“Capacity Building and Strengthening Institutional Arrangement”

Workshop: “Best Available Techniques (BAT)

BAT on Metal Industries
(Non-Ferrous)

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Index

1. Introduction

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.

1. Introduction

- Refractory Metals
- Ferro Alloys
- Alkali and Alkaline Earth Metals.
- Nickel and Cobalt.
- Carbon and Graphite.

Mining and ore treatment at the mine site are not covered.

1. Introduction

Non-ferrous metals are produced from a variety of primary and econdary 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.

2. Main environmental issues

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.

2. Main environmental issues

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.

2. Main environmental issues

- 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.

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

2. Main environmental issues

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.

2. Main environmental issues

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:

2. Main environmental issues

- 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).

2. Main environmental issues

- For the production of ***Lead, Zinc*** and ***Cadmium***: dust, metal compounds, VOCs (including dioxins), odours, SO2, 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, NOx, other acid gases such as chlorine and SO2. Residues such as sludge, filter dust and slag and wastewater (metal compounds and organic compounds).

2. Main environmental issues

- For the production of ***Mercury***: mercury vapour, dust, metal compounds, odours, SO2, 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.

2. Main environmental issues

- 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.

2. Main environmental issues

- For the production of ***Carbon*** and ***graphite***: PAHs, hydrocarbons, dust, odours, SO2, wastewater prevention, residues such as filter dust.
- It is not possible to conclude the **Best Available Techniques** for all of the common process stages because of the influence of the specific metal group.
- The selection of 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 etc.

3. BAT for productive cycles

- The Best Available Techniques included in this section for the common processes are:

. Materials handling and storage;

. Process control;

. Fume and gas collection;

. Sulphur removal;

. Prevention and destruction of dioxins; and

. Removal of mercury from process gases.

3. BAT for productive cycles

Emissions

•***Emissions*** to the environment depend on the collection or batement 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:

Reported range of current emissions

Abatement Technique	Reported emissions Component	minimum	maximum	Specific emission (amount per t of metal produced)
Fabric filter, hot EP and cyclone.	Dust (Metals dependent on composition)	< 1 mg/Nm³	100 mg/Nm³	100 - 6000 g/t
Carbon filter	Total C	< 20 mg/Nm³		
Afterburner (including temperature quench for dioxin)	Total C	< 2 mg/Nm³	100 mg/Nm³	10 - 80 g/t
	Dioxin (TEQ)	< 0.1 ng/Nm³	5 ng/Nm³	5 - 10 µg/t
	PAH (EPA)	< 1 µg/Nm³	2500 µg/Nm³	
	HCN	< 0.1 mg/Nm³	10 mg/Nm³	
Wet or semi-dry scrubber	SO_2	< 50 mg/Nm³	250 mg/Nm³	500 - 3000 g/t
	Hydrocarbon	<10 mgC/Nm³	200 mgC/Nm³	
	Chlorine	< 2 mg/Nm³		
Alumina scrubber	Dust	< 1 mg/Nm³	20 mg/Nm³	
	Hydrocarbon	< 1 mgC/Nm³	50 mgC/Nm³	
	PAH (EPA)	< 20 µg/Nm³	2000 µg/Nm³	
Chlorine recovery	Chlorine	< 5 mg/Nm³		
Optimised combustion Low NO_x burner	NO_x	10 mg/Nm³	500 mg/Nm³	
Oxidising scrubber	NO_x		< 100 mg/Nm³	
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/Nm³	6 mg/Nm³	
	Hydrocarbons	20 mgC/Nm³	200 mgC/Nm³	

3. BAT for productive cycles

Emissions to Air

Emissions to air arise from the storage, handling, pre-treatment, pyro-metallurgical and hydrometallurgical stages.

- 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;

3. BAT for productive cycles

Emissions to Air

- Roofline collection of fume is very energy consuming and should be a last resort.
- Sulphur capture is an important requirement when ulphidic 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.

3. BAT for productive cycles

Emissions to Air

The process choice depends on the existence of local markets for sulphur dioxide.

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:

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 µgC/Nm^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) > 99.1% conversion (single contact)	Including mercury scrubber using Boliden/Norzink process or thiosulphate scrubber Hg < 1 ppm in acid produced
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.

3. BAT for productive cycles

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.

3. BAT for productive cycles

Emissions to Water

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.						

3. BAT for productive cycles

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.

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

3. BAT for productive cycles

Process Residues

- 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.

3. BAT for productive cycles

Process Residues

- The recovery of residues has to be 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.

3. BAT for productive cycles

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.

3. BAT for productive cycles

Energy recovery

- 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.

4. Conclusions

- 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.

- 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.

- 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.

4. Conclusions

• 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.

• 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.

5. References

Best Available Techniques in the Non Ferrous Metals Industries

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http://eippcb.jrc.es/pages/FActivities.htm
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