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Reference Document on Best Available Techniques in the Non Ferrous Metals Industries

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Executive Summary

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This reference document on best available techniques in the non-ferrous metal industry reflects the information exchange carried out according to Article 16 (2) of Council Directive 96/61/EC. The document has to be seen in the light of the preface that describes the objective of the document and its use.

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, (+ 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 13 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.
- Receipt, storage and handling of raw materials.
- Pre-processing and pre-treatment of raw materials and transfer to production processes.
- Metal production processes - furnace types and process control techniques.
- Gas collection and air abatement techniques.
- 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, dioxin 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.

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 pre-treatment to remove coating materials.

In Europe, ore deposits containing 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 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, stand-alone 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 sulphur-containing fuels 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 dioxins due to the presence of small amounts of chlorine in the secondary raw materials; the destruction and/or capture of dioxin 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 fugitive 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, wastewater (metal compounds), residues such as furnace linings, sludge, filter dust and slag. Dioxin formation during treatment of secondary copper materials is also an issue.
- For the production of aluminium: fluorides (incl. HF), dust, metal compounds, SO_2, COS, PAH, VOCs, green house gases (PFCs and CO_2), dioxins (secondary), chlorides and HCl. Residues such as bauxite residue, Spent Pot Lining, filter dust and salt slag and wastewater (oil and ammonia).
- For the production of lead, zinc and cadmium: dust, metal compounds, VOCs (including dioxins), odours, SO_2, other acid gases, wastewater (metal compounds), residues such as sludge, the iron rich residues, filter dust and slag.
- For the production of precious metals: VOCs, dust, metal compounds, dioxins, odours, NO_x, other acid gases such as chlorine and SO_2. Residues such as sludge, filter dust and slag and wastewater (metal compounds and organic compounds).
- For the production of mercury: mercury vapour, dust, metal compounds, odours, SO_2, other acid gases, wastewater (metal compounds), residues such as sludge, filter dust and slag.
- For the production of refractory metals, hardmetal powder and metal carbides: dust, solid hardmetal and metal compounds, wastewater (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 needs to 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, wastewater (metal compounds), residues such as filter dust, sludge and slag.

- For the production of alkali and alkaline earth metals: chlorine, HCl, dioxin, SF_6, dust, metal compounds, CO_2, SO_2, wastewater (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, wastewater (metal compounds and organic compounds), residues such as sludge, filter dust and slag.
- For the production of carbon and graphite: PAHs, hydrocarbons, dust, odours, SO_2, wastewater 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. The following tables summarise the furnaces used for the production of non-ferrous metals:

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

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	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.
Vanyucov	Copper	Concentrates	
ISA Smelt/Ausmelt	Copper, lead,	Intermediates, concentrates and secondary materials.	
QSL	Lead	Concentrates and secondary	
Kivcet	Lead Copper	Concentrates and secondary	
Noranda	Copper	Concentrates	
El Teniente	Copper	Concentrates	
TBRC 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, high carbon ferro-manganese.	Concentrates, most secondary	For ferro-manganese production it is only used together with energy recovery.
Inco Flash Furnace	Copper, nickel	Concentrates	
Outokumpu 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	
Outokumpu Flash Converter	Copper (converter)	Matte	
Noranda Converter	Copper (converter)	Matte	
Mitsubishi Converter	Copper (converter)	Matte	

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.

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 electro-winning. 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 containing 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 the following table:

Abatement Technique	**Reported emissions**			**Specific emission** (amount per t of metal produced)
	Component	**minimum**	**maximum**	
Fabric filter, hot EP 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 dioxin)	Total C	< 2 mg/Nm^3	100 mg/Nm^3	10 - 80 g/t
	Dioxin (TEQ)	< 0.1 ng/Nm^3	5 ng/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	<10 mgC/Nm^3	200 mgC/Nm^3	
	Chlorine	< 2 mg/Nm^3		
Alumina scrubber	Dust	< 1 mg/Nm^3	20 mg/Nm^3	
	Hydrocarbon	< 1 mgC/Nm^3	50 mgC/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, EP, lime/carbon adsorption and fabric filter	PAH (EPA)	0.1 mg/Nm^3	6 mg/Nm^3	
	Hydrocarbons	20 mgC/Nm^3	200 mgC/Nm^3	

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 dioxins and VOCs.

Uncaptured gases or fugitive emissions, however, are not treated. Dust emissions also occur from storage, handling and the pre-treatment of raw materials where fugitive 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 fugitive emissions are significant.

The following table shows that fugitive or uncaptured emissions are important issues:

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

Comparison of abated and fugitive dust loads at a primary copper smelter

Many processes use sealed cooling and process water systems but there is still the potential to discharge heavy metals to water. The methods to reduce water use and wastewater 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 needs to ensure that these recovery operations are operated to a high environmental standard.

5. Key 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 for the production and associated processes. 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 key 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 fugitive 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 to accept the anticipated range of raw material. 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.

The following table 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 Covered conveyors	Closed drum, bins and hoppers	Prevention of water contamination and fugitive 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 Bunded areas.	Back venting of delivery lines
Process gases:	All	Overhead pipeline Reduced pressure pipeline (Chlorine, CO)	Certified storage	Pressure loss monitoring, Alarms for toxic gases.
Solvents	Cu, Ni, Zn group, PM, Carbon	Overhead pipeline 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.

Summary of raw material and handling techniques

Furnace design, the use of suitable pre-treatment 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 fugitive emissions. Systems that maintain furnace sealing or hood deployment should be used. Examples are: through electrode additions of material; additions via tuyeres 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.

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 after-burning if this is considered necessary to avoid local, regional or long-range air quality problems or if dioxins 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 dioxins**

The presence of dioxins or their formation during a process needs to be considered for many of the pyro-metallurgical 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 dioxins 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 dioxin formation.
- 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 if necessary 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.
- 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 dioxins and to recover metals.

The emission concentrations that are associated with the above techniques range from <0.1 to 0.5 ng/Nm³ TEQ depending on the feed, the smelting or melting process and the techniques or combination of techniques that are used for dioxin 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 pre-treatment of secondary material to minimise organic contamination of the feed.
- The use of sealed furnaces or other process units to prevent fugitive 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, pre-treatment, pyro-metallurgical and hydrometallurgical stages. Transfer of materials is particularly important. Data provided has confirmed that the significance of fugitive emissions in many processes is very high and that fugitive 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 fugitive emissions must be considered at all stages of process design and development. The hierarchy of gas collection from all of the process stages is:

- Process optimisation and minimisation of emissions;
- Sealed reactors and furnaces;
- 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 the following table, 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 the value will be 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
Materials handling and storage.	Dust and metals.	Correct storage, handling and transfer. Dust collection and fabric filter if necessary.
Grinding, drying.	Dust and metals.	Process operation. Gas collection and fabric filter.
Sintering/roasting Smelting Converting Fire refining	VOCs, dioxins.	Afterburner, adsorbent or activated carbon addition.
	Dust and metal compounds.	Gas collection, gas cleaning in fabric filter, heat recovery.
	Carbon monoxide	Afterburner if necessary
	Sulphur dioxide	sulphuric acid plant (for sulphidic ores) or scrubber
Slag treatment.	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. Hydrogen.	Sealed process, recovery and re-use. 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 if necessary.
Thermal refining.	Dust and metals.	Gas collection and fabric filter.
	Sulphur dioxide.	Scrubber if necessary.
Molten salt electrolysis	Fluoride, chlorine, PFCs	Process operation. Gas collection, scrubber (alumina) and fabric filter.
Electrode baking, graphitisation	Dust, metals, SO_2, Fluoride, PAHs, tars	Gas collection, condenser and EP, afterburner or alumina scrubber and fabric filter. Scrubber if necessary for SO_2.
Metal powder production	Dust and metals	Gas collection and fabric filter.
Powder production	Dust, Ammonia	Gas collection and recovery. Acid medium scrubber.
High temperature reduction	Hydrogen.	Sealed process, re-use.
Electro-winning.	Chlorine. Acid mist.	Gas collection and re-use. Wet scrubber. De-mister.
Melting and casting.	Dust and metals.	Gas collection and fabric filter.
	VOCs, dioxins (organic feed)	Afterburner (Carbon injection)

Note. 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.

Summary of sources and treatment/abatement options

A summary of the emission levels associated with abatement systems that are considered to be BAT for the non-ferrous metal processes is shown in the following table. 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 Metals - dependent on dust composition	Depends on characteristics of dust.
Carbon or Bio filter	Total organic C < 20 mg/Nm^3	Phenol < 0.1 mg/Nm^3
Afterburner (including temperature quench for dioxin removal)	Total organic C < 5 - 15 mg/Nm^3 Dioxin < 0.1 - 0.5 ng/Nm^3 TEQ PAH (OSPAR 11) < 200 µgCNm^3 HCN < 2 mg/Nm^3	Designed for gas volume. Other techniques are available to reduce dioxins further by carbon/lime injection, catalytic reactors/filters.
Optimised combustion conditions	Total organic C < 5 - 50 mg/Nm^3	
Wet EP 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 Tar < 10 mg/Nm^3 Chlorine < 2 mg/Nm^3	
Alumina scrubber	Dust 1 - 5 mg/Nm^3 Hydrocarbon < 2 mg/Nm^3 PAH (OSPAR 11) < 200 µgC/Nm^3	
Chlorine recovery	Chlorine < 5 mg/Nm^3.	Chlorine is re-used. Possible accidental fugitive releases.
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, EP, lime/carbon adsorption and fabric filter	PAH (OSPAR 11) < 200 µgC/Nm^3 Hydrocarbons (volatile) < 20 mgC/Nm^3 Hydrocarbons (condensed) < 2 mgC/Nm^3	
Note. Collected emissions only. Associated emissions are given as daily averages based on continuous monitoring during the operating period and 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 the value will be 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.		

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 EP 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

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 wastewaters can contain soluble and non-soluble metal compounds, oil and organic material. The following table summarises the potential wastewaters, the metals produced, minimisation and treatment methods.

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

Overview of BAT for wastewater streams

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

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. The following table 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 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	Recovery of other valuable metals
	Precious metals (PMs)	Skimmings and slag	Internal recycle
Slag treatment	Cu and Ni	Cleaned slag	Construction material. Matte produced
Melting furnace	All metals	Skimmings Slag and salt slag.	Return to process after treatment. Metal recovery, recovery of salt and other material
Electro-refining	Cu	Electrolyte bleed Anode remnants Anode slime	Recovery of Ni. Return to converter Recovery of precious metals
Electro-winning	Zn, Ni, Co, PMs	Spent electrolyte	Re-use in leaching process
Fused salt electrolysis	Al	Spent Pot Lining Excess bath Anode stubs	Carburant or disposal Sale as electrolyte 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
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 EPs	Filter dust	Return to process Recovery of other metals
Wet abatement systems	Most – using scrubbers or wet EPs	Filter sludge	Return to process or recovery of other metals (e.g. Hg). Disposal
Wastewater treatment sludge	Most	Hydroxide or sulphide sludges.	Safe disposal, re-use Re-use
Digestion	Alumina	Red mud	Safe disposal, re-use of liquor

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:

- Production of steam and electricity from the heat raised in waste heat boilers.
- The use of the heat of reaction to smelt or roast concentrates or melt scrap metals in a converter.
- The use of hot process gases to dry feed materials.
- Pre-heating of a furnace charge using the energy content of furnace gases or hot gases from another source.
- The use of recuperative burners or the pre-heating of combustion air.
- The use as a fuel gas of CO produced.
- The heating of leach liquors from hot process gases or liquors.
- The use of plastic contents in some raw materials as a fuel, provided that good quality plastic cannot be recovered and VOCs and dioxins are not emitted.
- The use of low-mass refractories where practicable.

6. 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, fugitive emissions and also specific emission and consumption data, process residues, wastewater and aspects related to small and medium-sized companies. Chapter 13 contains further recommendations.