Directive). |
| IPTS | Institute for Prospective Technological Studies. |
| IR | Infra red. |
| Irony material | Is material that includes discrete iron components as well as the desired metal (Al, Cu). |
| ISA | Refers to Mount Isa in Australia |
| ISF<br>ISP | Imperial Smelting Furnace or Imperial Smelting process |
| Isokinetic sampling | Sampling technique where the velocity at which the sample enters the sampling nozzle is the same as the flow velocity in the duct. |
| ITEQ | International toxic equivalent. |
| | |
| **J** | |
| Jaw crusher | A machine for reducing the size of materials by impact or crushing between a fixed plate and an oscillating plate. |
| JRC | Joint Research Centre. |
| | |
| **K** | |
| Kaldo | Top blowing rotary converter used for primary smelting of Cu, precious metals and Pb concentrates as well as smelting of waste electronic equipment. |
| Kiln | See furnace - commonly used to refer to 'rotary kiln' which is a type of combustor commonly used, particularly for hazardous waste. |
| KRS | See Ausmelt/ISA Smelt |
| | |
| **L** | |

| ENGLISH TERM | MEANING |
|---|---|
| ~~Leachate~~ | ~~Solution obtained by leaching, e.g. water that has percolated through soil containing soluble substances and that contains certain amounts of these substances in solution.~~ |
| Launder | A channel used to convey molten metal or slag. |
| LCV | Low calorific value |
| Leachate | Solution obtained by leaching, e.g. water that has percolated through soil containing soluble substances and that contains certain amounts of these substances in solution. |
| Leaching | Passage of a solvent through a porous or crushed material in order to extract components from the liquid phase. For example, gold can be extracted by heap leaching of a porous ore or pulverised tailings. Other methods are tank leaching of ore, concentrates or tailings and in-situ leaching. |
| Leakage | Gaseous or liquid spills out of system/equipment due to system/equipment failure. |
| L-EX-EW | Leach-Extraction-Electrowin |
| Liquation | Is a refining technique that involves heating a molten metal to temperature where the solubility of impurities decreases so that they can be separated. |
| LNB | Low $NO_X$ burner. |
| | |
| **M** | |
| Make-up water | Water added to a process to start or maintain a reaction, prepare a solution, mix reactants, dilute reactants. |
| Mass balance | Approach to monitoring, consisting of accounting for inputs, accumulation, outputs and the generation or destruction of the substance of interest, and accounting for the difference by classifying it as a release to the environment. The result if a mass balance is usually a small difference between a large input and a large output, also taking into account the uncertainties involved. Therefore, mass balances are only applicable in practice when accurate input, output and uncertainties quantities can be measured. |
| Matte | A mixture of sulphides that forms when sulphide metal ores containing, e.g. nickel, copper, cobalt, are smelted. |
| Measurement | Set of operations for determining the value of a quantity. |
| Measuring system | Complete set of measuring instruments and other equipment, including all operating procedures used for carrying out specified measurements. |
| Melting capacity | The aggregate 'plated' capacity of the furnaces at an installation where the hourly rate multiplied by 24 should be used if appropriate. |
| Metals Environmental Risk Assessment Guidance (MERAG) | Metals Environmental Risk Assessment Guidance (MERAG) was created by a consortium of researchers, metals associations, scientific panel reviewers and governmental reviewers (UK Government, Department for Environment Food and Rural Affairs (Defra)) for use in chemicals management and environmental quality standard setting for metals and allow consideration of site-specific conditions by the assessor through the introduction of metal-specific concepts |
| Mineral processing (benefaction, ore dressing, mineral dressing, milling | Processes to produce marketable mineral products (concentrates) from ore. This is usually carried out on the mine site, the plant being referred to as mineral processing plant (mill or concentrator). The essential purpose is to reduce the bulk of the ore which must be transported to, and processed by, subsequent processes, e.g. smelting, by using methods to separate the valuable (desired) minerals from the gangue. The marketable product of this is called 'concentrate'; the remaining material is called 'tailings'. Mineral processing includes various procedures that rely on the mineral's physical characteristics, i.e. particle size, density, magnetic properties, colour, or physico-chemical properties, i.e. surface tension, hydrophobicity, wetability. |
| Mineral processing plant (mill or concentrator) | Facility where mineral processing is carried out. |
| Mineral resource | Concentration or occurrence of natural, solid, inorganic or fossilised organic material in or on the Earth's crust in such a form and quantity and of such a grade or quality that it has reasonable prospects for economic extraction. The location, quantity, grade, geological characteristics and continuity of a mineral resource are known, estimated or interpreted from specific geological evidence and knowledge. |

| ENGLISH TERM | MEANING |
|---|---|
| Mining | Methods and techniques to extract ore from the ground, including support facilities, e.g. stockpiles, workshops, transport, ventilation, and supporting activities in the mine itself or in the vicinity. |
| Mining operation | Any extraction of ore from which mineral substances are taken, where the corporate intent is to make an operating profit or build continuously towards a profitable enterprise. |
| Monitoring | Systematic surveillance of the variations of a certain chemical or physical characteristic of emissions, discharges, consumptions, equivalent parameters or technical measures, etc. This is based on repeated measurement or observation at an appropriate frequency in accordance with documented and agreed procedures, and is done to provide useful information. |
| Mother liquor | Waste water stream directly arising from a synthesis or chemical reaction, generally highly concentrated in products, starting material or by-products, especially the initial aqueous discharges. |
| MS | Member State of the European Union. |
| | |
| **N** | |
| N | Normal - refers to volume of gases under normal conditions with a temperature of 0 °C and pressure of 1 atmosphere (101.3kPa). |
| NA | Not applicable OR not available (depending on the context). |
| Nameplate | Officially rated plant capacity. |
| Nameplate (or nominal) capacity | Quantity of production that a unit is able to produce by design at normal operating conditions. |
| NaOH | Sodium hydroxide. Also called caustic soda. |
| n/d | No data. |
| N D | Not detectable. |
| NFM | Non-ferrous metal (BREF). |
| NGO(s) | Non-Governmental organisation(s). |
| NJ | New Jersey a type of distillation column |
| NOEC | No observed effect concentration. |
| Non-ferrous material | All materials that are not ferrous. |
| $NO_X$ | The sum of nitrogen oxide (NO) and nitrogen dioxide ($NO_2$) expressed as $NO_2$. |
| | |
| **O** | |
| OBM converter | A bottom blown converter used for ferro-nickel production. |
| Off-gas | General term for gas/air released during combustion processes or extraction processes at ambient temperatures. |
| Operational | Emissions occurring due to normal operational activities. Frequency, volumes and loads are usually known up-front or can be estimated or schedules. The above can be used for determining the best ratio of investment vs. efficiency when prioritising investments and determining best applicable emission reduction techniques. Fugitive emissions and pressure relief are considered to be operational since they occur under normal operational circumstances. |
| Operational data | Performance data on emissions/wastes and consumptions, e.g. raw materials, water and energy. Any other useful information on how to operate, maintain and control, including safety aspects, operability constraints of the technique, output quality, etc. |
| OEL | Occupational exposure limit. |
| Operating and maintenance costs | The cost of energy, labour, materials and environmental services required to operate and maintain the proposed technique during a single year. Operating and maintenance costs can include fixed annual costs associated with administration, insurance premiums and other general overheads. However, they exclude any costs associated with the financing and depreciation of the plant or equipment. These are covered through the use of a capital recovery factor when determining total annual costs or annual capital costs. As operating and maintenance costs are incurred yearly throughout the useful life of the technique, they are also known as ‘recurring’ costs. |

| ENGLISH TERM | MEANING |
|---|---|
| Operator (from the IPPC Directive) | Any natural or legal person who operates or controls the installation or, where this is provided for in national legislation, to whom decisive economic power over the technical functioning of the installation has been delegated. |
| Ore | Mineral or variety of accumulated minerals (including coal) of sufficient value as to quality and quantity that it/they may be mined at a profit. Most ores are mixtures of extractable minerals and extraneous rocky material described as 'gangue'. |
| Orebody (mineral deposit) | Naturally occurring geological structure consisting of an accumulation of a desired mineral and waste rock from which the mineral can be extracted at a profit, or with a reasonable expectation thereof. |
| OSPARCOM | Oslo and Paris convention for the protection of the marine environment of the North East Atlantic. |
| Output | Includes the 'waste out' (main output) and the other types of solid residues, emissions, waste water etc. produced during a waste treatment. |
| Oxidant | A material that can react highly exothermically when brought into contact with other materials, flammables in particular. |
| | |
| **P** | |
| PAH | Polycyclic aromatic hydrocarbons. |
| PAN | Polyacrylonitrile. |
| Parameter | Measurable magnitude representing the main features of a statistical group. |
| Particulate matter | Dust. |
| PB | Prebaked type of anode. |
| PCB | Printed circuit board - an electronic circuit in which the wiring between components and certain fixed components themselves are printed on an insulating board. This is the main use in this document. Flexible films and other substrates can be used instead of insulating board. |
| PCC | Post combustion chamber - a term applied to the zone after the initial combustion chamber where gas burnout occurs. Also referred to as the secondary combustion chamber or SCC. |
| PCDD/F | polychlorinated di-benzo para dioxin and polychlorinated di-benzo para furans. |
| Periodic sampling | Discrete/individual/separate/discontinuous/grab/spot sampling - individual samples taken in batched, time or effluent-volume dependent. Three formats can be identified:<br>• periodic time dependent sampling - discrete samples of equal volume are taken at equal time intervals<br>• periodic flow proportional sampling - discrete samples are taken of variable volumes at equal time intervals<br>• periodic samples taken at fixed flow intervals - discrete samples of equal volume are taken after the passage of a constant volume. |
| Permit (IPPC permit) (from the IPPC Directive) | Part or the whole of a written decision (or several such decisions) granting authorisation to operate all or part of an installation, subject to certain conditions which guarantee that the installation complies with the requirements of this Directive. A permit may cover one or more installations or parts of installations on the same site operated by the same operator. |
| PFPB | Point feeder prebake cells used for primary aluminium electrolysis. |
| PFC | Means polyfluorocarbon. |
| pH | Acidity or alkalinity of a solution. It is a number equivalent to the logarithm, to the base of 10, of the reciprocal of the concentration of hydrogen ions in an aqueous solution. |
| PGMs | Platinum group metals: Ir, Os, Pd, Pt, Rh, Ru. |
| Plant | Machinery or factory. A large item of equipment or an assembly of equipment, e.g. a plant for subcontract surface treatment, a plant for chromium electroplating. |
| PLC | Programmable logic control: digital computer used for the automation of industrial processes. |
| PLS | Pregnant leach solution produced by leaching minerals from a substrate. |

| ENGLISH TERM | MEANING |
|---|---|
| PM | Particulate matter.<br>Precious metals: Ag, Au and PGMs. |
| $PM_x$ | Particulate matter with an aerodynamic diameter less than or equal to a nominal x micrometres. |
| PNEC | Predicted no effect concentrations - the concentration at which no toxic effect is observed. |
| Pollutant | Individual substance or group of substances which can harm or affect the environment. |
| Pollution (from the IPPC Directive) | The direct or indirect introduction, as a result of human activity, of substances, vibrations, heat or noise into the air, water or land which may be harmful to human health or the quality of the environment, result in damage to material property, or impair or interfere with amenities and other legitimate uses of the environment. |
| Pollution source | The emission source. Pollution sources can be categorised as:<br>• point, or concentrated sources<br>• dispersed sources or fugitive emissions<br>• line sources, including mobile (transport) and stationary sources. |
| Post combustion | Ignition and burning of exhaust gas through the injection of air or the use of a burner. Used in order to reduce the amount of CO and (volatile) organic compounds. |
| Primary measure/technique | A measure/technique that in some way changes the way in which the core process operates thereby reducing raw emissions or consumptions (see also: end-of-pipe technique). |
| Process generated waste | The non-usable waste, e.g. waste lime, bottoms of storage tanks, sludges, is generated by the process/operations and is different from the target ‘waste out’. The reason for differentiating between the wastes is that the ‘waste out’ may be used for different purposes, but process generated waste is typically not re-used. |
| Production capacity | Production of ‘good castings’ and capacity based on the theoretical capacity of the foundry if it was operated for 24 hours, provided that it is technically able to operate that way. |
| PRTR | Pollutant release and transfer register. |
| | |
| **Q** | |
| | |
| **R** | |
| R | Recovery - codes given by EC legislation to recovery treatments. |
| R40 | Limited evidence of a carcinogenic effect (see also: R-phrases). |
| R45 | May cause cancer (see also: R-phrases). |
| R46 | May cause heritable genetic damage (see also: R-phrases). |
| R49 | May cause cancer by inhalation (see also: R-phrases). |
| R60 | May impair fertility (see also R-phrases). |
| R61 | May cause harm to the unborn child (see also R-phrases). |
| RCO | Regenerative Catalytic Oxidiser – a type of afterburner |
| Recovery | Defined by the EC Waste Framework Directive. Also used in this document as the treatment for the recovery of, or part of, material from the waste. |
| Recuperation | Is the recovery of heat. In this sector, it can be the use of process heat to preheat raw material, fuel or combustion air. Recuperative burners are designed to circulate hot gases within the burner system to achieve this, see also regenerative burners. |
| Recycle | Used in this document with two meanings:<br>• the recycling of some part of the waste to another industrial sector<br>• recycling within the WT installation.<br>The latter one is most commonly used in this document. |
| Reference conditions | Conditions that are specified, e.g. in connection with operating a process, collecting samples. |
| Release | Actual discharge (routine, usual or accidental) of an emission into the environment. |

| ENGLISH TERM | MEANING |
|---|---|
| Regenerative burners | These are designed to recover heat from hot gases using two or more refractory masses which are alternatively heated and then used to preheat combustion air, see also regenerative burners. |
| Residue | This term is used in this document covers all materials that are produced apart from the target material. |
| RF | Rotary furnace. |
| RLE | Roast-Leach-Electrowin. |
| RO | Reverse osmosis. |
| Roll crusher | A type of secondary crusher consisting of a heavy frame on which two rolls are mounted. These are driven so that they rotate towards one another. Rock fed in from above is nipped between the moving rolls, crushed and discharged at the bottom. |
| RTD | Research, technology and development. |
| RTO | Regenerative thermal oxidiser, a type of afterburner. |
| Run-off | Part of the precipitation and snowmelt that does not infiltrate but moves as overland flow. |
| | |
| **S** | |
| S | Sulphur. |
| Sampling | Process by which a portion of substance, material or product is removed to form a representative sample of the whole, for the purpose of examination of the substance, material or product under consideration. The sampling plan, the sampling and the analytical considerations should always be taken into account simultaneously. |
| SCR | Selective catalytic reduction. |
| Screening | Separating material into size fractions. |
| Semis | Semi finished products such as rod, wire, extrusions, ingots, etc. that are used as an input for the production of other finished products. |
| Separation | Processing methods to separate ore into concentrate and tailings. |
| SFT | Norwegian Pollution Control Authority. |
| Shaft furnace | A vertical furnace used to melt metal. |
| Slag | A product of smelting, containing mostly silicates, the substances not sought to be produced as matte or metal, and having a lower specific gravity than the latter. The slag of iron blast furnaces is essentially silicate of calcium, magnesium and aluminium; that of lead and copper smelting furnaces contains iron.<br>Solid residues from combustion processes. The term ‘bottom ash’ is the most frequently used term in this document. |
| Sludge | A suspension with a relatively high solids content. |
| SNCR | Selective non-catalytic reduction. |
| Solubility | Quantity of solute that dissolves in a given volume and type of solvent, at a given temperature and pressure, to form a saturated solution. The degree to which compounds are soluble depends on their ability, and that of other dissolved species, to form ions and aqueous complexes in a particular drainage chemistry. |
| Solubility product | The product of the concentrations of the ions of a dissolved electrolyte when in equilibrium with an undissolved substance. |
| SOP | Standard operating procedure. |
| $SO_X$ | Sulphur oxides - $SO_2$ and $SO_3$. |
| Sparge | To sprinkle, e.g. water, aerate a liquid with air or inject steam. In brewing, a spray of hot water sprinkled over the malt. |
| Specific emission | Emission related to a reference basis, such as production capacity, or actual production, e.g. grams per tonne or per unit produced, number of pieces of equipment, $m^2$ of material produced. |

| ENGLISH TERM | MEANING |
|---|---|
| Specific water consumption | The amount of fresh water consumed during production (surface water, groundwater), which is taken out from external resources. This fresh water demand is related to air dry net production and is expressed as $m^3/t$. Fresh water that is only used for cooling purposes, i.e. water that had no contact with fibres and additives, and that is directly discharged into the recipient is not included. Also waste water generated in steam and power plants on sit is not included. |
| Specification | Physico-chemical values given in legislation to certain compounds, e.g. lubricant oils. |
| SS | Suspended solids (see also: TSS). |
| SPL | Spent pot lining, the residues of the cathode system in primary aluminium production. |
| Start up, shut down operations | Operation whilst bringing an activity, an equipment item or a tank into or out of service or into or out of an idling state. Regularly oscillating activity phases are not to be considered as start ups or shut downs. |
| Substance (from the IPPC Directive) | A chemical element and its compounds, as defined in Art. 2(1) of the IPPC Directive. |
| Substantial change (from the IPPC Directive) | Change in operation which, in the opinion of the competent authority, may have significant negative effects on human beings or the environment, as defined in Art. 2(1) of the Directive. |
| SWPB | Side worked prebaked anode cell. |
| SX | Solvent extraction. |
| | |
| **T** | |
| Tapping | The act of opening of a furnace outlet to remove molten metal or slag. |
| TBRC | Top Blown Rotary Converter used for primary smelting of Cu, precious metals and Pb concentrates as well as smelting of waste electronic equipment. |
| TEQ | International toxicity equivalents (dioxins and furans).See also - ITEQ. |
| TROFF | Tilting rotating oxy-fuel furnace has similar uses to the TBRC. |
| TSA | Thermal swing adsorption. |
| TWA | Time weighted average. |
| TWG | Technical working group. |
| Technical oxygen | Oxygen from air that has been separated from nitrogen to give more than 97 % $O_2$ it is also referred to as tonnage oxygen. |
| | |
| **U** | |
| | |
| **V** | |
| VDI | Verein Deutscher Ingenieure. |
| Vitreous | This term meaning ‘glassy’ is applied to ceramic ware that as a result of a high degree of vitrification (as distinct from sintering) has an extremely low porosity. |
| Vitrification | The progressive partial fusion of a clay, or of a body, as a result of a firing process. |
| VOC | Volatile organic compound. |
| Volatile organic compound | Any organic compound having at 293.15 K a vapour pressure of 0.01 kPa or more, or having a corresponding volatility under the particular conditions of use. |
| VSS | Vertical stud Søderberg anode cell. |
| | |
| **W** | |
| Waste gas | Final gaseous discharge containing volatile organic compounds (VOC) or other pollutants from a stack or abatement equipment into air. |
| Waste treatment | Any of the installations that perform a waste treatment covered by the scope of this document. |

| ENGLISH TERM | MEANING |
|---|---|
| Waste water | Aqueous effluent from chemical processes, product make-up, raw material preparation, equipment cleaning, storage facilities, loading activities. Rainwater and indirect cooling water are not included because of the different definitions in the Member States for waste water. Instead rain waster and its need for treatment is dealt with separately. Cooling water is dealt with in the respective horizontal BREF on Industrial Cooling Systems. |
| WESP | Wet electrostatic precipitator. |
| WOX | Waelz oxide |
| WSA SNOX | A particular $SO_X$ and $NO_X$ reduction process. |
| WT | Waste treatment. |
| Wt-% | Percentage by weight |
| WW | Waste water. |
| WWT | Waste water treatment. |
| WWTP | Waste water treatment plant. |
| | |
| **Y** | |
| Yield | Mass ratio of concentrate to feed, calculated on a dry basis and expressed as a percentage. |

# 14 ANNEXES

## 14.1 Annex I: Specific cost data for metal production and abatement

This annex compiles data to allow cost evaluations for some process and abatement installations. The data given focusses on the process plant and main consumption data. Site-specific cost factors have been eliminated as far as possible. The information gives an order of magnitude of the cost range and allows a limited comparison of costs between techniques.

Data is not available for all of the metal groups and so this data is presented as an annex so that some costs, e.g. for furnaces, abatement, etc. can be referred to for these groups. Costs are mainly presented on the basis of cost per annual tonne of production. Reference is made where possible to the size of the process or of the abatement plant so that the data can be used to provide rough estimates for sectors that may not be represented.

Several sources presented data and all give the specific investment cost per tonne of metal produced per year. The data was supplied in a variety of currencies effective at the time of purchase. For the sake of direct comparisons, these currencies have been converted into Euros, using the exchange rate that was effective on 16 June 1999 - 1.06 USD = 1 EUR (Euro). The various exchange rates that operated since 1950 are given below so that the original costs can be derived if required.

| Year | DM/GBP | DM/ USD | USD/GBP | DM/EUR (1) | USD/EUR (1) |
|---|---|---|---|---|---|
| 1950 | 11.76 | 4.20 | 2.80 | - | - |
| 1960 | 11.71 | 4.17 | 2.81 | - | - |
| 1970 | 8.74 | 3.65 | 2.40 | - | - |
| 1980 | 4.23 | 1.82 | 2.33 | 2.48 | 1.36 |
| 1990 | 2.88 | 1.62 | 1.79 | 2.07 | 1.26 |
| 1993 | 2.48 | 1.65 | 1.50 | 1.90 | 1.15 |
| 1996 | 2.35 | 1.50 | 1.56 | 1.90 | 1.27 |
| 1998 | 2.91 | 1.76 | 1.66 | 1.97 | 1.12 |
| 2008 | NA | NA | 1.992 | NA | 1.487 |
| (1) since 1979 only. | | | | | |

**Table 14.1: Some currency exchange rates**

The cost data shown in this annex are an order of magnitude indication only.

Some sources also reported financing and operating costs for the particular installation. These may not be applicable to other sites because the costs of individual operations would include a substantial percentage of site and corporate specific cost components.

### 14.1.1 Influences on cost data

Some of the site-specific influences on costs referred to above are listed as follows:

- transport:
    - feed material transport costs (effect on treatment and refining charge)
    - transport costs for product(s).

- direct operating costs:
    - labour legislation, climatic conditions, arrangement of unit operations (in-plant transport costs), energy availability, available infrastructure, special environmental protection requirements.

- sales costs:
  - market access, infrastructure, climatic conditions.

- capital costs:
  - feed material shipment options, market access and market conditions/product sale, corporate structure.

- investment costs:
  - climatic conditions, available infrastructure, energy and consumables, specific local environmental protection requirements.

The above factors indicate that it is very difficult to give reliable cost data which could be used in a more general sense without the danger of misleading results. A complete and reliable economic calculation/evaluation can only be done for a site-specific investment. Only on such a basis are definite cost data available. For example, the following factors have an overwhelming influence on the economics of a project and cannot always be estimated in this annex:

- treatment and refining charges for concentrates
- costs for concentrates, flux, etc. and other purchases
- purchase price (after deductions) of secondary materials
- purchase price for refined metal
- sale of by-products like sulphuric acid or similar
- the selected country (taxes, labour, disposal and energy costs, inflation)
- the specific site (transport of pure materials and products)
- the infra structure (availability of energy, water, oxygen, maintenance)
- the plant capacity
- type and composition of feed
- time schedule and time of investment
- financing of the investment
- costs for construction and erection (inland execution).

Where costs are known accurately for specific installations they have been included but they are provided separately so that site variation can be taken into account. Comments have also been made where possible to illustrate how cost variations, e.g. waste disposal costs, can account for a significant variation in the costs.

The capital cost of emission control measures and equipment varies with the type of plant. While in existing plants, retrofit costs can be very high, integrated pollution control measures in new plants may be more cost effective [ 234, UBA Copper, lead, zinc and aluminium 2007 ]. Factors governing the capital cost of a fabric filter system include:

- the off-gas volume to cleaned
- the off-gas characteristics (dust and moisture content, temperature, presence of aggressive constituents)
- the need for additive dosing or flue dust recirculation (additional piping, silos, conveying systems)
- available floor area for construction; type of construction (arrangement options, shallow or pile foundation, overall height, filter area, number of compartments, duct routing etc.)
- the necessary stack height or need for stack lining (depending on off-gas composition)
- the necessary measuring equipment (platform, continuous monitoring equipment, access)
- extended scope of supplies (off-gas cooler, compressors, etc.).

Off-gases with low dust loads (e.g. secondary hood off-gases with fine dust loads <50 mg/m$^3$) normally require the addition of an additive (e.g. lime) to improve the dust collection efficiency. This not only drastically increases the raw gas dust load, but also the volume of collected dust that should be disposed of. For moist and/or aggressive off-gases, the filter may have to be heated or provided with a corrosion protection coating.]

The capital cost of a fabric filter designed for an off-gas flow rate of approximately 100000 m$^3$/h, including fan and filter media, was of the order of approximately EUR 650000 (secondary hood off-gas with low dust load) or approximately EUR 950000 (process off-gas with an elevated dust load). The total cost of a filter system including steel and concrete structures, ducting, stack and other equipment (see above) may amount to three or four times the capital cost of the filter.

Electricity consumption is the largest single contributor to the operating costs. Depending on the filter area, filter resistance, dust composition and concentration, the specific power consumption of a fabric filter ranges between 2 and 3 kWh/1000 m$^3$ off-gas. If, due to the specific additive used, the dust collected in the filter system cannot be further processed for metal recovery and should be landfilled, the additional cost will be substantial.

## 14.1.2 Specific investment costs for copper process plants

As explained above, the investment costs for copper plants are influenced also by a number of site specific factors and not only by the process technology and abatement techniques selected. Tables 14.2 to 14.5 give some technology-related data.

The tables indicate for green-field plants:

- the year of investment or cost determination
- the key plant sections covered
- the production capacity related to the cost indication.

The normal plant-related abatement techniques are included in the cost indication. The investment costs are indicated as specific cost per tonne of copper. The cost data shown are to be understood as an order of magnitude indication. Not included are costs for land, finance, inside and outside plant infrastructure, owner's costs during construction and all other investments, which are not directly connected with the plant sections mentioned.

| **Year** | **Installed cost (EUR per t/yr production capacity)** | **Product made and design capacity (t/yr)** | **Plant sections included** |
|---|---|---|---|
| 1977 | 2250 - 2450 | Anode copper 70000 t/yr | Material handling/storage, partial roasting & electric furnace smelting, PS converter, anode plant, EF slag cleaning, double catalysis acid plant |
| 1980 | 2450 - 2650 | Anode copper, 150000 - 160000 t/yr | Material handling/storage, Outotec flash, PS converter, anode plant, EF slag cleaning, double catalysis acid plant |
| 1981 | 1700 - 1850 | Anode copper, 280000 t/yr | Material handling/storage, Outotec flash, PS converter, anode plant, EF slag cleaning, double catalysis acid plant |
| 1981 | 2850 - 3000 | Anode copper 100000 t/yr | Material handling storage, Mitsubishi continuous smelting, anode plant, double contact acid plant |
| 1981 | 2250 - 2550 | Anode copper 120000 t/yr | Material handling/storage, INCO flash, PS converter, anode plant, double catalysis acid plant |
| 1992 | 2150 - 2250 | Anode copper 150000 t/yr | Material handling/storage, ISA Smelt, PS converter, anode plant, EF slag cleaning, double catalysis acid plant |
| 1994 | 2250 - 2350 | Anode copper 285000 t/yr | Material handling/storage, Outotec flash smelter, Flash converter, anode plant, double catalysis acid plant. Slag flotation not included |

| Year | Installed cost (EUR per t/yr production capacity) | Product made and design capacity (t/yr) | Plant sections included |
|---|---|---|---|
| 1995 | 2350 - 2750 | Anode copper 120000 t/yr | Material handling/storage, Outotec flash, PS converter, anode plant, EF slag cleaning, double catalysis acid plant |
| 1997 | 1950 - 2150 | Anode copper 160000 t/yr | Material handling storage, Mitsubishi continuous smelting, anode plant, double contact acid plant |
| 1998 | 2550 - 2650 | Anode copper 303000 t/yr | Outotec flash smelter, Flash converter, anode plant, double catalysis acid plant |
| 1998 | 2950 - 3150 | Anode copper 200000 t/yr | Material handling storage, Mitsubishi continuous smelting, anode plant, double contact acid plant |
| NB: (1) Cost indications are in the year indicated without consideration of escalation or adjustment! Original costs were in USD and have been converted using EUR = 1.06USD | | | |

**Table 14.2: Primary copper smelter/acid plant complexes**
**[ 90, Traulsen, H. 1998 ], [ 206, Traulsen, H. 1999 ]**

**Rönnskär Project,**

**Description of the project components for the development:**

- extension to quay for raw materials unloading
- enclosed conveyors for raw material handling
- mixing plant and conveyors
- Outotec flash furnace
- converter aisle with three Peirce-Smith converters of 250 t capacity
- ventilation air extraction system and fabric filter
- fire-refining and anode casting plant - 45 t/h extra capacity
- 33 % increase in copper electro-refinery, evaporator to produce copper sulphate
- refurbishment of sulphuric acid plants to handle 280000 Nm$^3$/h. Mercury removal stage
- process instrumentation
- civil engineering costs.

**Operational data**

Recent information is available for a specific process upgrade. In this instance the published costs are given below. The plant was under construction 1999 - 100000 t/yr extra production of copper.

**Economics**

Total project cost – 2 billion Swedish crowns (EUR 224 million). Anticipated pay back period 6.5 years.

| Year | Installed cost (EUR per t/yr production capacity) | Product made and design capacity (t/yr) | Plant sections included |
|---|---|---|---|
| 1990 | 1300 - 1500 | Anode copper 50000 t/yr | Material handling/storage, shaft furnace, converter, anode plant. |
| 1990 | 1100 - 1300 | Anode copper 80000 - 100000 t/yr | Material handling/storage, electric furnace, converter, anode plant. |
| 1991 | 1250 - 1400 | Anode copper, 60000 t/yr | Material handling/storage, TBR furnace, anode plant (1) |
| (1) The technical concept is different from the process now used at Metallo-Chimique and Elmet. Cost indications are in year indicated without consideration of escalation or adjustment! Original costs were in USD and have been converted using EUR = 1.06 USD. [ 90, Traulsen, H. 1998 ]. | | | |

**Table 14.3: Secondary copper smelters**
**Source - Boliden**

| Year | Installed cost (EUR per t/yr production capacity) | Product made and design capacity (t/yr) | Plant sections included |
|---|---|---|---|
| 1976 | 470 | Cathode copper 380000 t/yr | Conventional process concept with starter sheets and mechanisation |
| 1987 | 550 - 600 | Cathode copper 40000 t/yr | ISA process concept with permanent cathodes |
| 1990 | 400 - 450 | Cathode copper 180000 t/yr | ISA process concept with permanent cathodes |
| 1993 | 450 - 480 | Cathode copper 150000 t/yr | ISA process concept with permanent cathodes |
| 1994 | 650 | Cathode copper 280000 t/yr | Retrofit/expansion of an existing refinery based on the Kidd Creek concept with permanent cathodes |
| 1996 | 400 - 450 | Cathode copper 200000 t/yr | ISA Process concept with permanent cathodes |
| NB: Cost indications are in year indicated without consideration of escalation or adjustment! Original costs were in and have been converted using EUR = 1.06USD | | | |

**Table 14.4: Electrolytic copper refineries**
[ 90, Traulsen, H. 1998 ]

| Year | Installed cost (EUR per t/yr production capacity) | Product made and design capacity (t/yr) | Plant sections included |
|---|---|---|---|
| 1992 | 180 - 200 | Copper wire-rod 220000 t/yr | Continuous Southwire type rod line with shaft furnace for melting |
| 1995 | 280 - 320 | Copper wire-rod 80000 t/yr | Continuous Southwire type rod line with shaft furnace for melting |
| 1995 | 290 - 330 | Copper wire-rod 80000 t/yr | Continuous Contirod type rod line with shaft furnace for melting |
| NB: Cost indications are in year indicated without consideration of escalation or adjustment! Original costs were in USD and have been converted using EUR = 1.06USD | | | |

**Table 14.5: Copper wire-rod plants**
[ 90, Traulsen, H. 1998 ]

### 14.1.3 Specific investment costs for primary and secondary aluminium processes

**Primary Aluminium Smelters**
The following ranges are given as investment costs for conversions that are identified as possible options for upgrading existing plants or a modern new plant.

Side Worked Prebaked (SWPB) to Point Feeder Prebaked (CWPB-PF): EUR 400 - 1000 per tonne yearly production capacity
Centre Worked Prebaked to Point Feeder Prebaked: EUR 100 - 200 per tonne yearly production capacity
Vertical Stud Søderberg (VSS) to Point Feeder Prebaked: EUR 2500 - 4000 per tonne yearly production capacity
Conventional VSS to modernised VSS: EUR 100 - 250 per tonne yearly production capacity
New Point Feeder Prebaked (green site): EUR 4000 - 5000 per tonne yearly production capacity

The conversion of SWPB or VSS to Point Feeder Prebaked can in most cases never be achieved to a standard comparable to a completely new PFPB plant.

The operating cost for a primary smelter depends entirely on the factors given above, and will according to reports from various consultants be in the range EUR 950 - 1500 per. tonne, excluding capital costs.

Investment costs for abatement equipment will again depend on site-specific conditions, since this will determine the extent of additional equipment and work necessary in addition to the actual equipment installation. The following ranges can be given.

| | |
|---|---|
| Dry scrubbing unit: | EUR 150 - 250 per year tonne production |
| $SO_2$ seawater scrubber for pot gases: | EUR 40 - 70 per year tonne production |
| $SO_2$ alkali scrubber for pot gases: | EUR 100 - 200 per year tonne production |

**Cost data for secondary smelters**

**Process equipment costs:**

| | |
|---|---|
| Rotary furnace: | EUR 15 - 60 per year tonne |

**Abatement equipment costs:**

| | |
|---|---|
| Baghouse filter system: | EUR 30 - 75 per year tonne |
| Ceramic filter system: | EUR <30 per year tonne |

### 14.1.3.1 Use of metal pumping system in a secondary smelter

**Description**

Reverberatory furnace with side-well, charge well and pumped metal system (see Figure Figure 14.1).

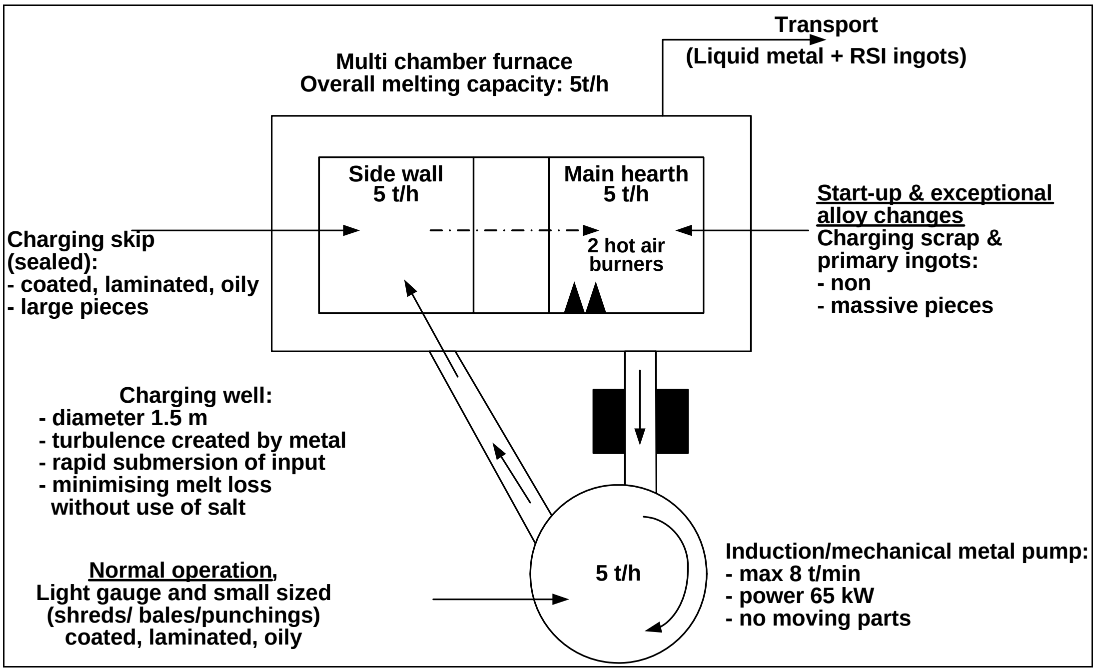

**Figure 14.1:** **Use of a metal pumping system**

**Achieved environmental benefits**

Elimination of salt flux and reduction of fume. Increased yield. Greater range of raw materials than simple reverberatory furnace, improved capture of furnace gases.

**Cross-media effects**
None were reported.

**Operational data**
Improvement in metal yield from 83 to 88 %, reduction in energy costs.

**Applicability**
This technique is applicable to new and upgraded furnaces.

**Economics**

- cost (1997)of 30 tonne furnace and EMP system £1800000 (EUR 2.73 million)
- estimated cost savings (energy, improved yield, flux savings and treatment savings) 832000 GBP (EUR 1.26 million) per year
- pay back 2.2 years
- cost of pumping system and charge well ~ £300000 (EUR 456000).

**Example plants**
BE, UK.

**Reference literature**
[ 119, McLellan 1998 ], [ 120, McLellan 1998 ].

### 14.1.4 Specific investment costs for Pb-Zn processes

Tables 14.6 to 14.9 give some data for primary and secondary lead smelters, for electrolytic Zinc plants as well as Pb-Zn shaft furnaces, for a Waelz kiln, a fuming plant and $H_2SO_4$-plants. Costs are given in USD per t/yr metal produced. Again the exchange rate USD to local currency is very important, which is time dependant.

The data presented includes:
- the year when those cost figures have been evaluated
- the volume of delivery
- the size of the smelter
- the specific investment costs per tonne of metal.

In case of Pb-Zn shaft furnaces, the investment costs are related to Zn production alone as well as to total Zn + Pb production. The costs only show the order of magnitude for such investments.

| Year | Installed cost (EUR per t/yr production capacity.) | Product made and design capacity (t/yr) | Plant sections included |
|---|---|---|---|
| 1980 | 660 | 100000 t/yr Pb | Sinter machine, Shaft furnace, $H_2SO_4$, lead refining |
| 1990 | 400 | 60000 t/yr Pb | Secondary, Plastics separation, Smelting, lead refining |
| 1990 | 635 | 30000 t/yr Pb | Secondary, Plastics separation, Smelting, lead refining (Same order of magnitude for CX-system) |
| 1997 | 625 | 100000 t/yr Pb | QSL-plant, $H_2SO_4$, without lead refining<br>(Kivcet and TBRC process should show similar investment costs) |
| 1997 | 330 | 30000 t/yr Pb | Secondary shaft furnace, lead refining |
| 1997 | 145 | 100000 t/yr Pb | Lead refining |
| 2009 | | 65000 t/yr Pb | EUR 70 million Ausmelt plant with installation and abatement and acid plant for 65000 t/year?? |

**Table 14.6: Lead processes**
[ 117, Krüger, J. 1999 ]

| Year | Installed cost (EUR per t/yr production capacity.) | Product made and design capacity (t/yr) | Plant sections included |
|---|---|---|---|
| 1980 | 1580 | 100000 t/yr Zn | Roasting, leaching, purification, electrolysis, $H_2SO_4$ plant, foundry |
| 1996 | 1530 | 100000 t/yr Zn | Roasting, leaching, purification, electrolysis, $H_2SO_4$ plant, foundry |
| 1997 | 1450 | 100000 t/yr Zn | Roasting, leaching, purification, electrolysis, $H_2SO_4$ plant, foundry |
| 2002 | 533 | 75000 t/y Zn | EUR 40 million for Roaster, WHB and water treatment, gas-cleaning , $H_2SO_4$ plant, cooling water installation, weak acid treatment |

**Table 14.7: Zinc processes**
[ 117, Krüger, J. 1999 ]

| Year | Installed cost (EUR per t/yr production capacity.) | Product made and design capacity (t/yr) | Plant sections included |
|---|---|---|---|
| 1980 | 1550 | 100000 t/yr Zn,<br>40000 t/yr Pb | Sinter-roasting, ISF, $H_2SO_4$ plant, Zn-refining |
| 1996 | 1380 | 100000 t/yr Zn,<br>40000 t/yr Pb | Sinter-roasting, ISF, $H_2SO_4$ plant, Zn-refining |
| 1996 | 2080 | 100000 t/yr Zn | Sinter-roasting, ISF, $H_2SO_4$ plant, Zn-refining |
| 1997 | 1790 | 100000 t/yr Zn,<br>40000 t/yr Pb | Sinter-roasting, ISF, $H_2SO_4$ plant, Zn-refining |
| 1997 | 2580 | 100000 t/yr Zn | Sinter-roasting, ISF, $H_2SO_4$ plant Zn-refining |
| 1994 | 2800 | 85000 t/yr Zn,<br>35000 t/yr Pb | Sinter-roasting, ISF, $H_2SO_4$ plant, Zn-refining |

**Table 14.8: Zinc and lead processes**
[ 117, Krüger, J. 1999 ]

| Year | Installed cost (EUR per t/yr production capacity) | Product made and Design Capacity (t/yr) | Plant sections included |
|---|---|---|---|
| 1980 | 480 | 21000 t/yr Waelz Oxide | Waelz kiln, cooler, filter |
| 1997 | 415 | 20000 t/yr slag | Drying, fuming, waste heat boiler, PSA, filter |

**Table 14.9: Zinc residues**
[ 117, Krüger, J. 1999 ].

## 14.1.5 Cost data for abatement techniques

### 14.1.5.1 Air abatement copper industry

The techniques applied for cleaning the off-gases and ventilation gases from copper operations are directed towards elimination of dust and gaseous matter including $SO_2$ and $SO_3$. Examples for widely applied gas-cleaning systems/equipment are: Dry gas-cleaning : Electrostatic precipitator (ESP), fabric filters (baghouses), cassette type filters, ceramic filters, etc.

**The following data is given for waste heat boiler, hot and wet ESPs, gas cooling and cleaning.**

The data for complete sulphuric acid plants is given later.

| **Application: Smelting Furnace Waste Heat Boiler** | |
|---|---|
| **Design basis:** | |
| Gas temperature:<br>Inlet:<br>Outlet: | <br>1300 - 1350 °C<br>300 - 400 °C |
| Gas flow | 100000 Nm$^3$/h |
| Steam production | 35 t/h |
| **Total installed costs:**<br>**Million EUR** | <br>**7.0 - 8.0** |

**Table 14.10: Indirect Gas Cooling - Energy Recovery**

| **Application: Smelter $SO_2$ gas-cleaning** | | |
|---|---|---|
| | **Flash furnace ESP** | **Flash furnace ESP** |
| Design basis:<br>Operating temperature<br>Gas flow<br>Dust inlet<br>Dust outlet<br>Efficiency | <br>300 - 400 °C<br>43000 Nm$^3$/h<br>10 - 20 g/Nm$^3$<br>150 - 200 mg/Nm$^3$<br>99.9 % | <br>300 - 400 °C<br>61000 Nm$^3$/h<br>10 - 15 g/Nm$^3$<br>200 - 300 mg/Nm$^3$<br>99.8 % |
| ESP characteristics: | 4 fields, 3000 m$^2$ collection area, single unit | 3 fields, 4800 m$^2$ collection area, single unit |
| Equipment supply costs: Total =<br>Million EUR | <br>1.0 (1) | <br>2.0 (1) |
| Main consumption:<br>Electricity | <br>250 kW installed | <br>400 kW installed |
| (1) Civil work, erection, etc. excluded; for installed costs approximately 80 - 100 % will have to be added. | | |

**Table 14.11: Dry ESP Gas Cleaning**
**Source: Lurgi Umwelt GmbH**

| **Baghouse, fabric filter** | | | |
|---|---|---|---|
| **Application:** | **Shaft furnace, converter & anode furnace** | **TBRC** | **Cooler & fabric filter** |
| Design basis:<br>Operating temperature<br>Gas flow<br>Dust outlet | <br>~ 100 °C<br>750000 Nm$^3$/h<br><10 mg/Nm$^3$ | <br>~ 100 °C<br>730000 Nm$^3$/h<br><10 mg/Nm$^3$ | <br>~ 100 °C<br>70000 Nm$^3$/h<br><10 mg/Nm$^3$ |
| Total installed cost: Million EUR | 20 (1) | 14 (2) | 2 - 2.5 (3) |
| Main consumption:<br>Electricity<br>Others | <br>2.5 - 3 kWh/1000 Nm$^3$<br>1 g/Nm$^3$ lime (4) | <br>2 - 3 kWh/1000 Nm$^3$ | <br>1.5 - 4 kWh/1000 Nm$^3$ |
| (1) Including ductwork and stack.<br>(2) Excluding duct work and stack.<br>(3) Total installed cost including gas cooler and stack.<br>(4) For anode furnace gas stream | | | |

**Table 14.12: Fabric filters**
[ 90, Traulsen, H. 1998 ]

| **Wet Electrostatic Precipitator for $SO_2$ gas treatment** | |
|---|---|
| Type: | Two wet ESPs in line |

| Application: | Final $SO_2$ gas-cleaning for further treatment. |
|---|---|
| Design basis: | |
| Operating temperature | 27 °C inlet |
| Gas flow | 88.00 Nm³/h |
| Precipitation efficiency for | |
| Dust | 99 % |
| Arsenic | 99 % |
| $H_2SO_4$ | 99 % |
| Total equipment supply costs:<br>Million EUR | 2.0 (1) |
| Main consumption:<br>Electricity | 112 kW |
| (1) Civil work, erection, etc. excluded; for installed costs approximately 60 - 80 % will have to be added. | |

**Table 14.13: Wet ESP gas Cleaning**
**Source: Lurgi Umwelt GmbH**

| Wet Gas Cooling and Cleaning System for Smelter $SO_2$ gases | | |
|---|---|---|
| System: | Wet gas-cleaning for furnace $SO_2$ gas | Wet gas cooling and cleaning section for combined $SO_2$ in furnace and converter gases |
| System equipment: | 1 radial flow scrubber, 1 ID fan, 2 in-line wet ESPs with a 2000 m² total collection area, acid cooler and acid circulation pumps, 1 cooling tower, 900 m³/h cooling media circulation. | 2 radial flow scrubbers, 3 lines with 2 in-line wet ESPs with 7000 m² total collection area, acid cooler and acid circulation pumps, 2 cooling towers, 2200 m³/h cooling media circulation. |
| Design basis: | | |
| Operating temperature | 390 °C inlet, 35 °C outlet | 370 °C inlet, 27 °C outlet |
| Gas flow | 96000 Nm³/h | 250000 Nm³/h |
| Precipitation efficiency for: | | |
| Dust | | |
| Arsenic | 96 - 97 % | 96 - 97 % |
| Mist | 99.0 % | 99.0 % |
| | >99.5 % | >99.5 % |
| Equipment supply costs:<br>Million EUR | **7.5 - 8 (1)** | **16 - 17 (2)** |
| Electricity consumption: | 828 kW | 1250 kW |
| (1) Civil work, erection, etc. excluded; for installed costs approximately 60 - 80 % will have to be added.<br>(2) Civil work, erection, etc. excluded; for installed costs approximately 70 - 100 % will have to be added. | | |

**Table 14.14: Wet ESP gas-cleaning**
**Source: Lurgi Umwelt GmbH**

The following cost data is given for abatement systems used in secondary copper processes and is provided by Austria. The costs are given in Austrian Schillings (ATS) and Euros (**EUR)**, site-specific investment, operating and disposal costs are given [ 157, Winter, B. et al. 1999 ].

| **Regenerative afterburner installation with reactor and fabric filter treating off-gases from a shaft furnace.** | | |
|---|---|---|
| Input data:<br>Volume of exhaust gas of 20000 Nm$^3$/h. | Quantity of metal produced<br>18000 t/yr Black Copper<br>Operating hours 6300 h/yr | |
| Output data:<br><0.1 ng ITEQ/Nm$^3$ PCDD/F | | |
| Description: Regenerative afterburner installed after a fabric filter treating 20000 Nm$^3$/h of dedusted gas with a reduction of 98 % for PCDD/F. | | Costs<br>ATS/t metal<br>(EUR/t metal) |
| Input factors for annual expenditure | | |

| | | |
|---|---|---|
| Investment costs (Million. ATS) | 12 +/-20 % | |
| Number of years | 15 | |
| Rate of interest (%) | 6 | |
| Annual repayment including Interest (Million. ATS/yr) | 1.24 | |
| Proportional investment costs including Interest | | 68.64<br>(4.99 EUR/t) |
| Maintenance + wear and tear<br>(% of investment costs = 0.24 Million ATS/yr) | 2 | 13.33<br>(0.97 EUR/t) |
| Proportional costs | | |
| Support fuel MJ/t | 1342 | 80.52 |
| Electrical energy consumption (kWh/t) at 0.9 ATS/kWh | 13.5 | 12.15 |
| Total costs | | ~ 175<br>(12.72 EUR/t) |

**Table 14.15: Afterburner, reactor and fabric filter**
**Source: Austrian cost data in [ 157, Winter, B. et al. 1999 ]**

| **Afterburner placed between a shaft furnace and waste heat boiler.** | | |
|---|---|---|
| Input data:<br>Volume of exhaust gas of 20000 Nm$^3$/h. | Quantity of metal produced 18000 t/yr Black copper<br>Operating hours 6300 h/yr | |
| Description: 98 % removal of PCDD/F | | Costs<br>ATS/t metal<br>(EUR/t metal) |
| Input factors for annual expenditure | | |
| Investment costs (Million. ATS) | 8 +/-20 % | |
| Number of years | 15 | |
| Rate of interest (%) | 6 | |
| Annual repayment including Interest (Million. ATS/yr) | 0.82 | |
| Proportional investment costs including Interest | | 45.76<br>(3.33 EUR/t) |
| Maintenance + wear and tear<br>(% of investment costs) | 2 | 8.89<br>(0.65 EUR/t) |
| Proportional costs | | |
| Support fuel MJ/t | 1304 | 78.24 |
| Electrical energy consumption (kWh/t) | 16.0 | 5.4 |
| Total costs | | ~ 138<br>(10.03 EUR/t) |

**Table 14.16: Afterburner**

**Source: Austrian cost data in [ 157, Winter, B. et al. 1999 ]**

| **Wet desulphurisation process to remove sulphur dioxide from scrap converter off-gases.** | | |
|---|---|---|
| Input data:<br>Volume of exhaust gas of 35000 Nm$^3$/h.<br>Average input $SO_2$ ~2300 mg/Nm$^3$, peak 4000 mg/Nm$^3$ | Quantity of metal produced 12000 t/yr raw copper<br>Operating hours 1200 h/yr | |
| Output data:<br>Annual average $SO_2$ <50 mg/Nm$^3$ - peak <200 mg/Nm$^3$ | | |
| Description | | Costs<br>ATS/t metal |

| | | (EUR/t metal) |
|---|---|---|
| Input factors for annual expenditure | | |
| Investment costs (Million. ATS) | 25 | |
| Number of years | 15 | |
| Rate of interest (%) | 6 | |
| Annual repayment including Interest (Million. ATS/yr) | 2.54 | |
| Proportional investment costs including Interest | | 214.51<br>(EUR 15.59/t) |
| Maintenance + wear and tear<br>(% of investment costs) | 2 | 41.67<br>(EUR 3.03/t) |
| Proportional costs | | |
| Cost of CaO kg/t at 1 ATS/kg | 6.74 | 6.74 |
| Disposal cost of gypsum kg/t at 0.2 ATS/kg | 22.99 | 4.6 |
| Electrical energy consumption (kWh/t) at 0.9 ATS/kWh | 16.39 | 14.75 |
| Total costs | | ~ 282<br>(EUR 20.49/t) |

**Table 14.17: Wet desulphurisation**[rr82]
**Source: Austrian cost data in [ 157, Winter, B. et al. 1999 ]**

| Semi-dry desulphurisation process to reduce sulphur dioxide from an anode furnace. | | |
|---|---|---|
| Input data:<br>Volume of exhaust gas of 80000 Nm$^3$/h. Pressure-drop 20 mbar.<br>$SO_2$ ~500 mg/Nm$^3$ | Quantity of metal produced<br>60000 t/yr anode copper<br>Operating hours 7000 h/yr | |
| Output data:<br>$SO_2$ ~ 50 mg/Nm$^3$, 95 % reduction of PCDD/F | | |
| Description | | Costs<br>ATS/t metal<br>(EUR/t metal) |
| Input factors for annual expenditure | | |
| Investment costs (Million. ATS) | 30 +/- 20 % | |
| Number of years | 15 | |
| Rate of interest (%) | 6 | |
| Annual repayment including Interest (Million. ATS/yr) | 3.09 | |
| Proportional investment costs including Interest | | 51.48<br>(EUR 3.74/t) |
| Maintenance + wear and tear<br>(% of investment costs) | 3 | 15<br>(EUR 1.09/t) |
| Proportional costs | | |
| CaO kg/t Cu | 7.35 | 7.35 |
| Carbon kg/t Cu | 1.87 | 6.53 |
| Combustion air | 23.33 | 3.97 |
| Disposal kg/t Cu | 13.42 | 26.83 |
| Electrical energy consumption (kWh/t) | 14.08 | 12.67 |
| Total costs | | ~ 124<br>(EUR 9.01/t) |

**Table 14.18: Semi-dry scrubber**

**Source: Austrian cost data in [ 157, Winter, B. et al. 1999 ]**

| Activated carbon final filter for black copper production. | | |
|---|---|---|
| Input data:<br>Volume of exhaust gas 20000 Nm$^3$/h.<br>Pressure drop 25 mbar | Quantity of metal produced 18000 t/yr<br>Black copper.<br>Operating hours 6300 h/yr | |
| Output data:<br>PCDD/F <0.1 ng ITEQ/Nm$^3$ | | |
| Description | | Costs<br>ATS/t metal<br>(EUR/t metal) |
| Input factors for annual expenditure | | |
| Investment costs (Million. ATS) | 12 | |
| Number of years | 15 | |
| Rate of interest (%) | 6 | |
| Annual repayment including Interest (Million. ATS/yr) | 1.24 | |
| Proportional investment costs including Interest | | 68.64<br>(EUR 4.99/t) |
| Maintenance + wear and tear<br>(% of investment costs) | 2 | 13.33<br>(EUR 0.97/t) |
| Proportional costs | | |
| Consumption and disposal of activated carbon kg/t at 6.5 ATS/kg | 1.4 | 9.1 |
| Electrical energy consumption (kWh/t) at 0.9 ATS/kWh | 17.51 | 15.76 |
| Total costs | | ~ 107<br>(EUR 7.78/t) |

**Table 14.19: Activated carbon filter**
**Source: Austrian cost data in [ 157, Winter, B. et al. 1999 ]**

| Selective catalytic reduction to reduce oxides of nitrogen. | | |
|---|---|---|
| Input data:<br>Volume of exhaust gas of 20000 Nm$^3$/h. | Quantity of metal produced 18000 t/yr Black copper.<br>Operating hours 6300 h/yr | |
| Output data:<br>$NO_X$ <100 mg/Nm$^3$, 98 % reduction of PCDD/F | | |
| Description | | Costs<br>ATS/t metal<br>(EUR/t metal) |
| Input factors for annual expenditure | | |
| Investment costs (Million. ATS) | 10 | |
| Number of years | 15 | |
| Rate of interest (%) | 6 | |
| Annual repayment including Interest (Million. ATS/yr) | 1.03 | |
| Proportional investment costs including Interest | | 57.2<br>(EUR 4.16/t) |
| Maintenance + wear and tear<br>(% of investment costs) | 2 | 11.11<br>(EUR 0.81/t) |
| Proportional costs | | |

| | | |
|---|---|---|
| Cost of Ammonia kg/t at 1.8 ATS/kg<br>Replacement catalyst $m^3$/yr at 200000 ATS/$m^3$<br>Energy for reheat MJ/t at 60 ATS/GJ<br>Electrical energy consumption (kWh/t) at 0.9 ATS/kWh | 2.07<br>0.5<br>284<br>19.03 | 3.73<br>5.56<br>17.01<br>17.13 |
| Total costs | | ~ 112<br>(EUR 8.14/t) |

**Table 14.20: SCR**
***Source*: Austrian cost data in [ 157, Winter, B. et al. 1999 ]**

The following data was supplied in 2007 by Germany for the review of the NFM BREF [ 234, UBA Copper, lead, zinc and aluminium 2007 ].

The capital cost of emission control measures and equipment varies with the type of plant. While in existing plants, retrofit costs can be very high, integrated pollution control measures in new plants may be more cost-effective. Factors governing the capital cost of a fabric filter system include:

- the off gas volume to cleaned
- the off gas characteristics (dust and moisture content, temperature, presence of aggressive constituents)
- the need for additive dosing or flue dust recirculation (additional piping, silos, conveying systems)
- available floor area for construction; type of construction (arrangement options, shallow or pile foundation, overall height, filter area, number of compartments, duct routing etc.)
- the necessary stack height or need for stack lining (depending on off gas composition)
- the necessary measuring equipment (platform, continuous monitoring equipment, access)
- extended scope of supplies (off gas cooler, compressors etc.).

Off gases with low dust loads (e.g. secondary hood off gases with fine dust loads <50 mg/Nm$^3$) normally require the addition of an additive (e.g. lime) to improve the dust collection efficiency. This not only drastically increases the raw gas dust load, but also the volume of collected dust that has to be disposed of. For moist and/or aggressive off gases, the filter may have to be heated or provided with a corrosion protection coating.

At the time of publication of the VDI guideline the capital cost of a fabric filter designed for an off gas flow rate of approx. 100000 m$^3$/h, including fan and filter media, was of the order of approx. EUR 650000 (secondary hood off gas with low dust load) or approx. EUR 950000 (process off gas with elevated dust load). The total cost of a filter system including steel and concrete structures, ducting, stack and other equipment (see above) may amount to three or four times the capital cost of the filter [ 219, VDI (D) 2102 2007 ].

Electricity consumption is the largest single contributor to the operating costs. Depending on the filter area, filter resistance, dust composition and concentration, the specific power consumption of a fabric filter ranges between 2 and 3 kWh/1000 Nm$^3$ off gas. If, due to the specific additive used, the dust collected in the filter system cannot be further processed for metal recovery and has to be landfilled, the additional cost will be substantial.

### 14.1.5.2 Air abatement - aluminium industry

The following cost data is given for abatement systems used in secondary aluminium processes and is provided by Austria. The costs are given in Austrian Schillings (ATS) and Euros (EUR), site-specific investment, operating and disposal costs are given [ 142, Boin, U. et al. 1998 ].

| **Simple flow injection process using a fabric filter.** |
|---|

| **Simple flow injection process using a fabric filter.** | | |
|---|---|---|
| Input data:<br>Volume of exhaust gas of 40000 $Nm^3/h$ that contains ~ 600 $mg/Nm^3$ dust, 500 mg $SO_2/Nm^3$,. 300 mg $HCl/Nm^3$ and 50 mg $HF/Nm^3$. | Quantity of metal produced 40000 t/yr Al<br>Operating hours 5500 h/yr | |
| Output data:<br><5 $mg/Nm^3$ dust <300 mg $SO_2/Nm^3$, <30 mg $HCl/Nm^3$ and <5 mg $HF/Nm^3$. | | |
| Description | | Costs<br>ATS/t metal<br>(EUR/t metal) |
| Input factors for annual expenditure<br>Investment costs (Million. ATS)<br>Number of years<br>Rate of interest (%)<br>Annual repayment including Interest (Million. ATS/yr)<br>Proportional investment costs including Interest | <br>15<br>15<br>6<br>1.54 | 38.61<br>(EUR 2.81/t) |
| Maintenance + wear and tear<br>(% of investment costs) | 3 | 11.25<br>(EUR 0.82/t) |
| Proportional costs<br>Consumption of CaO (kg/t metal)<br>Electrical energy consumption (kWh/h) | <br>22<br>102 | <br>22<br>14.03 |
| Technology costs | | 86<br>(EUR 6.25/t) |
| Disposal of filter dust (kg/t metal) | 35 - 60 | 70 - 240<br>(EUR 5.09 - 17.44/t) |
| Total costs | | ~ 156 - 326<br>(EUR 11.34 - 23.69/t) |

**Table 14.21: Dry scrubber and fabric filter**
[ 142, Boin, U. et al. 1998 ]

The range of the total costs is influenced by the variability of the disposal cost for filter dust. This factor will be a significant variable over EU.

| **Semi-dry reduction process using spray absorber, fabric filter and absorbent recirculation.** | | |
|---|---|---|
| Input data:<br>Volume of exhaust gas of 40000 $Nm^3/h$,. ~ 600 $mg/Nm^3$ dust, 1000 mg $SO_2/Nm^3$, 300 mg $HCl/Nm^3$ and 50 mg $HF/Nm^3$ | Quantity of metal produced 40000 t/yr Al<br>Operating hours 5500 h/yr | |
| Output data:<br><5 $mg/Nm^3$ dust <200 mg $SO_2/Nm^3$, <10 mg $HCl/Nm^3$, <1 mg $HF/Nm^3$ and <0.1 ng $PCDD/F/Nm^3$. | | |
| Description | | Costs<br>ATS/t metal<br>(EUR/t metal) |
| Input factors for annual expenditure<br>Investment costs (Million. ATS)<br>Number of years<br>Rate of interest (%)<br>Annual repayment including Interest (Million. ATS/yr)<br>Proportional investment costs including Interest | <br>20<br>15<br>6<br>2.06 | 51.48<br>(EUR 3.74/t) |

| | | |
|---|---|---|
| Maintenance + wear and tear (% of investment costs) | 3 | 15<br>(EUR 1.09/t) |
| Proportional costs | | |
| Consumption of CaO (kg/t metal) | 22 | 22 |
| Consumption of activated carbon (kg/t metal) | 1 | 3.5 |
| Electrical energy consumption (kWh/h) | 110 | 15.13 |
| Technology costs | | 107.11<br>(EUR 7.78/t) |
| Disposal of filter dust (kg/t metal) | 35 - 60 | 70 - 240<br>(5.09 - 17.44/t) |
| Total costs | | ~ 180 - 350<br>(EUR 13.08 - 25.44/t) |

**Table 14.22: Semi-dry scrubber and fabric filter**
**[ 142, Boin, U. et al. 1998 ]**

The range of the total costs is influenced by the variability of the disposal cost for filter dust. This factor will be a significant variable over EU.

| **Semi-dry reduction process using spray absorber, fabric filter and absorbent recirculation for sulphur dioxide free gas.** | | |
|---|---|---|
| Input data:<br>Volume of exhaust gas of 40000 Nm$^3$/h,. ~ 600 mg/Nm$^3$ dust. | Quantity of metal produced 40000 t/yr Al<br>Operating hours 5500 h/yr | |
| Output data:<br><5 mg/Nm$^3$ dust, <0.1 ng PCDD/F/Nm$^3$. | | |
| Description | | Costs ATS/t metal (EUR/t metal) |
| Input factors for annual expenditure | | |
| Investment costs (Million. ATS) | 14 | |
| Number of years | 15 | |
| Rate of interest (%) | 6 | |
| Annual repayment including Interest (Million. ATS/yr) | 1.44 | |
| Proportional investment costs including Interest | | 36.04<br>(EUR 2.62/t) |
| Maintenance + wear and tear (% of investment costs) | 3 | 10.5<br>(0.76 EUR/t) |
| Proportional costs | | |
| Consumption of $NaHCO_3$ (kg/t metal) at 3ATS/kg | 12 | 36 |
| Electrical energy consumption (kWh/h) at 1 ATS/kWh | 110 | 15.13 |
| Technology costs | | 97.67<br>(EUR 7.1t) |
| Disposal of filter dust (kg/t metal) | 15 - 30 | 15 - 30<br>(EUR 1.09 - 2.18/t) |
| Total costs | | ~ 110 - 130 |

| | | |
|---|---|---|
| | | (EUR<br>7.99 - 9.45/t) |

**Table 14.23: Semi-dry scrubber and fabric filter**
[ 142, Boin, U. et al. 1998 ]

The range of the total costs is influenced by the variability of the disposal cost for filter dust. This factor will be a significant variable over EU. In this particular example the filter dust is based on sodium bicarbonate and sodium chloride and is suitable for processing in a salt recovery process.

| **Wet processes using electrostatic precipitator and scrubber.** | | |
|---|---|---|
| **Input data:** Volume of exhaust gas of 40000 Nm$^3$/h ~ 600 mg dust/Nm$^3$, 1000 mg/Nm$^3$ $SO_2$, 300 mg HCl/Nm$^3$ and 50 mg HF/Nm$^3$ | Volume of metal produced 40000 t/yr Al<br>Operating hours 5500 h/yr | |
| **Output data:** ~5 - 15 mg dust/Nm$^3$, <50 mg $SO_2$/Nm$^3$, <5 mg HCl/Nm$^3$ and <1 mg HF/Nm$^3$ | | |
| | | **Costs ATS/t metal (EUR/t metal)** |
| **Input factors for annual expenditure** | | |
| Investment costs (Million. ATS) | 17 | |
| Number of years | 15 | |
| Rate of interest (%) | 6 | |
| Annual repayment including Interest (Million. ATS/yr) | 1.75 | |
| **Proportional investment costs including interest** | | 43.76<br>(EUR 3.18/t) |
| **Maintenance + wear and tear**<br>(% of investment costs) | 2 | 8.5<br>(EUR 0.62/t) |
| **Proportional costs** | | |
| Water consumption (m$^3$/t metal) and waste water disposal | 0.3 | 1.5 - 9 |
| Consumption of CaO (kg/t metal) | 11 | 11 |
| Electrical energy consumption (kWh/h) | 90 | 12.38 |
| **Technology costs** | | 77.14 - 84.64<br>(EUR 5.61 - 6.15/t) |
| Disposal of filter dust (kg/t metal) | 10 - 35 | 20 - 140<br>(1.45 - 10.17 EUR/t) |
| Disposal of neutralisation sludge (kg/t metal) | 15 | 22.5 - 45<br>(EUR 1.64 - 3.28/t) |
| **Total costs** | | ~ 120 - 270<br>(EUR 8.72 - 19.62/t) |

**Table 14.24: Wet scrubber and ESP**
[ 142, Boin, U. et al. 1998 ]

The range of the total costs is influenced by the variability of the disposal cost for filter dust and sludge. This factor will be a significant variable over EU.

| **Combination of semi-dry process with series scrubber using a spray absorber and fabric filter.** | | |
|---|---|---|
| Input data:<br>Volume of exhaust gas of 40000 $Nm^3/h$, 600 $mg/Nm^3$ dust, 1000 $SO_2/Nm^3$, 300 mg $HCl/Nm^3$ and 50 mg $HF/Nm^3$. | Quantity of metal produced 40000 t/yr Al<br>Operating hours 5500 h/yr | |
| Output data:<br><5 mg dust/$Nm^3$, <50 mg $SO_2/Nm^3$, <5 mg $HCl/Nm^3$, <1 mg $HF/Nm^3$ and the reduction of PCDD/F to under 0.1 ng ITEQ/$Nm^3$. | | |
| | | Costs ATS/t metal (EUR/t metal) |
| Input factors for annual expenditure | | |
| Investment costs (Million. ATS) | 22 | |
| Number of years | 15 | |
| Rate of interest (%) | 6 | |
| Annual repayment including Interest (Million. ATS/yr) | 2.27 | |
| Proportional investment costs including Interest | | 56.63<br>(EUR 4.16/t) |
| Maintenance + wear and tear (% of investment costs) | 3 | 16.5<br>(EUR 1.2/t) |
| Proportional costs | | |
| Consumption of CaO (kg/t metal) | 11 | 11 |
| Consumption of activated carbon (kg/t metal) | 1 | 3.5 |
| Electrical energy consumption (kWh/h) | 160 | 22 |
| Technology costs | | 109.63<br>(EUR 7.97/t) |
| Disposal of filter dust (kg/t metal) | 25 - 50 | 50 - 200<br>(EUR 3.63 - 14.53/t) |
| Total costs | | ~160 - 310<br>(EUR 11.63 - 22.53/t) |

**Table 14.25: Semi-dry scrubber and fabric filter**
**[ 142, Boin, U. et al. 1998 ]**

The range of the total costs is influenced by the variability of the disposal cost for filter dust. This factor will be a significant variable over EU.

#### 14.1.5.2.1 Costs associated with deSOX

Cost data has been compiled for a variety of process variations and abatement systems. Some costs are included where available with the examples given earlier in this chapter. The cost data is very site-specific and depends on a number of factors but the ranges given may enable some comparisons to be made. Other cost data is provided in an appendix to this note so that costs for processes and abatement systems over the whole of the non-ferrous metal industry can be compared.

The Netherlands have made a comparison between the cost effectiveness of deSOX abatement techniques of two smelters. The cost effectiveness method that is used is the method described in Section 4.13 of the Netherlands Emission Guideline for Air (NER) and in the BREF cross-media effects and economics as shown in Table 14.26. [ 241, Netherlands SOX paper 2008 ].

| Cost, effects and cost effectiveness | Plant A | Plant B |
|---|---|---|
| Costs:<br>total investments, EUR million<br>capital costs, EUR K<br>fixed operation costs, EUR K<br>variable operating costs, EUR K<br>total brute (=net) yearly costs, EUR K | • 32.4<br>• 4975<br>• 1002<br>• 7571<br>• 13548 (A) | • 23.5<br>• 3839<br>• 680<br>• 1624<br>• 6143 |
| Effects:<br>yearly unabated load, Ktonne<br>yearly remaining emission, Ktonne<br>avoided $SO_2$ in Ktonne | • 2.67<br>• 0.45<br>• 2.2 (B) | • 2.0<br>• 0.3<br>• 1.7 |
| Cost effectiveness, EUR per kg:<br>-with gas reheating (A/(B(1)1000))<br>(to prevent occurring of blue mist)<br>- without gas reheating | • 6.2<br>• 3.7 | • 3.6 |

**Table 14.26: Cost effectiveness according to NER methodology**

Data from [ 303, Canadian Al Rapport final in French.pdf 2008 ].

- seawater scrubber: EUR 248 - 905.5/t $SO_2$ (annual base): 6 reference plants in Norway
- NaOH-scrubber: EUR 1367 - 1627/t $SO_2$ (annual base): 1 reference plant in Norway, 4 in the US
- double alkali scrubber: EUR 1183 - 1270/t $SO_2$ (annual base)
- calcium (carbonate): EUR 1810/t $SO_2$ (annual base)
- calcium (lime): 1954 EUR/t $SO_2$ (annual base).

### 14.1.5.3 Sulphuric acid plants

| Gas Cooling and Cleaning section, Double Contact Sulphuric Acid Plant. Applied to copper smelter | | |
|---|---|---|
| Gas cooling and cleaning system: | Wet gas cooling and cleaning section for combined $SO_2$ gas of furnace and converter gases | Wet gas cooling and cleaning section for combined $SO_2$ gas of furnace and converter gases |
| Equipment supplied: | 2 radial flow scrubber, 3 lines with 2 in-line wet ESPs, acid cooler and acid circulation pumps, 2 cooling tower, 2200 $m^3/h$ cooling media circulation | 1 reversed jet scrubber, 1 cooling tower, 3 lines first stage wet ESPs, 2 lines second stage wet ESPs, acid cooler, $SO_2$ stripper, acid circulation pumps, 2 cooling towers,<br>6 - 24 $m^3/h$ weak acid effluent |
| Contact acid plant: | Double catalysis sulphuric acid plant | Double catalysis sulphuric acid plant |
| Equipment supplied: | Single strand,<br>4 pass converter with inter-pass absorption after the 2nd pass | Single strand,<br>5 pass converter with inter-pass absorption after the 3rd pass |

| **Gas Cooling and Cleaning section, Double Contact Sulphuric Acid Plant. Applied to copper smelter** | | |
|---|---|---|
| Design basis gas-cleaning :<br>Operating temperature<br>Gas flow<br>Precipitation efficiency for dust | 370 °C inlet, 27 °C outlet<br>91000 - 123000 Nm³/h<br>96.7 % | 370 °C inlet, 27 °C outlet<br>45000 - 115000 Nm³/h<br>96.7 % |
| Design basis contact plant:<br>Gas flow<br>$SO_2$<br>Conversion $SO_2/SO_3$<br>$H_2SO_4$ production | 91000 - 123000 Nm³/h<br>10 - 15.1 % (av. 13 %)<br>>99.5 %<br>1700 t/d | 45000 - 115000 Nm³/h<br>6 - 11.3 %<br>>99.5 %<br>1350 t/d |
| Installed costs:<br>Million EUR | 44 - 45 | 51 - 52 |
| Main consumption:<br>Electricity<br>Fuel oil<br>Natural gas<br>Catalyst<br>Labour | (1)<br>75 - 80 kWh/t acid<br><br>3 - 4 Nm³/t acid<br>0.02 - 0.04 l/t acid<br>0.1 h/t acid | (1)<br>55 - 60 kWh/t acid<br>2 - 3 kg/t acid<br><br>0.02 - 0.04 l/t acid<br>0.1 h/t acid |
| (1) reference t acid = nominal design production | | |

**Table 14.27: Copper smelter sulphuric acid plants**
[ 90, Traulsen, H. 1998 ]

| **Sulphuric acid plants<br>Lead/Zinc smelters** | | | |
|---|---|---|---|
| **Year** | **Components** | **Cost (EUR per t/yr of acid)** | **Acid production** |
| 1995 | Double contact plant | 40 | 800000 t/yr acid |
| 1996 | Double contact plant + Hg removal | 155<br>120 | 100000 t/yr acid<br>200000 t acid |
| 1997 | Double contact plant + Hg removal | 130<br>100 | 100000 t/yr acid<br>200000 t acid |
| 2009 | Addition of 5th bed with blower capacity increase | Total cost EUR 8 million | Updated costs provided by Lurgi (Outotec) |
| 2009 | Change of catalyst in 4th bed to incorporate caesium promoted catalyst | Total cost EUR 700000 | Updated costs provided by Lurgi (Outotec) |
| 2009 | $H_2O_2$ scrubber for 100000 t/yr acid plant | Total cost EUR 25 million | Updated costs provided by Lurgi (Outotec) |

**Table 14.28: Sulphuric acid plants**
[ 117, Krüger, J. 1999 ]

### 14.1.5.4 Effluent treatment systems

| **Neutralisation of weak acid from a sulphuric acid plant and other acidic process water** | |
|---|---|
| System equipment: | Thickeners, tanks, pumps, filter press |
| Application: | Weak acid resulting from an $SO_2$ gas flow of 200000 Nm³/h |
| Design basis:<br>Flow | 32 m³/h weak acid |
| Installed cost:<br>Million EUR | 2.5(1) |
| Main consumption: | |

| | |
|---|---|
| Electricity | 200 kW |
| Lime milk (10 %) | 15 m³/h |
| $H_2SO_4$ (10 % | 0.8 m³/h |
| $FeSO_4.7\ H_2O$ | 80 kg/h |
| (1) Civil work, erection, etc. excluded; for installed costs approximately 90 - 110 % will have to be added. SOURCE: Lurgi Umwelt GmbH | |

**Table 14.29: Weak acid neutralisation**

2005 – Waste water treatment plant for 350 to 400 $m^3$/hr for a zinc/lead plant producing 140000 t/yr metal with lime and Fe $Cl_3$ treatment, settlement tanks and sludge filter press. Cost EUR 3 million. Local treatment for weak acid is undertaken at additional cost.

## 14.2 Annex II: International regulations (overview)

In this section, a rough overview of important regulations on an international level effecting the copper production industry is given. International regulations and agreements have been worked out on different levels. Besides the European level, the different international committees of the United Nations like UNEP, UNCED, UNECE, WHO, IFCS have to be mentioned and the implications of the Kyoto and Montreal Protocols taken into account. In addition, the OECD is working in the field of environmental protection. Important international regulations, effecting the pollution of the different environmental media are [ 121, Rentz, O. et al. 1999 ]:

### 14.2.1 Long Range Treaty on Air Pollution (LRTAP)

International efforts to reduce the adverse effects of the transboundary acidification on forests, aquatic ecosystems, and human health, by way of internationally co-ordinated emission reductions, were undertaken in the 1979 Convention on Long Range Trans-boundary Air Pollution (LRTAP). After coming into force in 1983, the LRTAP Convention was augmented by:

- the 1984 Protocol on long-term financing;
- the 1985 Helsinki Protocol reducing sulphur emissions or their transboundary fluxes by at least 30 %;
- the 1988 Sofia Protocol on the freezing of the emission of nitrogen oxides;
- the 1991 Geneva Protocol on the control of the emission of volatile organic compounds; and
- the 1994 Oslo Protocol on the further reduction of the emission of sulphur dioxide
- the 1998 Aarhus Protocols on Persistent Organic Compounds (POPs) and on Metals.

### 14.2.2 Basel Conventions

The Basel Conventions declare the responsibility of OECD states regarding the control of transboundary movements of hazardous wastes and their disposal. It was adopted in March 1989 and entered into force in May 1992. In 1996, more than 100 countries plus the EC are parties to the Convention. The conventions comprise Technical Guidelines for waste management activities. In this guidelines materials are divided into substances with a ban for export (list A) and substances, which still can be exported to non-OECD countries. A decision adopted by the parties in 1994 prohibits with immediate effect the export from OECD countries of hazardous wastes destined for final disposal in non-OECD countries. The decision also phased out similar exports destined for recycling or recovery operations before banning them completely on 31 December 1997.

### 14.2.3 OECD-Council decision on Trans-frontier Movements of Hazardous Wastes

As a reaction of the "Basel Convention" of the United Nations, the council of the OECD ratified the council decision C 88(90). A three-tiered system was proposed to delineate controls to be applied to transfrontier movements: Wastes destined for recovery operations included on the green list would move among OECD Member countries toward recovery operations subject to all existing controls normally applied in commercial transactions. A notification procedure would exist for wastes destined for recovery operations included in the yellow list and wastes destined for recovery operations included in the amber list or red list would be subject to stricter or more rigorous controls.

### 14.2.4 Protection of the aquatic environment

There are several international activities concerning the protection of the aquatic environment. The most important ones are the Oslo Paris Commission (OSPARCOM) for the protection of the maritime environment of the North Sea and the Northeast Atlantic and the Helsinki commission of the countries bordering the East Sea (HELCOM) for the protection of their maritime environment.

In addition, there exist several international agreements on the pollution prevention of the main European seas (Nordseeschutzkonferenz), lakes (Bodensee) and rivers (e.g. Rhine (IKSR), Elbe(IKSE), Donau (IKSD), Oder (IKSO)). For example, there are two international agreements dating from 1978 concerning the pollution prevention of the River Rhine referring to chemical contamination and chlorides.

### 14.2.5 Global Environment Monitoring System (WHO/UNEP)

UNEP and WHO operate the GEMS (Global Environment Monitoring System) environmental pollution monitoring programmes for urban air quality (AIR), food, human exposure assessment location (HEAL), and water. The objectives of GEMS as defined at its inception are:

- to strengthen monitoring and assessment capabilities in the participating countries,
- to increase the validity and comparability of environmental data and information,
- top produce global/regional assessments in selected fields and compile environmental information at a global level.