

Section VI.B.5.

Guidance by source category: Annex C, Part III Source Categories

Primary base metals production

Coordinated by Mr. Patrick Finlay (Canada)

# Draft Guidelines on Best Available Techniques (BAT) for Primary Base Metals Smelting

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## **1.0 Process Description**

The technical processes involved in the extraction and refining of base metals (nickel, lead, copper, zinc and cobalt) generally proceed as shown in Figure 1. Key metal recovery technologies that are used to produce refined metals can be categorized as follows:

- Pyrometallurgical technologies use heat to separate desired metals from unwanted materials. These processes exploit the differences between constituent oxidation potential, melting point, vapour pressure, density, and/or miscibility when melted.
- Hydrometallurgical technologies use differences between constituent's solubility and/or electrochemical properties while in aqueous acid solutions to separate desired metals from unwanted materials; and
- Vapo-metallurgical technologies apply to the Inco Carbonyl Process whereby nickel alloys are treated with carbon monoxide gas to form nickel carbonyl.

Generally, primary base metals smelting facilities process ore concentrates. Most primary smelters have the technical capability to supplement primary concentrate feed with secondary materials (e.g., recyclables).

Figure 1 provides a generic flow sheet showing the main production processes associated with primary smelting and refining.

Unintentional production of POPs are thought to originate through high temperature thermal metallurgical processes, therefore hydrometallurgical processes are not considered in this paper on BAT for primary base metals smelting.

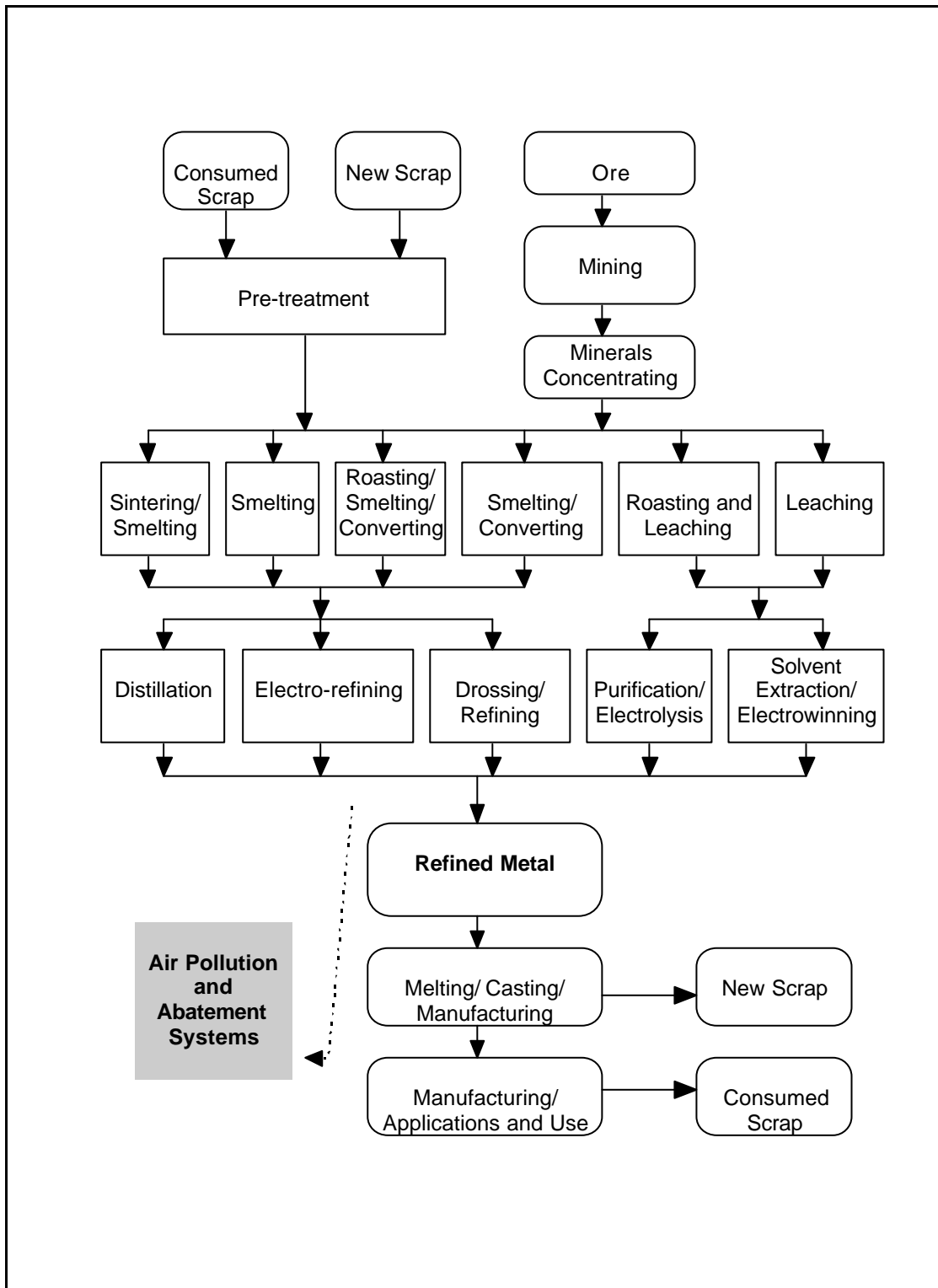


Figure 1: Generic flowsheet for primary base metals smelting and refining.

## 2.0 Sources of Unintentional POPs

Primary base metals smelters can be sources of unintentional produced persistent organic pollutants. The formation and release of UPOPs from primary smelters are not well understood, and it has been shown that emissions of PCDD/PCDF can range significantly between operations using similar processes.

### 2.1 Releases to Air

#### 2.1.1 General Information on Emissions from Base Metals Smelting<sup>1</sup>

*“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 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.”*

#### 2.1.2 Emissions of PCDD and PCDF

*“There is limited published information on dioxin/furan mechanisms of formation for the base metals smelting sector, most of which is based on European experience for secondary base metal smelters. There are a few general statements that dioxins and furans might be present in some of the raw materials for secondary base metals smelting and that oils and organic materials are present in many of these raw materials. The presence of oils and other organic materials in scrap or other sources of carbon (partially burnt fuels and reductants 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 dioxins and furans. This process is known as de novo synthesis which is dependent on catalysts such as copper and iron. Although dioxins and furans are destroyed at high temperature (above 850°C) in the presence of oxygen, the process of de novo synthesis is still possible as the gases are cooled.”<sup>2</sup>*

Available information on emissions of PCDD and PCDF from a variety of source sectors (e.g., incinerators, steel electric arc furnaces, iron sintering plants) suggest that process

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<sup>1</sup> European Commission, *Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, May 2000, <http://eippcb.jrc.es>

<sup>2</sup> Charles E. Napier Co. Ltd., *Generic Dioxin/Furan Emission Testing Protocol for the Base Metals Smelting Sector*, prepared for Environment Canada, Final 2002/02/08.

technologies and techniques, and associated off-gas conditioning can influence the formation and subsequent release of PCDD/PCDF.

Canadian base metals smelting and refining facilities undertook emissions testing for PCDD and PCDF, and results from their emission test work showed that concentration levels varied with the type of off-gas conditioning system.

Note, smelting facilities in Canada generally process sulphide concentrates, and at some facilities, also process some secondary materials. Off-gas conditioning varies from extensive cleaning (e.g., de-dusting) and conversion to sulphuric acid, to dedusting by fabric filter, to dedusting by electrostatic precipitator (ESP). These facilities produce nickel, copper, lead, zinc and co-product metals. There were eleven participating facilities in the Canadian test program, conducting approximately 20 emission tests on 16 different sources. No two facilities had the same combination and configuration of production processes and off-gas conditioning systems, further complicating any possible analysis. As such, the observations noted below are general in nature.

Where off-gases were cleaned (i.e., dedusted, scrubbed) and processed through an acid plant for conversion of sulphur dioxide (SO<sub>2</sub>) rich off-gases to sulphuric acid, emission test results showed concentrations below 5 pg TEQ/m<sup>3</sup>.

Where off-gases were dedusted by baghouse, concentration levels typically ranged from a few picograms TEQ/m<sup>3</sup> to <30 pg TEQ/m<sup>3</sup>.

Where off-gases were dedusted by ESP, concentration levels ranged from approximately 30 pg TEQ/m<sup>3</sup> to approximately 500 pg TEQ/m<sup>3</sup>.

## **2.2 Releases to Other Media**

No information was found on releases of unintentional POPs from primary base metals smelters to media other than air.

## **3.0 Alternate Processes for Base Metals Smelting**

In accordance with the POPs Convention, when consideration is being given to proposals for construction of a new base metals smelting facility, priority consideration should be given to alternate processes, techniques or practices that have similar usefulness but which avoid the formation and release of the identified substances.

As indicated in Figure 1, there is a wide range of processes used in the primary production of base metals smelting. The processes used to produce crude and/or refined base metals from primary sources will depend to a large extent on the available ore or concentrate (i.e., laterite ore vs. sulphide ore), and other considerations (properties of the desired metal(s),

properties of the feed materials, available fuel and energy sources, capacity/ production, economics, etc.).

The formation and release of unintentional POPs is considered to be a result of high temperature thermal metallurgical operations. Consideration should be given to hydrometallurgical processes (e.g., leaching, electrowinning) where technically feasible, as alternatives to pyrometallurgical processes (e.g., roasting, smelting, converting, fire refining) when considering proposals for the construction and commissioning of new base metals smelting facilities or processes.

#### **4.0 Primary and Secondary Measures**

There is a paucity of information on the release of UPOPs from primary base metals smelting operations. No techniques were identified specifically for the primary base metals smelting sector to prevent or control the unintentional formation and release of PCDD/PCDF and other unintentional POPs. The following measures identified below constitute general measures which may result in lower pollutant emissions at primary base metals smelters, including releases of PCDD/PCDF.

The extent of emission reduction possible with implementation of primary measures only is not readily known. It is therefore recommended that consideration be given to implementation of both primary and secondary measures.

#### **4.1 Primary Measures**

Primary measures are understood to be pollution prevention measures that will prevent or minimize the formation and release of the identified substances (PCDD, PCDF, HCB and PCB). These are sometimes referred to as process optimization or integration measures. Pollution prevention is defined as: *The use of processes, practices, materials, products or energy that avoid or minimize the creation of pollutants and waste, and reduce overall risk to human health or the environment.*

Primary measures which may assist in reducing the formation and release of pollutant emissions include:

##### **1. Use of Hydrometallurgical Processes:**

Use of hydrometallurgical processes rather than pyrometallurgical processes where possible, as a significant means to preventing emissions. Closed-loop electrolysis plants will contribute to prevention of pollution.

## 2. Quality Control of (Scrap) Feed Material

The presence of oils, plastics and chlorine compounds in scrap feed materials should be avoided to reduce the generation of PCDD/PCDF during incomplete combustion or by de-novo synthesis. Feed material should be classified according to composition and possible contaminants. Selection and sorting to prevent the addition of material that is contaminated with organic matter or precursors can reduce the potential for PCDD/PCDF formation. Storage, handling and pre-treatment techniques will be determined by feed size distribution and contamination.

Methods to be considered are:<sup>3</sup>

- Oil removal from feed (e.g. thermal de-coating and de-oiling processes followed by afterburning to destroy any organic material in the off-gas)
- Use of milling and grinding techniques with good dust extraction and abatement. The resulting particles can be treated to recover valuable metals using density or pneumatic separation.
- Elimination of plastic by stripping cable insulation (e.g. possible cryogenic techniques to make plastics friable and easily separable)
- Sufficient blending of material to provide a homogenous feed in order to promote steady-state conditions.

## 3. Effective Process Control:

Process control systems should be utilized to maintain process stability and operate at parameter levels that will contribute to the minimization of PCDD/PCDF generation, such as maintaining furnace temperature above 850 °C to destroy PCDD/PCDF. Ideally, PCDD/DF emissions would be monitored continuously to ensure reduced releases. Continuous emissions sampling of PCDD/PCDF has been demonstrated for some sectors (e.g. waste incineration), but research is still developing in this field. In the absence of continuous PCDD/PCDF monitoring, other variables such as temperature, residence time, gas components and fume collection damper controls should be continuously monitored and maintained to establish optimum operating conditions for the reduction of PCDD/PCDF.

## 4. Use flash smelting technology

The most effective pollution prevention option is to choose a process that entails lower energy usage and lower emissions. Where pyrometallurgical techniques are used, use of flash smelting technology rather than older technologies (e.g., roasters, blast furnace, etc.) is a significant means to reducing energy use and to reducing emissions. Flash smelting will also result in high concentration of sulphur dioxide in the off-gas stream,

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<sup>3</sup> European Commission, *Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p. 232.



which would permit the efficient fixation or recovery of sulphur dioxide prior to off-gas venting.

***Other general measures for primary base metals smelting:***

5. Maximize SO<sub>2</sub> Content for Sulphur Fixation

Processes should be operated to maximize the concentration of the sulphur dioxide in the off-gas (where processing sulphide ores or concentrates). It is important, therefore, that a process be selected that uses oxygen-enriched air (or pure oxygen) to raise the SO<sub>2</sub> content of the process gas stream and reduce the total volume of the stream, thus permitting efficient fixation of sulphur dioxide.

## 4.2 Secondary Measures

Secondary measures are understood to be pollution control technologies or techniques, sometimes described as 'end-of-pipe' treatments.

Secondary measures which may assist in reducing the formation and release of pollutant emissions include:

1. High Efficiency Gas Cleaning and Conversion of SO<sub>2</sub> to Sulphuric Acid

For SO<sub>2</sub> rich off-gases (typically 5% or greater) generated by pyrometallurgical processing of sulphide ores or concentrates, high efficiency pre-cleaning of off-gases followed by conversion of SO<sub>2</sub> to sulphuric acid are together considered BAT for this type of source. Emission concentrations of PCDD/PCDF with use of this combination of techniques are < 5 pg TEQ/m<sup>3</sup>.

For conversion to sulphuric acid, a double-contact, double-absorption process is considered BAT. A double-contact, double-absorption plant should emit no more than 0.2 kg of sulphur dioxide per ton of sulphuric acid produced (based on a conversion efficiency of 99.7%).<sup>4</sup>

SO<sub>2</sub> rich off-gases from smelting facilities pass through a gas cleaning train, which typically includes high efficiency dedusting, prior to the sulphuric acid plant.

This combination of techniques has the co-benefit of controlling dust and SO<sub>2</sub> emissions, in addition to PCDD/PCDF.

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<sup>4</sup> World Bank, *Pollution Prevention and Abatement Handbook*: Chapters on Copper, Nickel, Lead, and Zinc smelting, July 1998. URL: [www.worldbank.org](http://www.worldbank.org)

Other techniques for sulphur fixation, which may require pre-cleaning of off-gases prior to conversion/recovery, may potentially contribute to the minimization of PCDD/PCDF emissions. These techniques include:<sup>5</sup>

- Recovery as liquid sulphur dioxide (absorption of clean, dry off-gas in water or chemical absorption by ammonium bisulfite or dimethyl aniline); and
- Recovery as elemental sulphur, using reductants such as hydrocarbons, carbon, or hydrogen sulfide.

### 1. Fume and Gas Collection<sup>6</sup>:

Air emissions should be controlled at all stages of the process, from material handling, smelting and material transfer points, to control the emission of PCDD/PCDF. Sealed furnaces are essential to contain fugitive emissions while permitting heat recovery and collecting off-gases for process recycling. Proper design of hooding and ductwork is essential to trap fumes. Furnace or reactor enclosures may be necessary. If primary extraction and enclosure of fumes is not possible, the furnace should be enclosed so that ventilation air can be extracted, treated and discharged. Roofline collection of fume should be avoided due to high energy requirements. The use of intelligent damper controls can improve fume capture and reduce fan sizes and hence costs. Sealed charging cars or skips used with a reverberatory furnace can significantly reduce fugitive emissions to air by containing emissions during charging.

### 3. High Efficiency Dust Removal:

The smelting process generates high volumes of particulate matter with large surface area on which PCDD/PCDF can adsorb. These dusts and metal compounds should be removed to reduce PCDD/PCDF emissions. Very high efficiency dust removal techniques should be employed, for example, ceramic filters, high efficiency fabric filters or the gas cleaning train prior to a sulphuric acid plant.

Preference should be given to fabric filters over wet scrubbers, wet electrostatic precipitators (ESPs), or hot ESPs for dust control. Dust from dust control equipment should be returned to the process. Returned/collected dust should be treated in high temperature furnaces to destroy PCDD/PCDF and recover metals. Dust that is captured but not recycled will need to be disposed of in a secure landfill or other acceptable manner.

Fabric filter operations should be constantly monitored by devices to detect bag failure.

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<sup>5</sup> Ibid.

<sup>6</sup> European Commission, *Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p. 187-188.

## **5.0 Emerging Research**

Catalytic Oxidation: Selective catalytic reduction (SCR) has been used for controlling NO<sub>x</sub> emissions from a number of industrial processes. Modified SCR technology (i.e., increased reactive area) and select catalytic processes have been shown to decompose PCDD and PCDF contained in off-gases, likely through catalytic oxidation reactions. This may be considered as an evolving technique with potential for effectively reducing POPs emissions from base metals smelting operations and other applications.

## 6.0 Summary of Measures

The following tables present a summary of the measures discussed in previous sections.

**Table 6.1 Measures for New Iron Sintering Plants**

Measure	Description	Considerations	Other comments
<b><i>New Primary Base Metals Smelting Operations</i></b>			
<b>Alternate Processes</b>	Priority consideration should be given to alternate processes with potentially less environmental impacts than pyrometallurgical base metals smelting.	Hydrometallurgical processes are a significant means to preventing emissions. Closed-loop electrolysis plants will contribute to prevention of pollution.	
<b>Performance Requirements</b>	New primary base metals smelting operations should be permitted to achieve stringent performance and reporting requirements associated with best available techniques.	Consideration should be given to the primary and secondary measures listed in Table 6.2 below.	Performance requirements for achievement should take into consideration achievable emission levels of PCDD/PCDF identified in Section 7.0.

**Table 6.2 Summary of Primary and Secondary Measures for Primary Base Metals Smelting Operations**

Measure	Description	Considerations	Other Comments
<b><i>Primary Measures</i></b>			
Use of Hydrometallurgical Processes	Use of hydrometallurgical processes rather than pyrometallurgical processes where possible, as a significant means to preventing emissions. Closed-loop electrolysis plants will contribute to prevention of pollution.	Use of hydrometallurgical processes will depend in large part on the ore and concentrate to be processed (e.g. laterite or sulphide).	
Quality Control of (Scrap) Feed Material	Selection and sorting to prevent the addition of material that is contaminated with organic matter or precursors can reduce the potential for PCDD/PCDF formation.	Methods to be considered are: <ul style="list-style-type: none"> <li>Oil removal from feed (e.g. thermal de-coating and de-oiling processes followed by afterburning to destroy any organic material in the off-gas)</li> <li>Use of milling and grinding techniques with good dust extraction and abatement. The resulting</li> </ul>	

Measure	Description	Considerations	Other Comments
		<p>particles can be treated to recover valuable metals using density or pneumatic separation.</p> <ul style="list-style-type: none"> <li>• Elimination of plastic by stripping cable insulation (e.g. possible cryogenic techniques to make plastics friable and easily separable).</li> <li>• Sufficient blending of material to provide a homogenous feed in order to promote steady-state conditions.</li> </ul>	
Effective Process Control	Process control systems should be utilized to maintain process stability and operate at parameter levels that will contribute to the minimization of PCDD/PCDF generation. In the absence of continuous PCDD/PCDF monitoring, other variables such as temperature, residence time, gas components and fume collection damper controls should be continuously monitored and maintained to establish optimum operating conditions for the reduction of PCDD/PCDF.	For example, furnace temperatures should be maintained above 850 °C to destroy PCDD/PCDF.	
Use flash smelting technology	Where pyrometallurgical techniques are used, use of flash smelting technology rather than older technologies (e.g., roasters, blast furnace, etc.) is a significant means to reducing energy use and to reducing emissions.	Flash smelting will also result in high concentration of sulphur dioxide in the off-gas stream, which would permit the efficient fixation or recovery of sulphur dioxide prior to off-gas venting.	
<i>Other general measures to prevent and reduce pollutant emissions:</i>			
Maximize SO <sub>2</sub> Content for Sulphur Fixation	Processes should be operated to maximize the concentration of the sulphur dioxide in the off-gas (where processing sulphide ores or concentrates), to enable recovery or fixation of the sulphur. Preference should be given to processes that use oxygen-enriched air (or pure oxygen) to raise the SO <sub>2</sub> content of the process gas stream and reduce the total volume of the stream.		
<b>Secondary Measures</b>			

Measure	Description	Considerations	Other Comments
<i>The following secondary measures can effectively reduce emissions of PCDD/PCDF and should be considered as examples of best available techniques.</i>			
High Efficiency Gas Cleaning and Conversion of SO <sub>2</sub> to Sulphuric Acid	SO <sub>2</sub> rich off-gases, high efficiency pre-cleaning of off-gases followed by conversion of SO <sub>2</sub> to sulphuric acid should be employed, and are together considered BAT.	This combination of techniques has the co-benefit of controlling dust and SO <sub>2</sub> emissions, in addition to PCDD/PCDF.	Emission concentrations of PCDD/PCDF with use of high efficiency gas cleaning and conversion of SO <sub>2</sub> to sulphuric acid are < 5 pg TEQ/m <sup>3</sup> .
Fume and Gas Collection	Air emissions should be controlled at all stages of the process, from material handling, smelting and material transfer points, to control the emission of PCDD/PCDF.		
High Efficiency Dust Removal	<p>Dusts and metal compounds should be removed to reduce PCDD/PCDF emissions. Very high efficiency dust removal techniques should be employed, for example, ceramic filters, high efficiency fabric filters or the gas cleaning train prior to a sulphuric acid plant.</p> <p>Dust from dust control equipment should be returned to the process. Returned/collected dust should be treated in high temperature furnaces to destroy PCDD/PCDF and recover metals.</p> <p>Fabric filter operations should be constantly monitored by devices to detect bag failure.</p>	<p>Preference should be given to fabric filters over wet scrubbers, wet electrostatic precipitators (ESPs), or hot ESPs for dust control.</p> <p>Dust that is captured but not recycled will need to be disposed of in a secure landfill or other acceptable manner.</p>	

## 7.0 Achievable Levels

Levels achieved at primary base metals smelting operations are noted as follows:

<b>Primary Base Metals Smelting Source Type</b>	<b>Achievable Level</b>
Acid Plant Tail Gas (recovery of sulphur dioxide in off-gas from pyrometallurgical sources)	< 5 pg TEQ/Rm <sup>3</sup>
Off-gas dedusted by baghouse	< 5 pg ITEQ/Rm <sup>3</sup> to <30 pg TEQ/Rm <sup>3</sup>
Off-gas dedusted by ESP	30 pg TEQ/Rm <sup>3</sup> to < 500 pg TEQ/Rm <sup>3</sup>

No final country emission limits were identified for emissions PCDD/PCDF, HCB or PCBs unintentionally produced by primary base metals smelters.