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# Development of guidelines on best available techniques and provisional guidance on best environmental practices relevant to the provisions of Article 5 and Annex C of the Stockholm Convention on Persistent Organic Pollutants

## DRAFT GUIDELINES ON BAT FOR THERMAL PROCESSES IN THE METALLURGICAL INDUSTY

Note by the Secretariat

The following attachments were provided by Mr. Patrick Finlay (Canada) who coordinated there development:

(a) Attachment 1, draft guidelines on best available techniques for secondary copper smelting;

(b) Attachment 2, draft guidelines on best available techniques for iron sintering;

(c) Attachment 3, draft guidelines on best available techniques for secondary aluminium smelting;

(d) Attachment 4, draft guidelines on best available techniques for secondary zinc smelting;

(e) Attachment 5, draft guidelines on best available techniques for secondary lead smelting;

(f) Attachment 6, draft guidelines on best available techniques for primary aluminium production; and

(g) Attachment 7, draft guidelines on best available techniques for magnesium production.

This note and its attachments have not been formally edited.

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[1] UNEP/POPS/EGB.2/1.

# Attachment 1

# Draft Guidelines on Best Available Techniques (BAT) for Secondary Copper Smelting

## List of Contents

## 1.0 Process Description

Secondary copper smelting is comprised of pyro-metallurgical processes dependant on the copper content of the feed material, size distribution and other constituents. Feed sources are copper scrap, sludge, computer scrap, drosses from refineries and semi-finished products. These materials may contain organic materials like coatings or oil, and installations take this into account by using de-oiling and de-coating methods or by correct design of the furnace and abatement system. [1] Copper can be infinitely recycled without loss of its intrinsic properties.

*"Secondary copper recovery is divided into 4 separate operations: scrap pre-treatment, smelting, alloying, and casting. Pre-treatment includes the cleaning and consolidation of scrap in preparation for smelting. Smelting consists of heating and treating the scrap for separation and purification of specific metals. Alloying involves the addition of 1 or more other metals to copper to obtain desirable qualities characteristic of the combination of metals.*

*Scrap pre-treatment may be achieved through manual, mechanical, pyrometallurgical, or hydrometallurgical methods. Manual and mechanical methods include sorting, stripping, shredding, and magnetic separation. Pyrometallurgical pre-treatment may include sweating (the separation of different metals by slowly staging furnace air temperatures to liquefy each metal separately), burning insulation from copper wire, and drying in rotary kilns to volatilize oil and other organic compounds. Hydrometallurgical pre-treatment methods include flotation and leaching to recover copper from slag. Leaching with sulphuric acid is used to recover copper from slime, a byproduct of electrolytic refining.*

*Smelting of low-grade copper scrap begins with melting in either a blast or a rotary furnace, resulting in slag and impure copper. If a blast furnace is used, this copper is charged to a converter, where the purity is increased to about 80 to 90 percent, and then to a reverberatory furnace, where copper of about 99 percent purity is achieved. In these fire-refining furnaces, flux is added to the copper and air is blown upward through the mixture to oxidize impurities.*

*These impurities are then removed as slag. Then, by reducing the furnace atmosphere, cuprous oxide (CuO) is converted to copper. Fire-refined copper is cast into anodes, which are used during electrolysis. The anodes are submerged in a sulphuric acid solution containing copper sulphate. As copper is dissolved from the anodes, it deposits on the cathode. Then the cathode copper, which is as much as 99.99 percent pure, is extracted and recast. The blast furnace and converter may be omitted from the process if average copper content of the scrap being used is greater than about 90 percent.*

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[1] European Commission*, Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p. 201-202.

*In alloying, copper-containing scrap is charged to a melting furnace along with 1 or more other metals such as tin, zinc, silver, lead, aluminium, or nickel. Fluxes are added to remove impurities and to protect the melt against oxidation by air. Air or pure oxygen may be blown through the melt to adjust the composition by oxidizing excess zinc. The alloying process is, to some extent, mutually exclusive of the smelting and refining processes described above that lead to relatively pure copper.*

*The final recovery process step is the casting of alloyed or refined metal products. The molten metal is poured into moulds from ladles or small pots serving as surge hoppers and flow regulators. The resulting products include shot, wire bar, anodes, cathodes, ingots, or other cast shapes."*[2]

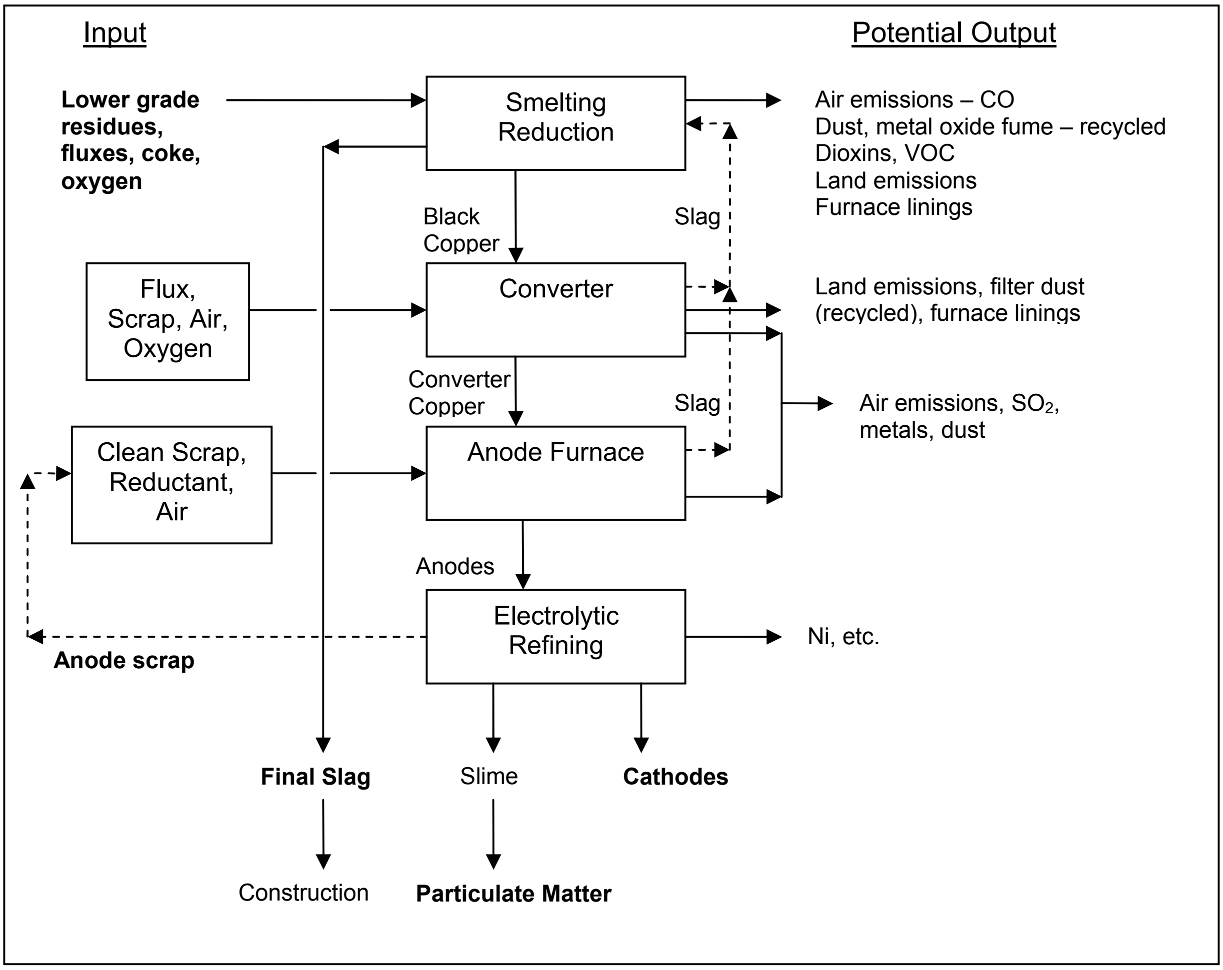

Figure 1 Secondary Copper Smelting[3]

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[2] US Environmental Protection Agency, *Background Report AP-42 Section 12.9, Secondary Copper Smelting, Refining and Alloying*, January 1995. URL: www.epa.gov/ttn/chief/ap42/ch12/final/c12s09.pdf

[3] European Commission, *Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p. 217.

## *2.0 Sources of Unintentionally Produced POPs*

The formation of polychlorinated dibenzoparadioxins (PCDD) and polychlorinated dibenzofurans (PCDF) is probable due to the presence of chlorine from plastics and trace oils in the feed material. As copper is the most efficient metal to catalyse PCDD/PCDF formation, copper smelting is a concern.

### 2.1 Emissions of PCDD/PCDF

PCDD/PCDF are formed during base metals smelting through incomplete combustion or by de-novo synthesis when organic and chlorine compounds such as oils and plastics are present in the feed material. Secondary feed often consists of contaminated scrap.

*"PCDD/PCDF or their precursors may be present in some raw materials and there is a possibility of de-novo synthesis in furnaces or abatement systems. PCDD/PCDF are easily adsorbed onto solid matter and may be collected by all environmental media as dust, scrubber solids and filter dust.*

*The presence of oils and other organic materials on 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 PCDD/PCDF. This process is known as de-novo synthesis and is catalysed by the presence of metals such as copper or iron.*

*Although PCDD/PCDF 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 through the "reformation window". This window can be present in abatement systems and in cooler parts of the furnace e.g. the feed area. Care taken in the design of cooling systems to minimise the residence time in the window is practised to prevent de-novo synthesis."*[4]

### 2.2 General Information on Emissions from Secondary Copper Smelters[5]

Airborne emissions consist of nitrogen oxides ($NO_x$), carbon monoxide (CO), dust and metal compounds, organic carbon compounds and PCDD/Fs. Off-gases usually contain little or no sulphur dioxide ($SO_2$) provided sulphidic material is avoided. Scrap treatment and smelting generate the largest quantity of atmospheric emissions. Dust and metal compounds are emitted from most stages of the process and are more prone to fugitive emissions during charging and tapping cycles. Particulate matter is removed from

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[4] European Commission, *Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p. 133.

[5] European Commission, *Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p. 218-229.

collected and cooled combustion gases by electrostatic precipitators (ESPs) or fabric filters. Fume collection hoods are used during the conversion and refining stages due to the batch process which prevents a sealed atmosphere. $NO_x$ is minimised in low $NO_x$ burners, while CO is burnt in hydrocarbon afterburners. Burner control systems are monitored to minimize CO generation during smelting.

Process, surface and cooling water can be contaminated by suspended solids, metal compounds and oils. Most process and cooling water is recycled. Wastewater treatment methods are used before discharge. By-products and residues are recycled in the process as these contain recoverable quantities of copper and other non-ferrous metals. Waste material generally consists of acid slimes which are disposed of on site.

## *3.0 New Secondary Copper Smelters*

The Stockholm Convention states that when proposals are considered to construct new facilities or significantly modify existing facilities using processes that release POPs, priority consideration should be given to alternative processes, techniques or practices that have similar usefulness but which avoid the formation and release of these chemicals.[6]

No information is available on alternate processes to smelting for secondary copper processing.

### 3.1 Recommended Processes for New Secondary Copper Smelters[7]

Process design and configuration is influenced by the variation in feed material and quality control. Processes considered as BAT for smelting/reduction include the Blast Furnace, Mini-Smelter (totally enclosed), Sealed Submerged Electric Arc furnace, and ISA Smelt. The Top Blown Rotary Furnace (totally enclosed) and Peirce-Smith converter are BAT for converting. The submerged electric arc furnace is sealed and cleaner than other designs if the gas extraction system is adequately designed and sized.

Clean copper scrap devoid of organic contamination can be processed using the reverberatory hearth furnace, the hearth shaft furnace and Contimelt process. These are considered to be BAT in configuration with suitable gas collection and abatement systems.

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[6] Stockholm Convention on Persistent Organic Pollutants, 2001. URL: www.pops.int/documents/convtext/convtext_en.pdf

[7] European Commission*, Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p. 262.

## 3.2 Performance Requirements for New Secondary Copper Smelters[8]

New secondary copper smelters should be designed and operated to achieve reductions in emissions levels as shown:

- <0.1 ng /Nm$^3$ TEQ for PCDD/PCDF

  Methods to achieve targeted emissions level:
    - high efficiency dust removal systems (e.g. fabric filters)
    - afterburners and quenching
    - adsorption on activated carbon

- <5 mg/Nm$^3$ for particulate matter

  Methods to achieve targeted emissions level:
    - high efficiency dust removal systems (e.g. fabric filters)

## *4.0 Primary and Secondary Measures*

Primary and secondary measures of PCDD/PCDF reduction and elimination are discussed below.

### 4.1 Primary Measures

Primary measures are regarded as pollution prevention techniques to reduce or eliminate the generation and release of POPs. Possible measures include:

1. Pre-sorting of Feed Material:

   The presence of oils, plastics and chlorine compounds in the feed material 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. Storage, handling and pre-treatment techniques will be determined by feed size distribution and contamination.

   Methods to be considered are: [9]

    - 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)

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[8] European Commission*, Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p. 268.

[9] European Commission*, Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p. 232.

- 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

2. 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.

## 4.2 Secondary Measures

Secondary measures are pollution control techniques. These methods do not eliminate the generation of contaminants, but serve as means to contain and prevent emissions.

1. Fume and Gas Collection[10]:

   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.

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[10] European Commission*, Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p. 187-188.

2. 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. Fabric filters are the most effective technique, while wet/dry scrubbers and ceramic filters are also to be considered. Collected dust must be treated in high temperature furnaces to destroy PCDD/PCDF and recover metals.

   Fabric filter operations should be constantly monitored by devices to detect bag failure. Other developments include online cleaning methods and use of catalytic coatings to destroy PCDD/PCDF [11].

3. Afterburners and quenching:

   Afterburners (post-combustion) should be used at a minimum temperature of 950°C to ensure full combustion of organic compounds.[12] This stage is to be followed by rapid quenching of hot gases to temperatures below 250°C. Oxygen injection in the upper portion of the furnace will promote complete combustion. [13]

   It has been observed that PCDD/PCDF are formed in the temperature range of 250 to 500°C. These are destroyed above 850°C in the presence of oxygen. Yet, *de novo* synthesis is still possible as the gases are cooled through the reformation window present in abatement systems and cooler areas of the furnace. Proper operation of cooling systems to minimise reformation time should be implemented.[14]

4. Adsorption on Activated Carbon:

   Activated carbon treatment should be considered for PCDD/PCDF removal from smelter off-gases. Activated carbon possesses large surface area on which PCDD/PCDF can be adsorbed. Off-gases can be treated with activated carbon using fixed or moving bed reactors, or by injection of carbon particulate into the gas stream followed by removal as a filter dust using high efficiency dust removal systems such as fabric filters.

5. Catalytic Oxidation:

   Catalytic oxidation is an emerging technology used in waste incinerators to eliminate PCDD/PCDF emissions. This process should be considered by secondary base

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[11] European Commission, *Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p.139-140.

[12] Hübner C., et. al., *State-Of-The-Art Measures For Dioxin Reduction In Austria*, 2000. URL: www.ubavie.gv.at/publikationen/Mono/M116s.htm

[13] European Commission, *Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p. 189.

[14] European Commission, *Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p. 133.

metals smelters as it has proven effective for PCDD/PCDF destruction in waste incinerators.

Catalytic oxidation processes organic compounds into water, carbon dioxide ($CO_2$) and hydrochloric acid using a precious metal catalyst to increase the rate of reaction at 370 to 450°C. In comparison, incineration occurs typically at 980°C. Catalytic oxidation has been shown to destroy PCDD/PCDF with shorter residence times, lower energy consumption and 99% efficiency, and should be considered. Off-gases should be de-dusted prior to catalytic oxidation for optimum efficiency. This method is effective for the vapour phase of contaminants. The resulting hydrochloric acid is treated in a scrubber while the water and $CO_2$ are released to the air after cooling.[15]

Fabric filters used for dust removal can also be treated with a catalytic coating to promote oxidation of organic compounds at elevated temperature.

## *5.0 Summary of Measures*

**Table 5.1 Measures for New Secondary Copper Smelters**

| Measure | Description | Considerations | Other comments |
|---|---|---|---|
| ***New Secondary Copper Smelters*** | | | |
| **Recommended Processes** | Various recommended smelting processes should be considered for new facilities. | Processes to be considered include:<br>- The blast Furnace, mini-smelter, Top Blown Rotary Furnace, Sealed Submerged Electric Arc furnace, ISA Smelt, and the Peirce-Smith converter.<br>- The reverberatory hearth furnace, the hearth shaft furnace and Contimelt process to treat clean copper scrap devoid of organic contamination. | These are considered to be BAT in configuration with suitable gas collection and abatement<br>The submerged electric arc furnace is sealed and cleaner than other designs if the gas extraction system is adequately designed and sized. |
| **Performance Requirements.** | New secondary copper smelters should be permitted to achieve stringent performance and reporting requirements associated with BAT. | Consideration should be given to the primary and secondary measures listed in Table 5.2 below. | Performance requirements for achievement should include:<br>- 0.1ng /$Nm^3$ TEQ for PCDD/PCDF<br>- 5 mg/$Nm^3$ for particulate matter |

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[15] Parvesse, T., Chemical Processing, *Controlling Emissions from Halogenated Solvents*, April 2001. URL: www.chemicalprocessing.com/Web_First/cp.nsf/ArticleID/NJEC-4VPKAW/

## Table 5.2 Summary of Primary and Secondary Measures for Secondary Copper Smelters

| Measure | Description | Considerations | Other Comments |
|---|---|---|---|
| ***Primary Measures*** | | | |
| **Pre-sorting of feed material** | The presence of oils, plastics and chlorine compounds in the feed material should be avoided to reduce the generation of PCDD/PCDF during incomplete combustion or by de-novo synthesis. | Processes to be considered include:<br>- Oil removal from feed material<br>- Use of milling and grinding techniques with good dust extraction and abatement.<br>- Elimination of plastic by stripping cable insulation | Thermal de-coating and de-oiling processes for oil removal should be followed by afterburning to destroy any organic material in the off-gas |
| **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. | PCDD/PCDF emissions may be minimized by controlling other variables such as temperature, residence time, gas components and fume collection damper controls after having established optimum operating conditions for the reduction of PCDD/PCDF. | Continuous emissions sampling of PCDD/PCDF has been demonstrated for some sectors (e.g. waste incineration), but research is still developing in this field. |
| ***Secondary Measures*** | | | |
| **Fume and Gas Collection** | Effective fume and off-gas collection should be implemented in all stages of the smelting process to capture PCDD/PCDF emissions. | Processes to be considered include:<br>- Sealed furnaces to contain fugitive emissions while permitting heat recovery and collecting off-gases. Furnace or reactor enclosures may be necessary<br>- Proper design of hooding and ductwork to trap fumes. | Roofline collection of fume is to be avoided due to high energy requirements. |
| **High Efficiency Dust Removal** | Dusts and metal compounds should be removed as this material possesses high surface area on which PCDD/PCDF easily adsorb. Removal of these dusts would contribute to the reduction of PCDD/PCDF emissions. | Processes to be considered include:<br>- Fabric filters (most effective method)<br>- wet/dry scrubbers and ceramic filters. | - Dust removal is to be followed by afterburners and quenching.<br>- Collected dust must be treated in high temperature furnaces to destroy PCDD/PCDF and recover |

| Measure | Description | Considerations | Other Comments |
|---|---|---|---|
| | | | metals. |
| **Afterburners and quenching** | Afterburners should be used at temperatures >950°C to ensure full combustion of organic compounds, followed by rapid quenching of hot gases to temperatures below 250°C. | Considerations include:<br>- PCDD/PCDF formation at 250-500°C, and destruction >850°C with $O_2$.<br>- Requirement for sufficient $O_2$in the upper region of the furnace for complete combustion.<br>- Need for proper design of cooling systems to minimise reformation time. | - De novo synthesis is still possible as the gases are cooled through the reformation window. |
| **Adsorption on Activated Carbon** | Activated carbon treatment should be considered as this material possesses large surface area on which PCDD/PCDF can be adsorbed from smelter off-gases. | Processes to be considered include:<br>- Treatment with activated carbon using fixed or moving bed reactors<br>-injection of carbon particulate into the gas stream followed by removal as a filter dust. | Lime/carbon mixtures can also be used. |
| **Catalytic Oxidation** | Catalytic oxidation is an emerging technology which should be considered due to its high efficiency and lower energy consumption. Catalytic oxidation transforms organic compounds into water, $CO_2$ and hydrochloric acid using a precious metal catalyst. | Considerations include:<br>- Process efficiency for the vapour phase of contaminants.<br>- Hydrochloric acid treatment using scrubbers while water and $CO_2$ are released to the air after cooling. | Catalytic oxidation has been shown to destroy PCDD/PCDF with shorter residence times, lower energy consumption and 99% efficiency.<br>Off-gases should be de-dusted prior to catalytic oxidation for optimum efficiency. |

## *6.0 Performance Standards*

Performance standards and timelines for achievement for new and existing secondary copper smelters are recommended as shown:

**Table 5.3 Performance Standards for New and Existing Secondary Copper Smelters**

| Type | Suggested Timeline | Emission Limit[16] |
|---|---|---|
| New | Entry into force | <0.1 ng /$Rm^3$ TEQ |

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[16] $Rm^3$ indicates a reference volume at 298 K (25°C), 101.3 kPa (1 atmosphere), dry gas basis and operating $O_2$ levels.

| | | |
|---|---|---|
| Existing | Within 10 years of entry into force | <0.1 ng /$Rm^3$ TEQ |

## 7.0 Performance Reporting

Performance reporting is recommended as follows:

Annual isokinetic emission testing should be conducted at secondary copper smelters and reported to the appropriate national or sub-national authority for:
- Polychlorinated dibenzoparadioxins;
- Polychlorinated dibenzofurans;
- Hexachlorobenzene; and
- Polychlorinated biphenyls.

Annual emission testing frequency could be reduced or suspended once emissions are shown to be 'eliminated' [17] on a continued and consistent basis.

This is considered as BAT for performance reporting.

Where isokinetic emission testing for the above substances is not possible (e.g. for fugitive emissions or some types of emission control technology or if analytical capacity is not readily available), emission factors associated with a similar plant type and operation are suggested as an interim performance reporting requirement until such time as annual emissions testing and analysis is available.

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[17] The Government of Canada has established levels of quantification (LOQ) for virtual elimination of PCDD/PCDF, HCB and PCBs in air as follows: <32 pg /$Rm^3$ TEQ, <6 ng /$Rm^3$ HCB, and <2 ng /$Rm^3$ PCB, respectively. Consideration should be given to appropriate emissions levels associated with elimination of these substances.

# Attachment 2

# DRAFT Guidelines on Best Available Techniques (BAT) for Iron Sintering

## List of Contents

## *1.0 Process Description*

Iron sintering plants are associated with the manufacture of iron and steel, often in integrated steel mills. The sintering process is a pre-treatment step in the production of iron, where fine particles of iron ores and in some plants, also secondary iron oxide wastes (collected dusts, mill scale), are agglomerated by combustion. Agglomeration of the fines is necessary to enable the passage of hot gases during the subsequent blast furnace operation.[1]

Sintering involves the heating of fine iron ore with flux and coke fines or coal to produce a semi-molten mass that solidifies into porous pieces of sinter with the size and strength characteristics necessary for feeding into the blast furnace. Moistened feed is delivered as a layer onto a continuously moving grate or "strand." The surface is ignited with gas burners at the start of the strand, and air is drawn through the moving bed causing the fuel to burn. Strand velocity and gas flow are controlled to ensure that "burn through" (i.e. the point at which the burning fuel layer reaches the base of the strand) occurs just prior to the sinter being discharged. The solidified sinter is then broken into pieces in a crusher and is air-cooled. Product outside the required size range is screened out, oversize material is recrushed, and undersize material is recycled back to the process. Sinter plants that are located in a steel plant recycle iron ore fines from the raw material storage and handling operations and from waste iron oxides from steel plant operations and environmental control systems. Iron ore may also be processed in on-site sinter plants.[2]

The flexibility of the sintering process permits conversion of a variety of materials, including iron ore fines, captured dusts, ore concentrates, and other iron-bearing materials of small particle size (e.g., mill scale) into a clinker-like agglomerate.[3]

Waste gases are usually treated for dust removal in a cyclone, electrostatic precipitator, wet scrubber or fabric filter.

Figure 1 provides a schematic of an iron sintering plant.

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[1] United Nations Environment Programme (UNEP), *Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases*, (Switzerland: UNEP Chemicals, 2003), p. 60

[2] Environment Canada, *Environmental Code of Practice for Integrated Steel Mills – CEPA 1999 Code of Practice,* (Canada: Public Works and Government Services, 2001), p. 18.

[3] William T. Lankford Jr., Norman L. Samways, Robert F. Craven, and Harold E. MacGannon, eds., *The Making, Shaping and Treating of Steel, 10th Edition*, (USA: Association of Iron and Steel Engineers, 1985), p. 305-6.

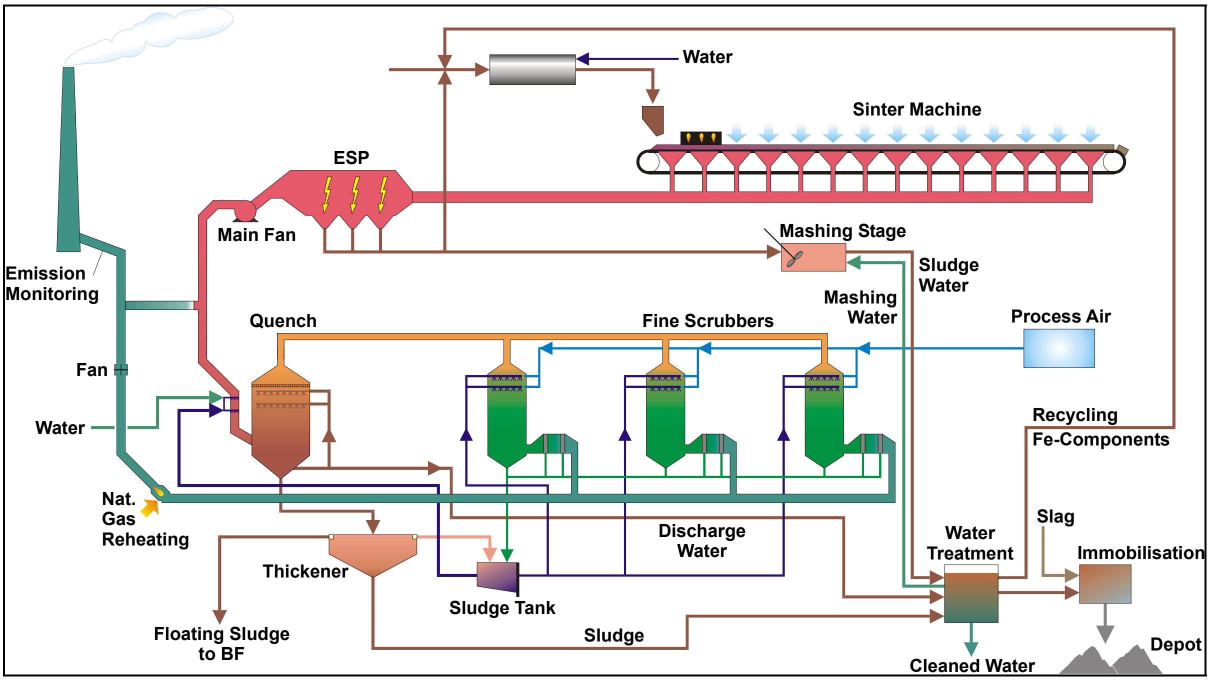

**Figure 1: Process Diagram from a Sinter Plant (Source: K. Hofstadler et al., *Dioxin at Sinter Plants and Electric Arc Furnaces – Emission profiles and removal efficiency*: downloaded May 2003 http://g5006m.unileoben.ac.at/downloads/Dioxin.doc )**

## *2.0 Sources of Unintentional POPs*

Iron sintering has been identified as a source of polychlorinated dibenzoparadioxins (PCDD) and polychlorinated dibenzofurans (PCDF). The formation and release of hexachlorobenzene (HCB) and polychlorinated biphenyls (PCB) are less understood from this potential source.

### 2.1 Emissions of PCDD and PCDF[4]

The processes by which PCDD/PCDF are formed are complex. PCDD/PCDF appear to be formed in the iron sintering process via *de novo* synthesis. PCDF generally dominate in the waste gas from sinter plants.

The PCDD/PCDF formation mechanism appears to start in the upper regions of the sinter bed shortly after ignition, and then the dioxin/furan and other compounds condense on cooler burden beneath as the sinter layer advances along the sinter strand towards the burn through point. The process of volatilization and condensation continues until the temperature of the cooler burden beneath rises sufficiently to prevent

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[4] William Lemmon & Associates Ltd., *Research on Technical Pollution Prevention Options for Iron Sintering, Draft of 2003/05/17* (Canada: prepared for the Canadian Council of Ministers of the Environment, 2003), p.20-21

condensation and the PCDD/PCDF exit with the flue gas. This appears to increase rapidly and peak just before burn through and then decrease rapidly to a minimum. This is supported by the dioxin/furan profile compared to the temperature profile along the sinter strand in several studies.

The quantity of PCDD and PCDF formed has been shown to increase with increasing carbon and chlorine content. Carbon and chloride are present in some of the sinter feed materials typically processed through a sinter plant.

## 2.2 Research findings of interest:[5]

It appears that the composition of the feed mixture has an impact on the formation of PCDD/PCDF i.e., increased chlorine content results in increased PCDD/PCDF formation while the replacement of coke as a fuel with anthracite coal appears to reduce PCDD/PCDF concentration.

The form of the solid fuel may also impact furan emissions. Coal, graphite, and activated coke in a Japanese laboratory research program reduced pentachlorinated dibenzofuran emissions by approximately 90 percent.

The operating parameters of the sintering process appear to have an impact on the formation of PCDD/PCDF.

## 2.3 General Information on Emissions from Iron Sintering Plants [6]

"*Emissions from the sintering process arise primarily from materials-handling operations, which result in airborne dust, and from the combustion reaction on the strand. Combustion gases from the latter source contain dust entrained directly from the strand along with products of combustion such as CO, $CO_2$, $SO_x$, $NO_x$, and particulate matter. The concentrations of these substances vary with the quality of the fuel and raw materials used and combustion conditions. Atmospheric emissions also include volatile organic compounds (VOCs) formed from volatile material in the coke breeze, oily mill scale, etc., and dioxins and furans, formed from organic material under certain operating conditions. Metals are volatilized from the raw materials used, and acid vapours are formed from the halides present in the raw materials.*

*Combustion gases are most often cleaned in electrostatic precipitators (ESPs), which significantly reduce dust emissions but have minimal effect on the gaseous emissions. Water scrubbers, which are sometimes used for sinter plants, may have lower particulate collection efficiency than ESPs but higher collection efficiency for gaseous emissions. Significant amounts of oil in the raw material feed may create explosive conditions in the ESP. Sinter crushing and screening emissions are usually controlled by*

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[5] Ibid.

[6] Environment Canada, *Environmental Code of Practice for Integrated Steel Mills – CEPA 1999 Code of Practice,* (Canada: Public Works and Government Services, 2001), p. 23-25.

*ESPs or fabric filters. Wastewater discharges, including runoff from the materials storage areas, are treated in a wastewater treatment plant that may also be used to treat blast furnace wastewater.*

*Solid wastes include refractories and sludge generated by the treatment of emission control system water in cases where a wet emission control system is used. Undersize sinter is recycled to the sinter strand.*"

## *3.0 New Iron Sintering Plants*

In accordance with the POPs Convention, when consideration is being given to proposals for construction of a new iron sintering plant, 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.

### 3.1 Alternate Processes to Iron Sintering

Alternate processes to iron sintering include:

The FASTMET process: This process converts iron oxide pellet feed, oxide fines, and/or steel mill wastes into metallic iron, and produces a direct reduced iron (DRI) product suitable for use in a blast furnace. Emission concentration of PCDD and PCDF from the FASTMET process is reported to be <0.1 ng TEQ/m$^3$.

Direct reduction processes: This technique processes iron ore to produce a DRI product which can be used as a feed material to steel manufacturing electric arc furnaces, iron making blast furnaces, or steelmaking basic oxygen furnaces.

Direct smelting processes: Direct smelting replaces the traditional combination of sinter plant, coke oven and blast furnace to produce molten iron. A number of direct smelting processes are evolving and are at various stages of development/commercialization.

### 3.2 Performance Requirements for New Iron Sintering Plants

If a new iron sintering is to be commissioned and installed, it is recommended that the process and associated controls and operations be permitted (and thus designed and operated) to attain emission levels of:

- <0.2 ng TEQ/m$^3$ for PCDD/PCDF[7]; and
- <20 mg/Rm3 for particulate matter;

, as well as hooding of the sinter strand to minimize fugitive emissions.

## *4.0 Primary and Secondary Measures*

Primary and secondary measures for reducing emissions of PCDD and PCDF from iron sintering processes are outlined below.

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 at existing plants.

### 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 have been identified which may assist in preventing and minimizing the formation and release of the identified substances. Emission reductions associated with implementation of the following primary measures only is not known. It is recommended that the following measures be implemented together with appropriate secondary measures to ensure the greatest minimization and reduction of emissions possible. Identified primary measures include:

1. Stable and consistent operation of the sinter strand: Research has shown that PCDD/PCDF are formed in the sinter bed itself, likely just ahead of the flame front as the hot gases are drawn through the bed. Disruptions to flame front (i.e., non-steady-state conditions) have been shown to result in higher PCDD/PCDF emissions.

   Sinter strands should be operated to maintain consistent and stable process conditions (i.e., steady-state operations, minimization of process upsets) in order to minimize the formation and release of PCDD, PCDF and other pollutants. Operating conditions to consistently manage include strand speed, bed

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[7] Based on the following: Canadian Council of Ministers of the Environment (CCME), *Canada-wide Standards for Dioxins and Furans from Iron Sintering Plants*, (Canada: CCME, March 2003), URL: www.ccme.ca

composition (consistent blending of revert materials, minimization of chloride input), bed height, use of additives (e.g., addition of burnt lime may help reduce PCDD, PCDF formation), minimization of oil content in mill scale, minimization of air in-leakage through the strand, ductwork and off-gas conditioning systems, and minimization of strand stoppages. This approach will also have beneficial operating performance improvements (e.g., productivity, sinter quality, energy efficiency).[8][9]

2. Continuous Parameter Monitoring: A continuous parameter monitoring system (CPMS) should be employed to ensure optimum operation of the sinter strand and off-gas conditioning systems. Various parameters are measured during emission testing to determine the correlation between the parameter value and the stack emissions. The identified parameters are then continuously monitored and compared to the optimum parameter values. Variances in parameter values can be alarmed and corrective action taken to maintain optimum operation of the sinter strand and/or emission control system.

   Operating parameters to monitor may include damper settings, pressure drop, scrubber water flow rate, average opacity, strand speed, etc.

   Operators of iron sintering plants should prepare a site-specific monitoring plan for the CPMS that addresses installation, performance, operation and maintenance, quality assurance and record keeping, and reporting procedures. Operators should keep records documenting conformance with the identified monitoring requirements and the operation and maintenance plan.[10]

3. Recirculation of Off-gases: Recycling of sinter off-gas (waste-gas) has been shown to minimize pollutant emissions, and reduce the amount of off-gas requiring end-of-pipe treatment. Recirculation of part of the off-gas from the entire sinter strand, or sectional recirculation of off-gas, can minimize formation and release of pollutants. The European Integrated Pollution Prevention and Control Bureau (EIPPCB) BREF document on Iron and Steel Production and the ECSC Steel Research and Technology Development Programme[11] provide additional information on this technique.[12]

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[8] European Integrated Pollution Prevention and Control Bureau (EIPPCB), *Best Available Techniques Reference Document on the Production of Iron and Steel*, (Seville, Spain, 2000), p.47.

[9] U.K. Environment Agency, *Integrated Pollution Prevention and Control (IPPC) Guidance for the Coke, Iron and Steel Sector*, (United Kingdom: Environment Agency, 2001), p. 39.

[10] U.S. Environmental Protection Agency, *National Emission Standards for Hazardous Air Pollutants: Integrated Iron and Steel Manufacturing; Final Rule*, (United-States: 40 CFR Part 63, Federal Register/ Vol. 68, No. 97, May 20, 2003), URL: www.epa.gov

[11] European Coal and Steel Community (ECSC), *The Impact of ECSC Steel Research on Steel Production and Sustainability*, downloaded 2003/09/15, URL: http://www.stahl-online.de//medien_lounge/medieninformationen/hintergrundmaterial.htm

[12] European Integrated Pollution Prevention and Control Bureau (EIPPCB), *Best Available Techniques Reference Document on the Production of Iron and Steel*, (Seville, Spain, 2000), p. 56-62

Recycling of iron sintering off-gases can reduce emissions of PCDD, PCDF, NOx and $SO_2$.

4. Feed material selection: Unwanted substances should be minimized in the feed to the sinter strand. Unwanted substances include POPs and other substances associated with the formation of PCDD, PCDF, HCB and PCB (e.g., chlorine/chlorides, carbon, precursors, oils, etc.).

   A review of feed inputs to determine its composition/structure and concentration of substances associated with POPs and their formation should be conducted. Options to eliminate or reduce the unwanted substance in the feed material should be identified. For example:

   - removal of the contaminant from the material (e.g., de-oiling of mill scales);
   - substitution of the material (e.g., replacement of coke breeze with anthracite);
   - avoid use of the contaminated material (e.g., avoid processing ESP sinter dusts which have been shown to increase PCDD/PCDF formation and release[13]);
   - specification of limits on permissible concentrations of unwanted substances (e.g., oil content in feed should be limited to less than 0.02 percent[14]).

   Documented procedures should be developed and implemented to carry out the appropriate changes.

5. Feed material preparation: Fine feed materials (e.g., collected dusts) should be adequately agglomerated before they are placed on the sinter strand and feed materials should be intimately mixed or blended. These measures will minimize formation and entrainment of pollutants in the waste gas, and will also minimize fugitive emissions.

## 4.2 Secondary Measures

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

*Primary measures identified earlier should be implemented together with appropriate secondary measures to ensure the greatest minimization and reduction of emissions*

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[13] Kasai, E. et al, Effect of Additives on the Dioxins Emissions in the Iron Ore Sintering Process. *ISIJ International*, Vol. 41 (2001), No.1, pp. 93-97.

[14] U.S. Environmental Protection Agency, *National Emission Standards for Hazardous Air Pollutants: Integrated Iron and Steel Manufacturing; Final Rule*, (United-States: 40 CFR Part 63, Federal Register/ Vol. 68, No. 97, May 20, 2003), URL: www.epa.gov

*possible. Measures that have been shown to effectively minimize and reduce PCDD and PCDF emissions include:*

1. Removal Techniques

   a. Adsorption/Absorption and High Efficiency De-dusting: This technique involves sorption of PCDD and PCDF to a material such as activated carbon together with effective particulate matter (de-dusting) control.

      For *regenerative activated carbon technology*[15] an ESP is used to reduce dust concentration in the off-gases prior to entry to the activated carbon unit. The waste gas passes through a slowly moving bed of char granules which acts as a filter/adsorption medium. The used char is discharged and transferred to a regenerator, where it is heated to elevated temperatures. PCDD and PCDF adsorbed to the char are decomposed and destroyed within the inert atmosphere of the regenerator. This technique has been shown to reduced emissions to 0.1 to <0.3 ng TEQ/m$^3$.

      Another sorption technique is the use of *lignite or activated carbon injection, together with a fabric filter*. PCDD and PCDF are sorbed onto the injected material, and the material is collected in the fabric filter. Along with good operation of the sinter strand, this technique is associated with PCDD/PCDF emission concentrations ranging from 0.1 to 0.5 ng TEQ/m$^3$.[16]

   b. Fine Wet Scrubbing System: The Airfine scrubbing system, developed by Voest Alpine Industries (Austria), has been shown to effectively reduce emission concentrations to 0.2 to 0.4 ng TEQ/m$^3$. The scrubbing system uses a counter current flow of water against the rising waste gas to scrub out coarse particles and gaseous components (e.g., sulphur dioxide ($SO_2$)), and to quench the waste gas. (Note, an ESP may also be used upstream for preliminary dedusting.) Caustic soda may be added to improve $SO_2$ absorption. A fine scrubber, the main feature of the system, follows, employing high-pressure mist jet co-current with the gas flow to remove impurities. Dual flow nozzles eject water and compressed air (creating microscopic droplets) to remove fine dust particles, PCDD and PCDF.[17,18]

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[15] William Lemmon & Associates Ltd., *Research on Technical Pollution Prevention Options for Iron Sintering, Draft of 2003/05/17* (Canada: prepared for the Canadian Council of Ministers of the Environment, 2003), p.29-30

[16] U.K. Environment Agency, *Integrated Pollution Prevention and Control (IPPC) Guidance for the Coke, Iron and Steel Sector*, (United Kingdom: Environment Agency, 2001), p. 135.

[17] William Lemmon & Associates Ltd., *Research on Technical Pollution Prevention Options for Iron Sintering, Draft of 2003/05/17* (Canada: prepared for the Canadian Council of Ministers of the Environment, 2003), p.29-30

[18] EIPPCB, *Best Available Techniques Reference Document on the Production of Iron and Steel*, (Seville, Spain, 2000), p. 72-74, URL: http://eippcb.jrc.es

This technique should be combined with effective treatment of the scrubber waste waters and waste water sludge should be disposed of in a secure landfill.[19]

***The following measures can assist in minimizing pollutant emissions, but should be combined with other measures (e.g., adsorption/absorption, recirculation of off-gases, etc.) for effective PCDD/PCDF formation and release.***

2. General Measures

a. De-dusting of the sinter off-gases. It has been suggested that effective removal of dust can help reduce emissions of PCDD and PCDF. Fine particles in the sinter off-gas have extremely large surface area for adsorption and condensation of gaseous pollutants, including PCDD and PCDF.[20] Best available technique for de-dusting is use of fabric filters to remove particulate matter. Use of fabric filters for sinter plants is associated with particulate matter emission concentrations of <10 to <30 mg/m$^3$.[21,22]

Other dedusting options that are commonly used for sinter plant off-gases include ESPs and wet scrubbers. Particulate removal efficiency is not as high as for fabric filters. Good performance of ESPs and high efficiency wet-gas scrubbers is associated with particulate matter concentrations of <30 to 50 mg/m$^3$. [23,24, 25]

Adequately sized capture and dedusting controls for both the feed and discharge ends should be required and put in place.

b. Hooding of the sinter strand: Hooding of the sinter strand reduces fugitive emissions from the process, and enables use of other techniques, such as waste gas recirculation.

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[19] Ibid.

[20] K. Hofstadler et al., *Dioxin at Sinter Plants and Electric Arc Furnaces – Emission profiles and removal efficiency*, (Austria: VOEST ALPINE Indstrienlagenbau GmbH, no date), Url: g5006m.unileoben.ac.at/downloads/Dioxin.doc (May 2003)

[21] United Nations Economic Commission for Europe (UNECE), Annex III Best available techniques for controlling emission of heavy metals, *Protocol to the 1979 Convention on Long-Range Transboundary Pollution on Heavy Metals (Aarhus)*, (Geneva: UNECE, 1998), URL: www.unece.org

[22] UK Environment Agency, *Integrated Pollution Prevention and Control (IPPC) Guidance for the Coke, Iron and Steel Sector*, (United Kingdom: Environment Agency, 2001), p. 131.

[23] Ibid.

[24] William Lemmon & Associates Ltd., *Research on Technical Pollution Prevention Options for Iron Sintering, Draft of 2003/05/17* (Canada: prepared for the Canadian Council of Ministers of the Environment, 2003), p.26.

[25] UNECE, Annex III Best available techniques for controlling emission of heavy metals, *Protocol to the 1979 Convention on Long-Range Transboundary Pollution on Heavy Metals (Aarhus)*, (Geneva: UNECE, 1998), URL: www.unece.org

## 3. Emerging BAT: - Destruction Technique

Catalytic Oxidation: Selective catalytic reduction (SCR) has been used for controlling NOx emissions from a number of industrial processes, including iron sintering. 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 emerging technique with potential for reducing POPs emissions from iron sintering plants and other applications.

A study investigating stack emissions from four sinter plants, noted that those with SCR had lower concentrations of PCDD/PCDF (0.995 – 2.06 TEQ/Nm$^3$) in the stack gases than a sinter plant without SCR (3.10 ng TEQ/Nm$^3$), and that the PCDD/PCDF degree of chlorination was lower for plants with SCR. It was concluded that SCR did indeed decompose PCDD/PCDF, but would not necessarily be sufficient as a stand alone PCDD/PCDF destruction technology to meet stringent emission limits. Add-on techniques (e.g., activated carbon injection) to SCR may be required. [26]

Further study of the use of SCR and other catalytic oxidation techniques at iron sintering applications is needed to determine its value and effectiveness in destroying and reducing PCDD/PCDF released from this source.

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[26] Wang, L-C, et al. Emission of polychlorinated dibenzo-p-dioxins and dibenzofurans from stack flue gases of sinter plants, *Chemosphere*, Vol. 50, Issue 9, March 2003, pg 1123-1129.

## 5.0 Summary of Measures

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

### Table 4.3.1 Measures for New Iron Sintering Plants

| Measure | Description | Considerations | Other comments |
|---|---|---|---|
| *New Iron Sintering Plants* | | | |
| **Alternate Processes** | Priority consideration should be given to alternate processes with potentially less environmental impacts than traditional iron sintering. | Examples include:<br>-FASTMET<br>-direct reduction of iron<br>-direct smelting | |
| **Performance Requirements.** | New iron sintering plants 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 4.3.2 below. | Performance requirements for achievement should include:<br>- <0.2 ng TEQ/Rm$^3$ for PCDD/PCDF<br>-<20 mg/Rm$^3$ for particulate matter |

### Table 4.3.2 Summary of Primary and Secondary Measures for Iron Sintering Plants

| Measure | Description | Considerations | Other Comments |
|---|---|---|---|
| *Primary Measures* | | | |
| **Stable and consistent operation of the sinter plant.** | The sinter strand should be operated to maintain stable consistent operating conditions (e.g., steady-state conditions, minimization of process upsets) to minimize formation of PCDD, PCDF and other pollutants. | Conditions to optimize operation of the strand include:<br>-minimization of stoppages<br>-consistent strand speed<br>-bed composition<br>-bed height<br>-additives (e.g., burnt lime)<br>-minimization of oil content<br>-minimization of air in-leakage | This approach will have co-benefits such as increased productivity, increased sinter quality and improved energy efficiency. |
| **Continuous Parameter Monitoring** | A continuous parameter monitoring system (CPMS) should be employed to ensure optimum operation of the sinter strand and off-gas conditioning systems.<br>Operators should prepare a site-specific monitoring plan for the CPMS and keep records that document conformance with the plan. | Correlations between parameter values and stack emissions (stable operation) should be established.<br>Parameters are then continuously monitored in comparison to optimum values. | |

| Measure | Description | Considerations | Other Comments |
|---|---|---|---|
| | | System can be alarmed and corrective action taken when significant deviations occur. | |
| **Recirculation of Waste Gases** | Waste gases should be recycled back to the sinter strand to minimize pollutant emissions and reduce the amount of off-gas requiring end-of-pipe treatment. | Recirculation of the waste gases can entail recycling of part of the off-gas from the entire sinter strand, or sectional recirculation of off-gas. | This technique will result in only a modest reduction of PCDD/PCDF. |
| **Feed material selection:** ***Minimization of feed materials contaminated with POPs or leading to POPs formation.*** | A review of feed materials and identification of alternate inputs and/or procedures to minimize unwanted inputs should be conducted.<br>Documented procedures should be developed and implemented to carry out the appropriate changes. | Examples include:<br>-removal of the contaminant from the material (e.g., de-oiling of mill scales)<br>-substitution of the material (e.g., replacement of coke breeze with anthracite)<br>-avoid use of the material (e.g., collected sinter ESP dust)<br>-specification of limits on permissible concentrations of unwanted substances (e.g., oil content in feed should be limited to less than 0.02 percent ) | |
| **Feed material preparation** | Fine material (e.g., collected dusts) should be agglomerated before being placed on the sinter strand. Feed materials should be intimately mixed before placement on the sinter strand. | | These measures will help reduce entrainment of pollutants in the waste gas, and minimize fugitive emissions. |
| ***Secondary Measures*** | | | |
| *The following secondary measures can effectively reduce emissions of PCDD/PCDF and should be considered as examples of best available techniques.* | | | |
| **Adsorption/ Absorption and high efficiency dedusting.** | Use of this technique should include an adsorption stage together with high efficiency particulate control as key components of the off-gas conditioning system. | Two adsorption techniques have been demonstrated:<br>(1) regenerative activated carbon technology where off-gases are first cleaned by ESP, and | These techniques are associated with the following emission concentration levels:<br>(1) <0.3 ng TEQ/m$^3$<br>(2) 0.1 to 0.5 ng TEQ/ m$^3$ |

| Measure | Description | Considerations | Other Comments |
|---|---|---|---|
| | | passed though moving adsorption bed (char) to both adsorb PCDD, PCDF, and to filter particulates. Adsorptive material is then regenerated. (2) injection of activated carbon, lignite or other similar adsorptive material into the gas stream followed by fabric filter dedusting. | |
| **Fine wet scrubbing of waste gases** | Use of this technique should include a preliminary counter current wet scrubber to quench gases and remove larger particles, followed by a fine scrubber using high pressure mist jet co-current with off-gases to remove fine particles and impurities. | | The fine wet scrubbing system under the trade name Airfine ® as developed by Voest Alpine Industries, has been shown to reduce emission concentrations to 0.2 to 0.4 ng TEQ/m$^3$. |
| *The following secondary measures should not be considered as BAT on their own. For effective minimization and reduction of PCDD, PCDF and other POPs, the following should be employed in concert with other identified measures.* | | | |
| **De-dusting of waste gases.** | Waste gases should be dedusted using high efficiency techniques, as this can help minimize PCDD/PCDF emissions. A recommended BAT for dedusting is the use of fabric filters.<br>Feed and discharge ends of the sinter strand should be adequately hooded and controlled to capture and dedust fugitive emissions. | Fabric filters have been shown to reduce sinter off-gas particulate emissions to <10 to <30 mg/m$^3$. | Other dedusting techniques used include ESPs and high efficiency scrubbers. Good performance of these technologies are associated with particulate concentrations of <30 to 50 mg/m$^3$. |
| **Hooding of the sinter strand** | The sinter strand should be hooded to minimize fugitive process emissions. | | Hooding of the strand will enable use of other measures, such as waste gas recirculation. |

# *6.0 Performance Standards*

## 6.1 Recommended Performance Standards

Performance standards and timelines for achievement for new and existing iron sintering plants are recommended as follows:

| Type | Suggested Timeline | Emission Limit Value |
|---|---|---|
| New | Entry into force | <0.2 ng TEQ/Rm$^3$ |
| Existing | Within 10 years of entry into force | <0.2 ng TEQ/Rm$^3$ |

## 6.2 Country Emission Limits for Iron Sintering

The following provides a brief overview of emission concentration limits that have been established for or are applicable to iron sintering operations.

| Country | Emission Limit | Comment |
|---|---|---|
| Austria | 0.4 ng I-TEQ/m3 | Applicable to new plants built after 2001 |
| Canada | 0.2 ng I-TEQ/Rm$^3$ | For new plants |
| | <1.35 ng I-TEQ/Rm$^3$ | For existing plants, to be achieved by 2002 |
| | <0.5 ng I-TEQ/Rm$^3$ | For existing plants, to be achieved by 2005 |
| | <0.2 ng I-TEQ/Rm$^3$ | For existing plants, to be achieved by 2010 |
| Germany | 0.1 ng I-TEQ/m$^3$ | Target |
| | 0.4 ng I-TEQ/m$^3$ | Upper limit |
| Japan | 0.1 ng WHO-TEQ/m$^3$ | For new plants |
| | 1 ng WHO-TEQ/m$^3$ | For existing plants |
| Netherlands | 0.1 ng I-TEQ/m$^3$ | Desirable |
| United Kingdom | 0.1 – 0.5 ng I-TEQ/m$^3$ | Benchmark emission values |
| Other | (PLEASE PROVIDE ANY ADDITIONAL INFORMATION ON EMISSION LIMITS) | |

## *7.0 Performance Reporting*

Performance reporting is recommended as follows:

Annual isokinetic emission testing should be conducted at iron sintering plants for:

- Polychlorinated dibenzoparadioxin (PCDD);
- Polychlorinated dibenzofuran (PCDF);
- Hexachlorobenzene (HCB); and
- Polychlorinated biphenyls (PCB).

, and reported to the appropriate national or sub-national authority. Annual emission testing could be reduced (i.e., frequency) or suspended once emissions are shown to be 'eliminated' [27] on a continued and consistent basis.

This is considered as BAT for performance reporting.

Where isokinetic emission testing for the above substances is not possible (e.g., analytical capacity is not readily available), emission factors associated with a similar plant type and operation, is suggested as an interim performance reporting requirement until such time as annual emissions testing and analysis is available. Emission factors for releases of PCDD/PCDF from iron sintering are presented in the *UNEP Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases*, May 2003 (URL: www.pops.int).

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[27] Consideration should be given to appropriate emission levels associated with 'elimination' of PCDD, PCDF, HCB and PCB. The Government of Canada has established levels of quantification (LOQ) for 'virtual elimination' of PCDD/PCDF, HCB and PCB in air as follows: <32 pg TEQ/Rm$^3$, <6 ng HCB/Rm$^3$, and <2 ng PCB/Rm$^3$, respectively.

# Attachment 3

# Draft Guidelines on Best Available Techniques (BAT) for Secondary Aluminium Smelting

## List of Contents

## *1.0 Process Description*

Processes used in secondary aluminium smelting are dependent on feed material. Pre-treatment, furnace type and fluxes used will vary with each installation. Production processes involve scrap pre-treatment and smelting/refining. Pre-treatment methods include mechanical, pyro- and hydrometallurgical cleaning. Smelting is conducted using reverberatory or rotary furnaces.

Feed consists of process scrap, used beverage cans (UBC), foils, extrusions, commercial scraps, turnings, and old rolled or cast metal. Skimmings and salt slags from the secondary smelting process are also recycled as feed. Pre-sorting of scrap into desired alloy groups can reduce processing time. Scrap is often contaminated with oil or coatings which must removed to reduce emissions and improve melting rate.[1]

*"Most secondary aluminium recovery facilities use batch processing in smelting and refining operations. The melting furnace is used to melt the scrap, and remove impurities and entrained gases. The molten aluminium is then pumped into a holding furnace. Holding furnaces are better suited for final alloying, and for making any additional adjustments necessary to ensure that the aluminium meets product specifications. Pouring takes place from holding furnaces, either into molds or as feedstock for continuous casters.*

*Smelting and refining operations can involve the following steps: charging, melting, fluxing, demagging, degassing, alloying, skimming, and pouring. Charging consists of placing pre-treated aluminium scrap into a melted aluminium pool (heel) that is maintained in melting furnaces. The scrap, mixed with flux material, is normally placed into the furnace charging well, where heat from the molten aluminium surrounding the scrap causes it to melt by conduction. Flux materials combine with contaminates and float to the surface of the aluminium, trapping impurities and providing a barrier (up to 6 inches thick) that reduces oxidation of the melted aluminium. To minimize aluminium oxidation (melt loss), mechanical methods are used to submerge scrap into the heel as quickly as possible.*

*Demagging reduces the magnesium content of the molten charge. In the past, when demagging with liquid chlorine, chlorine was injected under pressure to react with magnesium as the chlorine bubbled to the surface. The pressurized chlorine was released through carbon lances directed under the heel surface, resulting in high chlorine emissions. A more recent chlorine aluminium demagging process has replaced the carbon lance procedure. Chlorine gas is metered into the circulation pump discharge pipe. It is anticipated that reductions of chlorine emissions (in the form of chloride compounds) will be reported in the future. Other chlorinating agents or fluxes, such as anhydrous aluminium chloride or chlorinated organics, are used in demagging operations.*

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[1] European Commission*, Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p. 279.

*Degassing is a process used to remove gases entrained in molten aluminium. High-pressure inert gases are released below the molten surface to violently agitate the melt. This agitation causes the entrained gasses to rise to the surface to be absorbed in the floating flux.*

*Alloying combines aluminium with an alloying agent in order to change its strength and ductility. The skimming operation physically removes contaminated semisolid fluxes (dross, slag, or skimmings) by ladling them from the surface of the melt."* [2]

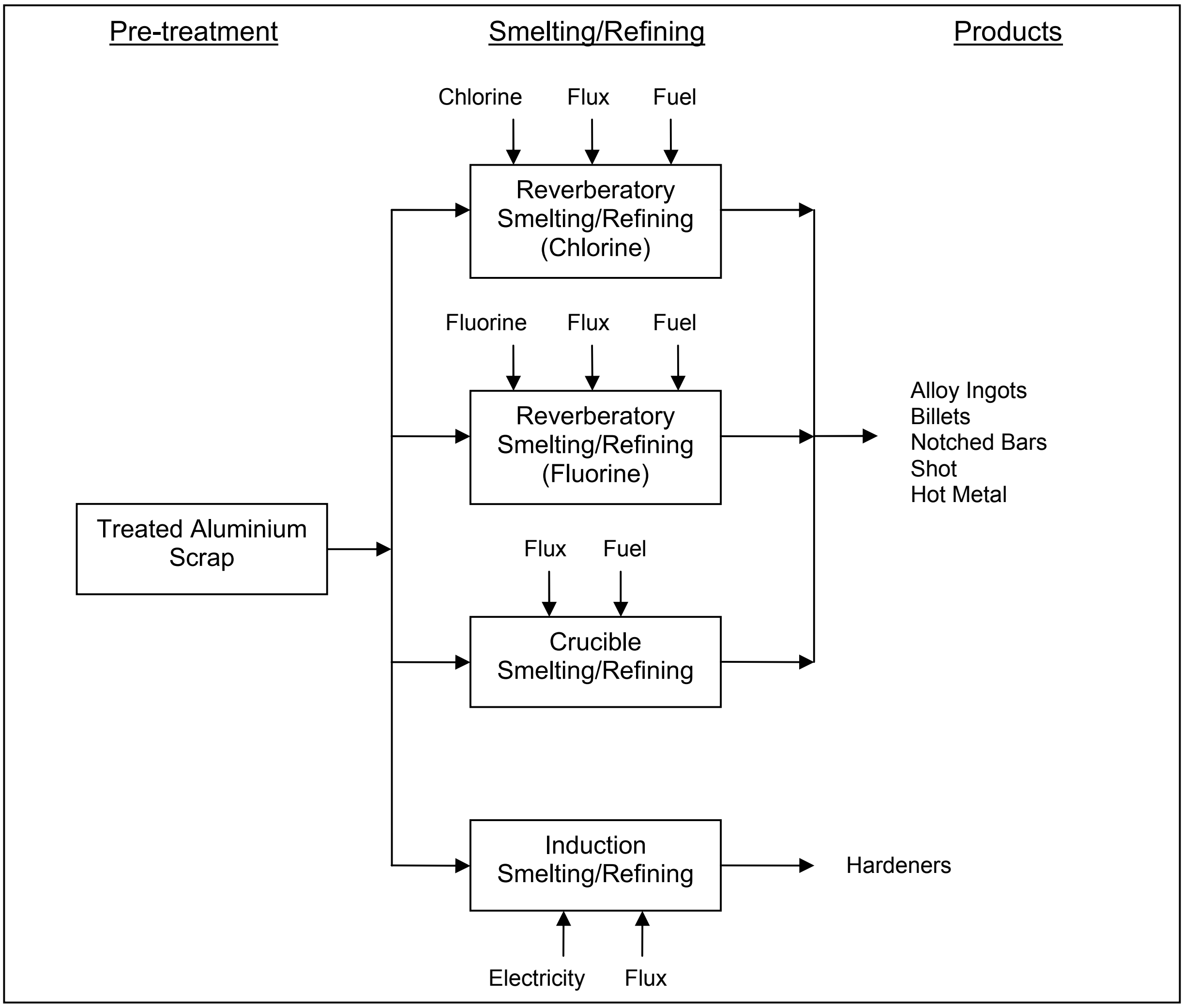

Figure 1 Secondary Aluminium Smelting[3]

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[2] US Environmental Protection Agency, *Background Report AP-42 Section 12.8, Secondary Aluminium Operations,* 1994. URL: www.epa.gov/ttn/chief/ap42/ch12/final/c12s08.pdf

[3] Ibid.

## *2.0 Sources of Unintentionally Produced POPs*

The generation of polychlorinated dibenzoparadioxins (PCDD) and polychlorinated dibenzofurans (PCDF) is probable due to the presence of organic contaminants and plastics in the feed material with the addition of chlorine and chlorides during the smelting process.

### 2.1 Emissions of PCDD/PCDF

PCDD/PCDF are formed during base metals smelting through incomplete combustion or by de-novo synthesis when organic and chlorine compounds such as oils and plastics are present in the feed material. Secondary feed often consists of contaminated scrap.

"*The presence of oils and other organic materials on 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 PCDD/PCDF. This process is known as de-novo synthesis and is catalysed by the presence of metals such as copper or iron.*

*Although PCDD/PCDF 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 through the "reformation window". This window can be present in abatement systems and in cooler parts of the furnace e.g. the feed area. Care taken in the design of cooling systems to minimise the residence time in the window is practised to prevent de-novo synthesis."*[4]

*"Poor combustion of fuel or the organic content of the feed material can result in the emission of organic materials. The provision of effective burner and furnace to controls is used to optimise combustion. Peak combustion rates from included organic materials needs to be taken into account if they are fed to the furnace. It is reported that pre-cleaning of scrap removes much of the organic material and improves the melting rate. The use of chlorine mixtures for degassing and magnesium removal and the use of chlorides (salt flux) will provide a source of chlorine for the potential formation of PCDD/PCDF."* [5]

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[4] European Commission*, Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p. 133.

[5] European Commission*, Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p.297.

## 2.2 General Information on Emissions from Secondary Aluminium Smelters [6]

Potential emissions to air include dust, metal compounds, chlorides, nitrogen oxides ($NO_x$), sulphur dioxide ($SO_2$) and organic compounds such as PCDD/PCDF and carbon monoxide (CO). Ammonia can also be generated from the improper storage, treatment and transport of skimmings. Chlorine compounds can be removed using wet/dry scrubbers and their formation minimised by good control and the use of mixtures of chlorine and inert gases. Low $NO_x$ burners and low sulphur fuels can be used to decrease emissions of $NO_x$ and $SO_2$.

*“After burning is used to destroy organic materials that escapes the combustion zone, while injection of treatment materials such as lime, sodium bi-carbonate and carbon is also practised. Most installations then use (high efficiency) bag filters or ceramic filters to remove dust and emissions can lie in the range 0.6 to 20 mg/Nm3. A spark arrester or cooling chamber often precedes them to provide filter protection. Energy recovery can be practised, most commonly re-cuperative burners are used*.

*Production of aluminium from secondary raw materials is essentially a dry process. Discharge of wastewater is usually limited to cooling water, which is often re-circulated and rainwater run-off from surfaces and roofs. The rainwater run-off can be contaminated by open storage of raw materials such as oily scrap and deposited solids*.

*Salt slags arise when mixtures of sodium and potassium chloride are used to cover the molten metal to prevent oxidation, increase yield and increase thermal efficiency. These slags are generally produced in rotary furnaces and can have an environmental impact if they are deposited on land. Skimmings are used as a raw material in other parts of the secondary aluminium industry and are sometimes pre-treated by milling and air classification to separate aluminium from aluminium oxide. Spent filters from metal treatment are usually disposed. In some cases when sodium bicarbonate is used for gas cleaning, solid residues can be recovered with the salt flux. Alternatively filter dust can be treated thermally to destroy dioxins. Furnace linings and dust can be recovered in the salt slag treatment processes or disposed.”*

## *3.0 New Secondary Aluminium Smelters*

The Stockholm Convention states that when proposals are considered to construct new facilities or significantly modify existing facilities using processes that release POPs, priority consideration should be given to alternative processes, techniques or practices

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[6] European Commission*, Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p.294-300.

that have similar usefulness but which avoid the formation and release of these chemicals.[7]

No information is available on alternate processes to smelting for secondary aluminium processing.

## 3.1 Recommended Processes for New Secondary Aluminium Smelters

Process design and configuration is influenced by the variation in feed material and quality control. Processes considered as BAT are the Reverberatory Furnace, Rotary and Tilting Rotary Furnaces, the Induction Furnace, and the Meltower Shaft Furnace. All techniques should be applied in conjunction with suitable gas collection and abatement systems.

## 3.2 Performance Requirements for New Secondary Aluminium Smelters[8]

New secondary aluminium smelters should be designed and operated to achieve reductions in emissions levels as shown:

- <0.1 ng/Nm$^3$ TEQ for PCDD/PCDF

  Methods to achieve targeted emissions level:
    - high efficiency dust removal systems (e.g. fabric filters)
    - afterburners and quenching
    - adsorption on activated carbon
    - catalytic oxidation

- <5 mg/Nm$^3$ for particulate matter

  Methods to achieve targeted emissions level:
    - high efficiency dust removal systems (e.g. fabric filters)

## *4.0 Primary and Secondary Measures*

Primary and secondary measures of PCDD/PCDF reduction and elimination are discussed below.

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[7] Stockholm Convention on Persistent Organic Pollutants, 2001. URL: www.pops.int/documents/convtext/convtext_en.pdf

[8] European Commission*, Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p.332.

## 4.1 Primary Measures

Primary measures are regarded as pollution prevention techniques to reduce or eliminate the generation and release of POPs. Possible measures include:

1. Pre-sorting of Feed Material:

   The presence of oils, plastics and chlorine compounds in the feed material should be avoided to reduce the generation of PCDD/PCDF during incomplete combustion or by de-novo synthesis. Sorting of feed material should be conducted prior to smelting to suit furnace type and abatement and to permit the transfer of unsuitable raw materials to other facilities better suited for their treatment. This will prevent or minimise the use of chloride salt fluxes during smelting.

   Scrap material should be cleaned of oils, paints and plastics during pre-treatment. The removal of organic and chlorine compounds will reduce the potential for PCDD/PCDF formation. Methods used include the swarf centrifuge, swarf drying or other thermal de-coating techniques. Thermal de-coating and de-oiling processes for oil removal should be followed by afterburning to destroy any organic material in the off-gas.[9]

   Scrap sorting using laser and eddy current technology is being tested. These methods could provide more efficient selection of materials for recycling and the ability to produce desired alloys in recycling plants.[10]

2. 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.

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[9] European Commission*, Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p.310.

[10] European Commission*, Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p.294-300.

## 4.2 Secondary Measures

Secondary measures are pollution control techniques. These methods do not eliminate the generation of contaminants, but serve as means to contain and prevent emissions.

1. Fume and Gas Collection[11]:

   Fume and off-gas collection should be implemented in the control of air emissions from all stages of the process. The use of sealed feeding systems and furnaces should be practiced. Fugitive emissions should be controlled by maintaining negative air pressure within the furnace to prevent leaks. If a sealed unit is not possible, hooding should be used. Furnace or reactor enclosures may be necessary. Where primary extraction and enclosure of fumes is not practicable, the furnace should be enclosed so that ventilation air can be extracted, treated and discharged.

2. High Efficiency Dust Removal:

   Particulate matter generated during the smelting process should be removed as this material possesses large surface area on which PCDD/PCDF can adsorb. Proper isolation and disposal of these dusts will aid in PCDD/PCDF control. Collected particulate should be treated in high temperature furnaces to destroy PCDD/PCDF and recover metals. Methods to consider are the use of fabric filters, wet/dry scrubbers and ceramic filters.

   Scrubbing off-gases with sodium bicarbonate will remove chlorides produced by the salt flux, resulting in sodium chloride, which can then be removed by fabric filters to be recharged to the furnace. In addition, use of a catalytic coating on fabric filter bags could destroy PCDD/PCDF by oxidation while collecting particulate matter on which these contaminants have adsorbed. [12]

3. Afterburners and quenching:

   Afterburners (post-combustion) should be used at a minimum temperature of 950°C to ensure full combustion of organic compounds.[13] This stage is to be followed by rapid quenching of hot gases to temperatures below 250°C. Oxygen injection in the upper portion of the furnace will promote complete combustion. [14]

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[11] European Commission, *Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p. 187-188.

[12] European Commission, *Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p.294-300.

[13] Hübner C., et. al., *State-Of-The-Art Measures For Dioxin Reduction In Austria*, 2000. URL: www.ubavie.gv.at/publikationen/Mono/M116s.htm

[14] European Commission, *Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p. 189.

It has been observed that PCDD/PCDF are formed in the temperature range of 250 to 500°C. These are destroyed above 850°C in the presence of oxygen. Yet, *de novo* synthesis is still possible as the gases are cooled through the reformation window present in abatement systems and cooler areas of the furnace. Proper operation of cooling systems to minimise reformation time should be implemented.[15]

4. Adsorption on Activated Carbon:

   Activated carbon treatment should be considered as this material is an ideal medium on which PCDD/PCDF can adsorb due to its large surface area. Off-gas treatment techniques include using fixed or moving bed reactors or injection of carbon into the gas stream followed by high efficiency dust removal systems such as fabric filters. Lime/carbon mixtures can also be used.

5. Catalytic Oxidation:

   Catalytic oxidation is an emerging technology used in waste incinerators to eliminate PCDD/PCDF emissions. This process should be considered by secondary base metals smelters as it has proven effective for PCDD/PCDF destruction in waste incinerators.

   Catalytic oxidation processes organic compounds into water, carbon dioxide ($CO_2$) and hydrochloric acid using a precious metal catalyst to increase the rate of reaction between 370 to 450°C, whereas incineration occurs typically at 980°C. Catalytic oxidation has been shown to destroy PCDD/PCDF with shorter residence times, lower energy consumption and 99% efficiency, and should be considered. Off-gases should be de-dusted prior to catalytic oxidation for optimum efficiency. This method is effective for the vapour phase of contaminants. The resulting hydrochloric acid is treated in a scrubber while the water and $CO_2$ are released to the air after cooling.[16]

## *5.0 Summary of Measures*

**Table 5.1 Measures for New Secondary Aluminium Smelters**

| Measure | Description | Considerations | Other comments |
|---|---|---|---|
| ***New Secondary Aluminium Smelters*** | | | |
| **Recommended Processes** | Various recommended smelting processes should be considered for new facilities. | Processes to be considered include: Reverberatory Furnace, Rotary and Tilting Rotary Furnaces, the Induction Furnace, | All techniques should be applied in conjunction with suitable gas collection and abatement systems. |

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[15] European Commission*, Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p. 133.

[16] Parvesse, T., Chemical Processing*, Controlling Emissions from Halogenated Solvents*, April 2001. URL: www.chemicalprocessing.com/Web_First/cp.nsf/ArticleID/NJEC-4VPKAW/

| Measure | Description | Considerations | Other comments |
|---|---|---|---|
| | | and the Meltower Shaft Furnace. | |
| **Performance Requirements.** | New secondary aluminium smelters should be permitted to achieve stringent performance and reporting requirements associated with BAT. | Consideration should be given to the primary and secondary measures listed in Table 5.2 below. | Performance requirements for achievement should include:<br>- 0.1 ng/Nm$^3$ TEQ for PCDD/PCDF<br>- 5 mg/Nm$^3$ for particulate matter |

## Table 5.2 Summary of Primary and Secondary Measures for Secondary Aluminium Smelters

| Measure | Description | Considerations | Other Comments |
|---|---|---|---|
| ***Primary Measures*** | | | |
| **Pre-sorting of feed material** | The presence of oils, plastics and chlorine compounds in the feed material should be avoided to reduce the generation of PCDD/PCDF during incomplete combustion or by de-novo synthesis. | Processes to be considered include:<br>- Prevention or minimisation of the use of chloride salts where possible.<br>- Cleaning scrap material of oils, paints and plastics during pre-treatment.<br>- Using thermal decoating techniques such as the swarf centrifuge or swarf dryer | Sorting of feed material should be conducted prior to smelting to suit furnace type and abatement and to permit the transfer of unsuitable raw materials to other facilities better suited for their treatment.<br>Thermal de-coating and de-oiling processes for oil removal should be followed by afterburning to destroy any organic material in the off-gas |
| **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. | PCDD/PCDF emissions may be minimized by controlling other variables such as temperature, residence time, gas components and fume collection damper controls after having established optimum operating conditions for the reduction of PCDD/PCDF. | Continuous emissions sampling of PCDD/PCDF has been demonstrated for some sectors (e.g. waste incineration), but research is still developing in this field. |
| ***Secondary Measures*** | | | |
| **Fume and Gas Collection** | Effective fume and off-gas collection should be implemented in the capture of air emissions from all stages of the process. | Processes to be considered include:<br>- Use of sealed feeding systems and furnaces.<br>- Control of fugitive emissions by maintaining negative air pressure within the furnace to | Where primary extraction and enclosure of fumes is not practicable, the furnace should be enclosed so that ventilation air can be extracted, treated and discharged. |

| Measure | Description | Considerations | Other Comments |
|---|---|---|---|
| | | prevent leaks.<br>- Use of hooding if a sealed unit is not possible.<br>- Use of furnace or reactor enclosures. | |
| **High Efficiency Dust Removal** | Particulate matter generated during the smelting process should be removed as this material possesses large surface area on which PCDD/PCDF can adsorb. Proper isolation and disposal of these dusts will aid in PCDD/PCDF control. | Processes to be considered include:<br>- Fabric filters, wet/dry scrubbers and ceramic filters.<br>- Catalytic coatings on fabric filter bags to destroy PCDD/PCDF by oxidation while collecting particulate matter on which these contaminants have adsorbed | Collected particulate should be treated in high temperature furnaces to destroy PCDD/PCDF and recover metals. |
| **Afterburners and quenching** | Afterburners should be used at temperatures >950°C to ensure full combustion of organic compounds, followed by rapid quenching of hot gases to temperatures below 250°C. | Considerations include:<br>- PCDD/PCDF formation at 250-500°C, and destruction >850°C with $O_2$.<br>- Requirement for sufficient $O_2$in the upper region of the furnace for complete combustion.<br>- Need for proper design of cooling systems to minimise reformation time. | - De novo synthesis is still possible as the gases are cooled through the reformation window. |
| **Adsorption on Activated Carbon** | Activated carbon treatment should be considered as this material is an ideal medium on which PCDD/PCDF can adsorb due to its large surface area. | Processes to be considered include:<br>- Treatment with activated carbon using fixed or moving bed reactors<br>- injection of carbon into the gas stream followed by high efficiency de-dusting methods such as fabric filters. | Lime/carbon mixtures can also be used. |
| **Catalytic Oxidation** | Catalytic oxidation is an emerging technology which should be considered due to its high efficiency and lower energy consumption. Catalytic oxidation transforms organic compounds | Considerations include:<br>- Process efficiency for the vapour phase of contaminants.<br>- Hydrochloric acid | Has been shown to destroy PCDD/PCDF with shorter residence times, lower energy consumption and 99% efficiency.<br>Off-gases should be de- |

| Measure | Description | Considerations | Other Comments |
|---|---|---|---|
| | into water, carbon dioxide ($CO_2$) and hydrochloric acid using a precious metal catalyst. | treatment using scrubbers while water and $CO_2$ are released to the air after cooling | dusted prior to catalytic oxidation for optimum efficiency. |

## *6.0 Performance Standards*

Performance standards and timelines for achievement for new and existing secondary aluminium smelters are recommended as shown:

**Table 5.3 Performance Standards for New and Existing Secondary Aluminium Smelters**

| Type | Suggested Timeline | Emission Limit[17] |
|---|---|---|
| New | Entry into force | <0.1 ng/$Rm^3$ TEQ |
| Existing | Within 10 years of entry into force | <0.1 ng/$Rm^3$ TEQ |

## *7.0 Performance Reporting*

Performance reporting is recommended as follows:

Annual isokinetic emission testing should be conducted at secondary aluminium smelters and reported to the appropriate national or sub-national authority for:

- Polychlorinated dibenzoparadioxins;
- Polychlorinated dibenzofurans;
- Hexachlorobenzene; and
- Polychlorinated biphenyls.

Annual emission testing frequency could be reduced or suspended once emissions are shown to be 'eliminated' [18] on a continued and consistent basis.

This is considered as BAT for performance reporting.

Where isokinetic emission testing for the above substances is not possible (e.g. for fugitive emissions or some types of emission control technology or if analytical capacity is not readily available), emission factors associated with a similar plant type and operation, is suggested as an interim performance reporting requirement until such time as annual emissions testing and analysis is available.

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[17] $Rm^3$ indicates a reference volume at 298 K (25°C), 101.3 kPa (1 atmosphere), dry gas basis and operating $O_2$ levels.

[18] The Government of Canada has established levels of quantification (LOQ) for virtual elimination of PCDD/PCDF, HCB and PCBs in air as follows: <32 pg/$Rm^3$ TEQ, <6 ng /$Rm^3$ HCB, and <2 ng /$Rm^3$ PCB, respectively. Consideration should be given to appropriate emissions levels associated with elimination of these substances.

# Attachment 4

# Draft Guidelines on Best Available Techniques (BAT) for Secondary Zinc Smelting

## List of Contents

## *1.0 Process Description*[1]

Secondary zinc smelting involves the processing of zinc scrap from various sources. Feed material includes dusts from copper alloy production and electric arc steel-making, residues from steel scrap shredding, and scrap from galvanizing processes. The process method is dependent on zinc purity, form and degree of contamination. Scrap is processed as zinc dust, oxides or slabs. The three general stages of production are pre-treatment, melting, and refining.

During pre-treatment, scrap is sorted according to zinc content and processing requirements, cleaned, crushed and classified by size. A sweating furnace is used to heat the scrap to 364°C. At this temperature, only zinc is melted while other metals remain solid. The molten zinc is collected at the bottom of the sweat furnace and recovered. The leftover scrap is cooled, recovered and sold to other processors.

Pre-treatment can involve leaching with sodium carbonate solution to convert dross and skimmings to zinc oxide, to be reduced to zinc metal. The zinc oxide product is refined at primary zinc smelters.

Melting processes use kettle, crucible, reverberatory, and electric induction furnaces. Impurities are separated from molten zinc by flux materials. Agitation allows flux and impurities to float on the surface as dross, which can be skimmed off. The remaining zinc is poured into moulds or transferred in a molten state for refining. Alloys can be produced from pre-treated scrap during sweating and melting.

Refining removes further impurities in clean zinc alloy scrap and in zinc vaporized during the melt phase in retort furnaces. Distillation involves vaporization of zinc at temperatures from 982 to 1249°C in muffle or retort furnaces and condensation as zinc dust or liquid zinc. Several forms can be recovered depending on temperature, recovery time, absence or presence of oxygen, and equipment used during zinc vapour condensation. Pot melting is a simple indirect heat melting operation where the final alloy cast into zinc alloy slabs is controlled by the scrap input into the pot. Distillation is not involved.

Final products from refining processes include zinc ingots, zinc dust, zinc oxide, and zinc alloys.

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[1] US Environmental Protection Agency, *Background Report AP-42 Section 12.14, Secondary Zinc Processing*, April 1981. URL: www.epa.gov/ttn/chief/ap42/ch12/final/c12s14.pdf

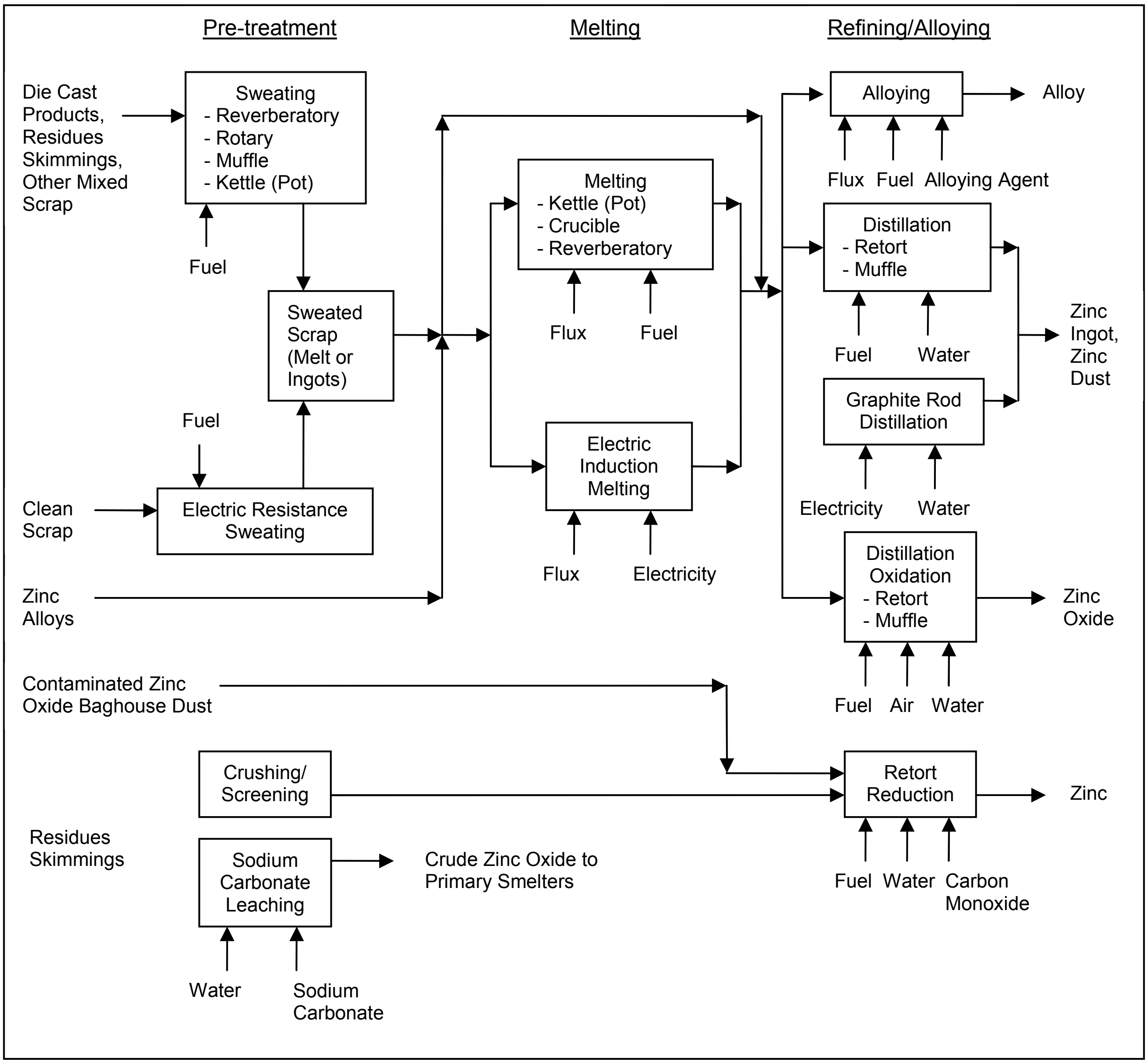

Figure 1 Secondary Zinc Smelting[2]

## 2.0 Sources of Unintentionally Produced POPs

The formation of polychlorinated dibenzoparadioxins (PCDD) and polychlorinated dibenzofurans (PCDF) may be possible if plastics and oils are present in the feed material.

### 2.1 Emissions of PCDD/PCDF

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[2] Ibid.

PCDD/PCDF are formed during base metals smelting through incomplete combustion or by de-novo synthesis when organic and chlorine compounds such as oils and plastics are present in the feed material. Secondary feed often consists of contaminated scrap.

*"The processing of impure scrap such as the non-metallic fraction from shredders is likely to involve production of pollutants including PCDD/PCDF. Relatively low temperatures are used to recover lead and zinc (340 and 440°C). Melting of zinc may occur with the addition of fluxes including zinc and magnesium chlorides."* [3]

The low temperatures used in zinc melting falls directly within the 250 to 500°C range in which PCDD/PCDF are generated. The addition of chloride fluxes provides a chlorine source. Formation is possible in the combustion zone by incomplete combustion of organic compounds and in the off-gas treatment cooling section through *de novo* synthesis. PCDD/PCDF adsorb easily onto particulate matter such as dust, filter cake and scrubber products and can be discharged to the environment through air emissions, wastewater and residue disposal.

*"Although PCDD/PCDF 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 through the "reformation window". This window can be present in abatement systems and in cooler parts of the furnace e.g. the feed area. Care taken in the design of cooling systems to minimise the residence time in the window is practised to prevent de-novo synthesis."* [4]

## 2.2 General Information on Emissions from Secondary Zinc Smelters[5]

Air emissions from secondary zinc smelting can escape as stack or fugitive emissions depending on the facility age or technology. Main contaminants are sulphur dioxide ($SO_2$), other sulphur compounds and acid mists, nitrogen oxides ($NO_x$), metals, especially zinc, and their compounds, dusts and PCDD/PCDF. $SO_2$ is collected and processed into sulphuric acid in acid plants when processing secondary material with high sulphur content. Fugitive $SO_2$ emissions can be controlled by good extraction and sealing of furnaces. $NO_x$ can be reduced using low $NO_x$ or oxy-fuel burners. Particulate matter is collected using high efficiency dust removal methods such as fabric filters and returned to the process.

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[3] UNEP, *Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases*, May 2003, p.78. URL: www.pops.int/documents/guidance/Toolkit_2003.pdf

[4] European Commission*, Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p. 133.

[5] European Commission*, Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p. 359-368.

Wastewater originates from process effluent, cooling water and runoff and is treated using wastewater treatment techniques. Process residues are recycled, treated using downstream methods to recover other metals, or safely disposed.

## *3.0 New Secondary Zinc Smelters*

The Stockholm Convention states that when proposals are considered to construct new facilities or significantly modify existing facilities using processes that release POPs, priority consideration should be given to alternative processes, techniques or practices that have similar usefulness but which avoid the formation and release of these chemicals.[6]

No information is available on alternate processes to smelting for secondary zinc processing.

### 3.1 Recommended Processes for New Secondary Zinc Smelters

Variation in feed material and desired product quality influences process design and configuration. These processes should be applied in combination with good process control, gas collection and abatement systems. Processes considered to be BAT include:

- *"Physical separation, melting and other high temperature treatment techniques followed by the removal of chlorides.*
- *The use of Waelz kilns, cyclone or converter type furnaces to raise the temperature to volatilise the metals and then form the oxides that are then recovered from the gases in a filtration stage."* [7]

### 3.2 Performance Requirements for New Secondary Zinc Smelters[8]

New secondary zinc smelters should be designed and operated to achieve reductions in emissions levels as shown:

- <0.1 ng/Nm$^3$ TEQ for PCDD/PCDF,

  Methods to achieve targeted emissions level:
    - high efficiency dust removal systems (e.g. fabric filters)
    - afterburners and quenching
    - adsorption on activated carbon

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[6] Stockholm Convention on Persistent Organic Pollutants, 2001. URL: www.pops.int/documents/convtext/convtext_en.pdf

[7] European Commission, *Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p. 396.

[8] European Commission, *Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p. 400.

- < 5 mg/Nm$^3$ for particulate matter
  Methods to achieve targeted emissions level:
  - high efficiency dust removal systems (e.g. fabric filters)

## *4.0 Primary and Secondary Measures*

Primary and secondary measures of PCDD/PCDF reduction and elimination are discussed below.

### 4.1 Primary Measures

Primary measures are regarded as pollution prevention techniques to reduce or eliminate the generation and release of POPs. Possible measures include:

1. Pre-sorting of Feed Material:

   Oils and plastics in zinc scrap should be separated from the furnace feed to reduce the formation of PCDD/PCDF from the incomplete combustion of organic compounds or by de-novo synthesis. Methods for feed storage, handling and pre-treatment are influenced by material size distribution, contaminants and metal content.

   Milling and grinding, in conjunction with pneumatic or density separation techniques, can be used to remove plastics. Thermal de-coating and de-oiling processes for oil removal should be followed by afterburning to destroy any organic material in the off-gas.[9]

2. 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.

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[9] European Commission*, Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p. 232.

## 4.2 Secondary Measures

Secondary measures are pollution control techniques to contain and prevent emissions. These methods do not prevent the formation of contaminants.

1. Fume and Gas Collection:

   Effective fume and off-gas collection should be implemented in all stages of the smelting process to capture PCDD/PCDF emissions.

   *"The fume collection systems used can exploit furnace-sealing systems and be designed to maintain a suitable furnace [vacuum] that avoids leaks and fugitive emissions. Systems that maintain furnace sealing or hood deployment can be used. Examples are through hood additions of material, additions via tuyeres or lances and the use of robust rotary valves on feed systems. An [effective] fume collection system capable of targeting the fume extraction to the source and duration of any fume will consume less energy. BAT for gas and fume treatment systems are those that use cooling and heat recovery if practical before a fabric filter…."*[10]

2. High Efficiency Dust Removal:

   Dusts and metal compounds generated from the smelting process should be removed as this particulate matter possesses high surface area on which PCDD/PCDF easily adsorb. Removal of these dusts would contribute to the reduction of PCDD/PCDF emissions. Techniques to be considered are the use of fabric filters, wet/dry scrubbers and ceramic filters. Collected particulate matter is usually recycled in the furnace.

   Fabric filters using high performance materials are the most effective option. Innovations regarding this method include bag burst detection systems, online cleaning methods, and catalytic coatings to destroy PCDD/PCDF. [11]

3. Afterburners and quenching:

   Afterburners (post-combustion) should be used at a minimum temperature of 950°C to ensure full combustion of organic compounds.[12] This stage is to be followed by rapid quenching of hot gases to temperatures below 250°C. Oxygen injection in the upper portion of the furnace will promote complete combustion. [13]

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[10] European Commission, *Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p. 397.

[11] European Commission, *Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p.139-140.

[12] Hübner C., et. al., *State-Of-The-Art Measures For Dioxin Reduction In Austria*, 2000. URL: www.ubavie.gv.at/publikationen/Mono/M116s.htm

[13] European Commission, *Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p. 189.

It has been observed that PCDD/PCDF are formed in the temperature range of 250 to 500°C. These are destroyed above 850°C in the presence of oxygen. Yet, *de novo* synthesis is still possible as the gases are cooled through the reformation window present in abatement systems and cooler areas of the furnace. Operation of cooling systems to minimise reformation time should be implemented.[14]

4. Adsorption on Activated Carbon:

   Activated carbon treatment should be considered for PCDD/PCDF removal from smelter off-gases. Activated carbon possesses large surface area on which PCDD/PCDF can be adsorbed. Off-gases can be treated with activated carbon using fixed or moving bed reactors, or injection of carbon particulate into the gas stream followed by removal as a filter dust using high efficiency dust removal systems such as fabric filters.

5. Catalytic Oxidation:

   Catalytic oxidation is an emerging technology used in waste incinerators to eliminate PCDD/PCDF emissions. This process should be considered by secondary base metals smelters as it has proven effective for PCDD/PCDF destruction in waste incinerators.

   Catalytic oxidation processes organic compounds into water, carbon dioxide ($CO_2$) and hydrochloric acid using a precious metal catalyst to increase the rate of reaction at 370 to 450°C. In comparison, incineration occurs typically at 980°C. Catalytic oxidation has been shown to destroy PCDD/PCDF with shorter residence times, lower energy consumption and 99% efficiency, and should be considered. Off-gases should be de-dusted prior to catalytic oxidation for optimum efficiency. This method is effective for the vapour phase of contaminants. The resulting hydrochloric acid is treated in a scrubber while the water and $CO_2$ are released to the air after cooling.[15]

## *5.0 Summary of Measures*

### Table 5.1 Measures for New Secondary Zinc Smelters

| Measure | Description | Considerations | Other comments |
|---|---|---|---|
| ***New Secondary Zinc Smelters*** | | | |

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[14] European Commission, *Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p. 133.

[15] Parvesse, T., Chemical Processing, *Controlling Emissions from Halogenated Solvents*, April 2001. URL: www.chemicalprocessing.com/Web_First/cp.nsf/ArticleID/NJEC-4VPKAW/

| Measure | Description | Considerations | Other comments |
|---|---|---|---|
| **Recommended Processes** | Various recommended smelting processes should be considered for new facilities. | Processes to be considered include:<br>- Physical separation, melting and other high temperature treatment techniques followed by the removal of chlorides.<br>- The use of Waelz kilns, cyclone or converter type furnaces to raise the temperature to volatilise the metals and then form the oxides that are then recovered from the gases in a filtration stage. | These processes should be applied in combination with good process control, gas collection and abatement systems. |
| **Performance Requirements.** | New secondary zinc smelters should be permitted to achieve stringent performance and reporting requirements associated with BAT. | Consideration should be given to the primary and secondary measures listed in Table 5.2 below. | Performance requirements for achievement should include:<br>- 0.1 ng/Nm$^3$ TEQ for PCDD/PCDF<br>- 5 mg/Nm$^3$ for particulate matter |

## Table 5.2 Summary of Primary and Secondary Measures for Secondary Zinc Smelters

| Measure | Description | Considerations | Other Comments |
|---|---|---|---|
| ***Primary Measures*** | | | |
| **Pre-sorting of feed material** | Oils and plastic in zinc scrap should be separated from the furnace feed to reduce the formation of PCDD/PCDF from incomplete combustion or by de-novo synthesis. | Processes to be considered include:<br>- Milling and grinding, in conjunction with pneumatic or density separation techniques, can be used to remove plastics.<br>- Oil removal conducted through thermal de-coating and de-oiling processes | Thermal de-coating and de-oiling processes for oil removal should be followed by afterburning to destroy any organic material in the off-gas. |
| **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. | PCDD/PCDF emissions may be minimized by controlling other variables such as temperature, | Continuous emissions sampling of PCDD/PCDF has been demonstrated for some sectors (e.g. waste incineration), but research is still developing in this field. |

| Measure | Description | Considerations | Other Comments |
|---|---|---|---|
| | | residence time, gas components and fume collection damper controls, after having established optimum operating conditions for the reduction of PCDD/PCDF. | |
| ***Secondary Measures*** | | | |
| **Fume and Gas Collection** | Effective fume and off-gas collection should be implemented in all stages of the smelting process to capture PCDD/PCDF emissions. | Processes to be considered include:<br>- Furnace-sealing systems to maintain a suitable furnace vacuum that avoids leaks and fugitive emissions.<br>- Use of hooding<br>- Hood additions of material, additions via tuyeres or lances and the use of robust rotary valves on feed systems. | BAT for gas and fume treatment systems are those that use cooling and heat recovery if practical before a fabric filter except when carried out as part of the production of sulphuric acid |
| **High Efficiency Dust Removal** | Dusts and metal compounds should be removed as this material possesses high surface area on which PCDD/PCDF easily adsorb. Removal of these dusts would contribute to the reduction of PCDD/PCDF emissions. | Processes to be considered include:<br>- Use of fabric filters, wet/dry scrubbers and ceramic filters. | Fabric filters using high performance materials are the most effective option. Collected particulate matter should be recycled in the furnace |
| **Afterburners and quenching** | Afterburners should be used at temperatures >950°C to ensure full combustion of organic compounds, followed by rapid quenching of hot gases to temperatures below 250°C. | Considerations include:<br>- PCDD/PCDF formation at 250-500°C, and destruction >850°C with $O_2$.<br>- Requirement for sufficient $O_2$in the upper region of the furnace for complete combustion.<br>- Need for proper design of cooling systems to minimise reformation time. | - De novo synthesis is still possible as the gases are cooled through the reformation window. |
| **Adsorption on Activated Carbon** | Activated carbon treatment should be considered as this material is an ideal medium for adsorption of PCDD/PCDF due to its large surface area. | Processes to be considered include:<br>- Treatment with activated carbon using fixed or moving bed reactors, | Lime/carbon mixtures can also be used. |

| Measure | Description | Considerations | Other Comments |
|---|---|---|---|
| | | - Injection of carbon particulate into the gas stream followed by removal as a filter dust. | |
| **Catalytic Oxidation** | Catalytic oxidation is an emerging technology which should be considered due to its high efficiency and lower energy consumption. Catalytic oxidation transforms organic compounds into water, $CO_2$ and hydrochloric acid using a precious metal catalyst. | Considerations include:<br>- Process efficiency for the vapour phase of contaminants.<br>- Hydrochloric acid treatment using scrubbers while water and $CO_2$ are released to the air after cooling. | Catalytic oxidation has been shown to destroy PCDD/PCDF with shorter residence times, lower energy consumption and 99% efficiency.<br>Off-gases should be de-dusted prior to catalytic oxidation for optimum efficiency. |

## 6.0 Performance Standards

Performance standards and timelines for achievement for new and existing secondary zinc smelters are recommended as shown:

**Table 5.3 Performance Standards for New and Existing Secondary Zinc Smelters**

| Type | Suggested Timeline | Emission Limit[16] |
|---|---|---|
| New | Entry into force | <0.1 ng /$Rm^3$ TEQ |
| Existing | Within 10 years of entry into force | <0.1 ng /$Rm^3$ TEQ |

## 7.0 Performance Reporting

Performance reporting is recommended as follows:

Annual isokinetic emission testing should be conducted at secondary zinc smelters and reported to the appropriate national or sub-national authority for:

- Polychlorinated dibenzoparadioxins;
- Polychlorinated dibenzofurans;
- Hexachlorobenzene; and
- Polychlorinated biphenyls.

Annual emission testing frequency could be reduced or suspended once emissions are shown to be 'eliminated' [17] on a continued and consistent basis.

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[16] $Rm^3$ indicates a reference volume at 298 K (25°C), 101.3 kPa (1 atmosphere), dry gas basis and operating $O_2$ levels.

This is considered as BAT for performance reporting.

Where isokinetic emission testing for the above substances is not possible (e.g. for fugitive emissions or some types of emission control technology or if analytical capacity is not readily available), emission factors associated with a similar plant type and operation are suggested as an interim performance reporting requirement until such time as annual emissions testing and analysis is available.

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[17] The Government of Canada has established levels of quantification (LOQ) for virtual elimination of PCDD/PCDF, HCB and PCBs in air as follows: <32 pg/Rm$^3$ TEQ, <6 ng/Rm$^3$ HCB, and <2 ng/Rm$^3$ PCB, respectively. Consideration should be given to appropriate emissions levels associated with elimination of these substances.

# Attachment 5

# Draft Guidelines on Best Available Techniques (BAT) for Secondary Lead Smelting

## List of Contents

## *1.0 Process Description*

*"Secondary lead smelters produce lead and lead alloys from lead-bearing scrap material. More than 60 percent of all secondary lead is derived from scrap automobile batteries. Other raw materials used in secondary lead smelting include wheel balance weights, pipe, solder, drosses, and lead sheathing.*

*Secondary lead smelting includes 3 major operations: scrap pre-treatment, smelting, and refining. Scrap pre-treatment is the partial removal of metal and nonmetal contaminants from leadbearing scrap and residue. Processes used for scrap pre-treatment include battery breaking, crushing, and sweating. Battery breaking is the draining and crushing of batteries, followed by manual separation of the lead from nonmetallic materials. This separated lead scrap is then sweated in a gas- or oil-fired reverberatory or rotary furnace to separate lead from metals with higher melting points. Rotary furnaces are usually used to process low-lead-content scrap and residue, while reverberatory furnaces are used to process high-lead-content scrap. The partially purified lead is periodically tapped from these furnaces for further processing in smelting furnaces or pot furnaces.*

*Smelting produces lead by melting and separating the lead from metal and non-metallic contaminants and by reducing oxides to elemental lead. Smelting is carried out in blast, reverberatory, and rotary kiln furnaces. In blast furnaces pre-treated scrap metal, rerun slag, scrap iron, coke, recycled dross, flue dust, and limestone are used as charge materials to the furnace. The process heat needed to melt the lead is produced by the reaction of the charged coke with blast air that is blown into the furnace. Some of the coke combusts to melt the charge, while the remainder reduces lead oxides to elemental lead. As the lead charge melts, limestone and iron float to the top of the molten bath and form a flux that retards oxidation of the product lead. The molten lead flows from the furnace into a holding pot at a nearly continuous rate.*

*Refining and casting the crude lead from the smelting furnaces can consist of softening, alloying, and oxidation depending on the degree of purity or alloy type desired. These operations can be performed in reverberatory furnaces; however, kettle-type furnaces are most commonly used. Alloying furnaces simply melt and mix ingots of lead and alloy materials. Antimony, tin, arsenic, copper, and nickel are the most common alloying materials. Oxidizing furnaces, either kettle or reverberatory units, are used to oxidize lead and to entrain the product lead oxides in the combustion air stream for subsequent recovery in high-efficiency baghouses."* [1]

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[1] US Environmental Protection Agency, *Background Report AP-42 Section 12.11, Secondary Lead Processing*, October 1986. URL: www.epa.gov/ttn/chief/ap42/ch12/final/c12s11.pdf

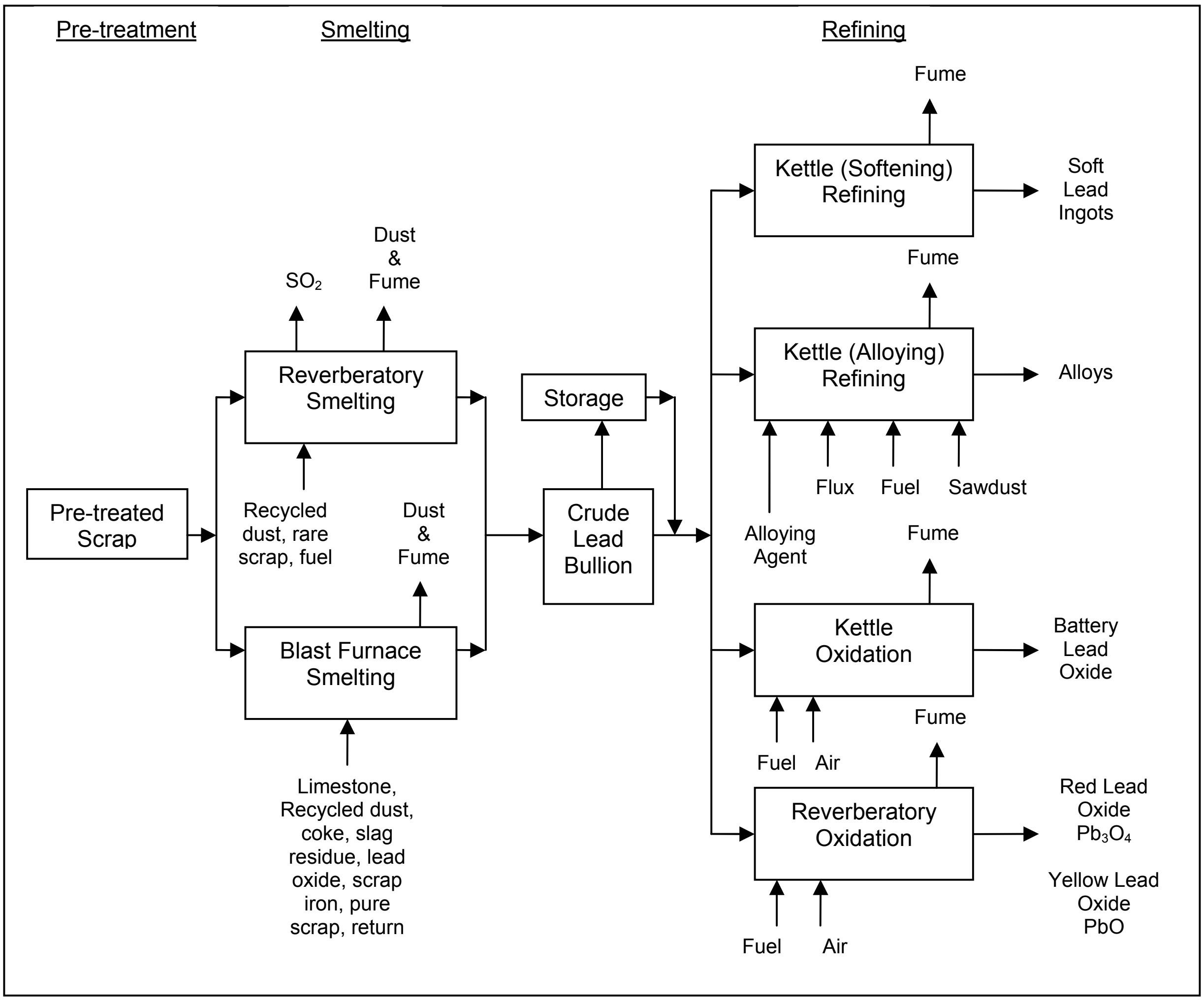

Figure 1 Secondary Lead Smelting[2]

## 2.0 *Sources of Unintentionally Produced POPs*

The formation of polychlorinated dibenzoparadioxins (PCDD) and polychlorinated dibenzofurans (PCDF) is probable due to the presence of chlorine from plastics and trace oils in the feed material.

### 2.1 Emissions of PCDD/PCDF

PCDD/PCDF are formed during base metals smelting through incomplete combustion or by de-novo synthesis when organic and chlorine compounds such as oils and plastics are present in the feed material.

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[2] Ibid.

*"PCDD/PCDF or their precursors may be present in some raw materials and there is a possibility of de-novo synthesis in furnaces or abatement systems. PCDD/PCDF are easily adsorbed onto solid matter and may be collected by all environmental media as dust, scrubber solids and filter dust.*

*The presence of oils and other organic materials on 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 PCDD/PCDF. This process is known as de-novo synthesis and is catalysed by the presence of metals such as copper or iron.*

*Although PCDD/PCDF 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 through the "reformation window". This window can be present in abatement systems and in cooler parts of the furnace e.g. the feed area. Care taken in the design of cooling systems to minimise the residence time in the window is practised to prevent de-novo synthesis."*[3]

## 2.2 General Information on Emissions from Secondary Lead Smelters[4]

Air emissions from secondary lead smelting can escape as stack or fugitive emissions depending on the facility age or technology. Main contaminants are sulphur dioxide ($SO_2$), other sulphur compounds and acid mists, nitrogen oxides ($NO_x$), metals, especially lead, and their compounds, dusts and PCDD/PCDF. $SO_2$ is collected and processed into sulphuric acid in acid plants. Fugitive $SO_2$ emissions can be controlled by good extraction and sealing of furnaces. $NO_x$ can be reduced using low $NO_x$ or oxy-fuel burners. Particulate matter is collected using high efficiency dust removal methods such as fabric filters and returned to the process.

Wastewater originates from process effluent, cooling water and runoff and is treated using wastewater treatment techniques. Process residues are recycled, treated using downstream methods to recover other metals, or safely disposed.

## *3.0 New Secondary Lead Smelters*

The Stockholm Convention states that when proposals are considered to construct new facilities or significantly modify existing facilities using processes that release POPs, priority consideration should be given to alternative processes, techniques or practices

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[3] European Commission*, Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p. 133.

[4] European Commission*, Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p. 359-368.

that have similar usefulness but which avoid the formation and release of these chemicals.[5]

No information is available on alternate processes to smelting for secondary copper processing.

## 3.1 Recommended Processes for New Secondary Lead Smelters

Variation in feed material and desired product quality influences process design and configuration. These processes should be applied in combination with good process control, gas collection and abatement systems. Processes considered as BAT include the blast furnace (with good process control), the ISA Smelt/Ausmelt furnace, the Top Blown Rotary furnace, the electric furnace and the rotary furnace.[6]

The submerged arc electric furnace is a sealed unit for mixed copper and lead materials. It is cleaner than other processes if the gas extraction system is well designed and sized.[7]

*"The injection of fine material via the tuyeres of a blast furnace has been successfully used and reduces the handling of dusty material and the energy involved in returning the fines to a sinter plant."*[8] This technique minimises dust emissions during charging and thus reduces the release of PCDD/PCDF through adsorption on particulate matter.

## 3.2 Performance Requirements for New Secondary Lead Smelters[9]

New secondary lead smelters should be designed and operated to achieve reductions in emissions levels as shown:

- <0.1 ng/Nm$^3$ TEQ for PCDD/PCDF

  Methods to achieve targeted emissions level:
  - high efficiency dust removal systems (e.g. fabric filters)
  - afterburners and quenching
  - adsorption on activated carbon

- < 5 mg/Nm$^3$ for particulate matter

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[5] Stockholm Convention on Persistent Organic Pollutants, 2001. URL: www.pops.int/documents/convtext/convtext_en.pdf

[6] European Commission, *Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p. 379.

[7] European Commission, *Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p. 395.

[8] European Commission, *Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p. 404.

[9] European Commission, *Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p. 400.

Methods to achieve targeted emissions level:

- high efficiency dust removal systems (e.g. fabric filters)

## *4.0 Primary and Secondary Measures*

Primary and secondary measures of PCDD/PCDF reduction and elimination are discussed below.

### 4.1 Primary Measures

Primary measures are regarded as pollution prevention techniques to reduce or eliminate the generation and release of POPs. Possible measures include:

1. Pre-sorting of Feed Material:

   Scrap should be sorted and pre-treated to remove organic compounds and plastics to reduce PCDD/PCDF generation from incomplete combustion or by de-novo synthesis. Whole battery feed or incomplete separation should be avoided. Feed storage, handling and pre-treatment techniques will be determined by material size distribution, contaminants and metal content.

   Milling and grinding, in conjunction with pneumatic or density separation techniques, can be used to remove plastics. Oil removal can be achieved through thermal de-coating and de-oiling processes. Thermal de-coating and de-oiling processes for oil removal should be followed by afterburning to destroy any organic material in the off-gas.[10]

2. 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.

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[10] European Commission*, Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p. 232.

> *"Particular attention is needed for the temperature measurement and control for furnaces and kettles used for melting the metals in this group so that fume formation is prevented or minimised."* [11]

## 4.2 Secondary Measures

Secondary measures are pollution control techniques to contain and prevent emissions. These methods do not prevent the formation of contaminants.

1. Fume and Gas Collection:

   Fume and off-gas collection should be implemented in all stages of the smelting process to control PCDD/PCDF emissions.

   *"The fume collection systems used can exploit furnace-sealing systems and be designed to maintain a suitable furnace depression that avoids leaks and fugitive emissions. Systems that maintain furnace sealing or hood deployment can be used. Examples are through hood additions of material, additions via tuyeres or lances and the use of robust rotary valves on feed systems. An [efficient] fume collection system capable of targeting the fume extraction to the source and duration of any fume will consume less energy. BAT for gas and fume treatment systems are those that use cooling and heat recovery if practical before a fabric filter except when carried out as part of the production of sulphuric acid."* [12]

2. High Efficiency Dust Removal:

   Dusts and metal compounds generated from the smelting process should be removed. This particulate matter possesses high surface area on which PCDD/PCDF easily adsorb. Removal of these dusts would contribute to the reduction of PCDD/PCDF emissions. Techniques to be considered are the use of fabric filters, wet/dry scrubbers and ceramic filters. Collected particulate should be recycled in the furnace.

   Fabric filters using high performance materials are the most effective option. Innovations regarding this method include bag burst detection systems, online cleaning methods, and catalytic coatings to destroy PCDD/PCDF. [13]

3. Afterburners and quenching:

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[11] European Commission, *Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p. 390.

[12] European Commission, *Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p. 397.

[13] European Commission, *Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p.139-140.

Afterburners (post-combustion) should be used at a minimum temperature of 950°C to ensure full combustion of organic compounds.[14] This stage is to be followed by rapid quenching of hot gases to temperatures below 250°C. Oxygen injection in the upper portion of the furnace will promote complete combustion.[15]

It has been observed that PCDD/PCDF are formed in the temperature range of 250 to 500°C. These are destroyed above 850°C in the presence of oxygen. Yet, *de novo* synthesis is still possible as the gases are cooled through the reformation window present in abatement systems and cooler areas of the furnace. Proper operation of cooling systems to minimise reformation time should be implemented.[16]

4. Adsorption on Activated Carbon:

Activated carbon treatment should be considered for PCDD/PCDF removal from smelter off-gases. Activated carbon possesses large surface area on which PCDD/PCDF can be adsorbed. Off-gases can be treated with activated carbon using fixed or moving bed reactors, or injection of carbon particulate into the gas stream followed by removal as a filter dust using high efficiency dust removal systems such as fabric filters.

5. Catalytic Oxidation:

Catalytic oxidation is an emerging technology used in waste incinerators to eliminate PCDD/PCDF emissions. This process should be considered by secondary base metals smelters as it has proven effective for PCDD/PCDF destruction in waste incinerators.

Catalytic oxidation processes organic compounds into water, carbon dioxide ($CO_2$) and hydrochloric acid using a precious metal catalyst to increase the rate of reaction at 370 to 450°C. In comparison, incineration occurs typically at 980°C. Catalytic oxidation has been shown to destroy PCDD/PCDF with shorter residence times, lower energy consumption and 99% efficiency, and should be considered. Off-gases should be de-dusted prior to catalytic oxidation for optimum efficiency. This method is effective for the vapour phase of contaminants. The resulting hydrochloric acid is treated in a scrubber while the water and $CO_2$ are released to the air after cooling.[17]

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[14] Hübner C., et. al., *State-Of-The-Art Measures For Dioxin Reduction In Austria*, 2000. URL: www.ubavie.gv.at/publikationen/Mono/M116s.htm

[15] European Commission, *Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p. 189.

[16] European Commission, *Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p. 133.

[17] Parvesse, T., Chemical Processing, *Controlling Emissions from Halogenated Solvents*, April 2001. URL: www.chemicalprocessing.com/Web_First/cp.nsf/ArticleID/NJEC-4VPKAW/

## 5.0 Summary of Measures

### Table 5.1 Measures for New Secondary Lead Smelters

| Measure | Description | Considerations | Other comments |
|---|---|---|---|
| ***New Secondary Lead Smelters*** | | | |
| **Recommended Processes** | Various recommended smelting processes should be considered for new facilities. | Processes to be considered include:<br>- Blast furnace (with good process control), ISA Smelt/Ausmelt furnace, Top Blown Rotary furnace, electric furnace and rotary furnace<br>- Submerged electric arc furnace (it is a sealed unit for mixed copper and lead materials, cleaner than other processes if gas extraction system is well designed and sized)<br>-injection of fine material via the tuyeres of a blast furnace reduces handling of dusty material | These processes should be applied in combination with good process control, gas collection and abatement systems. |
| **Performance Requirements.** | New secondary lead smelters should be regulated to fulfill stringent performance and reporting requirements associated with BAT. | Consideration should be given to the primary and secondary measures listed in Table 5.2 below. | Performance requirements for achievement should include:<br>- 0.1 ng/Nm$^3$ TEQ for PCDD/PCDF<br>- 5 mg/Nm$^3$ for particulate matter |

### Table 5.2 Summary of Primary and Secondary Measures for Secondary Lead Smelters

| Measure | Description | Considerations | Other Comments |
|---|---|---|---|
| ***Primary Measures*** | | | |
| **Pre-sorting of feed material** | Scrap should be sorted and pre-treated to remove organic compounds and plastics to reduce PCDD/PCDF generation from incomplete combustion or by de-novo synthesis. | Processes to be considered include:<br>- Avoidance of whole battery feed or incomplete separation.<br>- Milling and grinding, followed by pneumatic or density separation techniques, to remove plastics | Thermal de-coating and de-oiling processes for oil removal should be followed by afterburning to destroy any organic material in the off-gas |

| Measure | Description | Considerations | Other Comments |
|---|---|---|---|
| | | - Oil removal conducted through thermal de-coating and de-oiling processes | |
| **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. | PCDD/PCDF emissions may be minimized by controlling other variables such as temperature, residence time, gas components and fume collection damper controls after having established optimum operating conditions for the reduction of PCDD/PCDF. | Continuous emissions sampling of PCDD/PCDF has been demonstrated for some sectors (e.g. waste incineration), but research is still developing in this field. Particular attention is needed for the temperature measurement and control for furnaces and kettles used for melting the metals in this group so that fume formation is prevented or minimised |
| ***Secondary Measures*** | | | |
| **Fume and Gas Collection** | Fume and off-gas collection should be implemented in all stages of the smelting process to capture PCDD/PCDF emissions. | Processes to be considered include:<br>- Furnace-sealing systems to maintain a suitable furnace vacuum that avoids leaks and fugitive emissions.<br>- Use of hooding<br>- Hood additions of material, additions via tuyeres or lances and the use of robust rotary valves on feed systems. | BAT for gas and fume treatment systems are those that use cooling and heat recovery if practical before a fabric filter. |
| **High Efficiency Dust Removal** | Dusts and metal compounds should be removed as this material possesses high surface area on which PCDD/PCDF easily adsorb. Removal of these dusts would contribute to the reduction of PCDD/PCDF emissions. | Processes to be considered include:<br>- Use of fabric filters, wet/dry scrubbers and ceramic filters. | Fabric filters using high performance materials are the most effective option. Collected particulate matter should be recycled in the furnace. |
| **Afterburners and quenching** | Afterburners should be used at temperatures >950°C to ensure full combustion of organic compounds, followed by rapid quenching of hot gases to temperatures below 250°C. | Considerations include:<br>- PCDD/PCDF formation at 250-500°C, and destruction >850°C with $O_2$.<br>- Requirement for sufficient $O_2$in the upper region of the furnace for complete | - De novo synthesis is still possible as the gases are cooled through the reformation window. |

| Measure | Description | Considerations | Other Comments |
|---|---|---|---|
| | | combustion.<br>- Need for proper design of cooling systems to minimise reformation time. | |
| **Adsorption on Activated Carbon** | Activated carbon treatment should be considered as this material is an ideal medium for adsorption of PCDD/PCDF due to its large surface area. | Processes to be considered include:<br>- Treatment with activated carbon using fixed or moving bed reactors,<br>- Injection of carbon particulate into the gas stream followed by removal as a filter dust. | Lime/carbon mixtures can also be used. |
| **Catalytic Oxidation** | Catalytic oxidation is an emerging technology which should be considered due to its high efficiency and lower energy consumption. Catalytic oxidation transforms organic compounds into water, $CO_2$ and hydrochloric acid using a precious metal catalyst. | Considerations include:<br>- Process efficiency for the vapour phase of contaminants.<br>- Hydrochloric acid treatment using scrubbers while water and $CO_2$ are released to the air after cooling. | Catalytic oxidation has been shown to destroy PCDD/PCDF with shorter residence times, lower energy consumption and 99% efficiency.<br>Off-gases should be de-dusted prior to catalytic oxidation for optimum efficiency. |

## *6.0 Performance Standards*

Performance standards and timelines for achievement for new and existing secondary lead smelters are recommended as shown:

**Table 5.3 Performance Standards for New and Existing Secondary Lead Smelters**

| Type | Suggested Timeline | Emission Limit[18] |
|---|---|---|
| New | Entry into force | <0.1 ng/Rm$^3$ TEQ |
| Existing | Within 10 years of entry into force | <0.1 ng/Rm$^3$ TEQ |

## *7.0 Performance Reporting*

Performance reporting is recommended as follows:

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[18] Rm$^3$ indicates a reference volume at 298 K (25°C), 101.3 kPa (1 atmosphere), dry gas basis and operating $O_2$ levels.

Annual isokinetic emission testing should be conducted at secondary lead smelters and reported to the appropriate national or sub-national authority for:

- Polychlorinated dibenzoparadioxins;
- Polychlorinated dibenzofurans;
- Hexachlorobenzene; and
- Polychlorinated biphenyls.

Annual emission testing frequency could be reduced or suspended once emissions are shown to be 'eliminated' [19] on a continued and consistent basis.

This is considered as BAT for performance reporting.

Where isokinetic emission testing for the above substances is not possible (e.g. for fugitive emissions or some types of emission control technology or if analytical capacity is not readily available), emission factors associated with a similar plant type and operation are suggested as an interim performance reporting requirement until such time as annual emissions testing and analysis is available.

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[19] The Government of Canada has established levels of quantification (LOQ) for virtual elimination of PCDD/PCDF, HCB and PCBs in air as follows: <32 pg/Rm$^3$ TEQ, <6 ng/Rm$^3$ HCB, and <2 ng/Rm$^3$ PCB, respectively. Consideration should be given to appropriate emissions levels associated with elimination of these substances.

# Attachment 6

# Draft Guidelines on Best Available Techniques (BAT) for Primary Aluminium

## List of Contents

## *Process Description*

Primary aluminium production refers to aluminium produced directly from the mined ore, bauxite. The bauxite is refined into alumina by the Bayer Process, and then the alumina is reduced by electrolysis (the Hall-Héroult Process) into metallic aluminum. This chapter does not cover the secondary aluminium processes, which is covered in **section C.4.3 (Thermal Metallurgical Processes Part II Source Categories)**.

### The Bayer Process: Refining Bauxite to Alumina

Bauxite is converted to alumina using the Bayer Process. The bauxite ore is dried, crushed and ground into a powder and mixed with a solution of caustic soda to extract the alumina at elevated temperatures and pressures in digesters. A slurry is produced which contains dissolved sodium aluminate and a mixture of metal oxides called "red mud" that is removed in thickeners. The red mud is washed to recover the chemicals and is disposed. The aluminate solution is cooled and seeded with alumina to crystallize the hydrated alumina in precipitator tanks. The crystals are washed and then calcined in rotary kilns or fluid bed/fluid flash calciners to produce the aluminium oxide or alumina, which is a white powder resembling table salt.

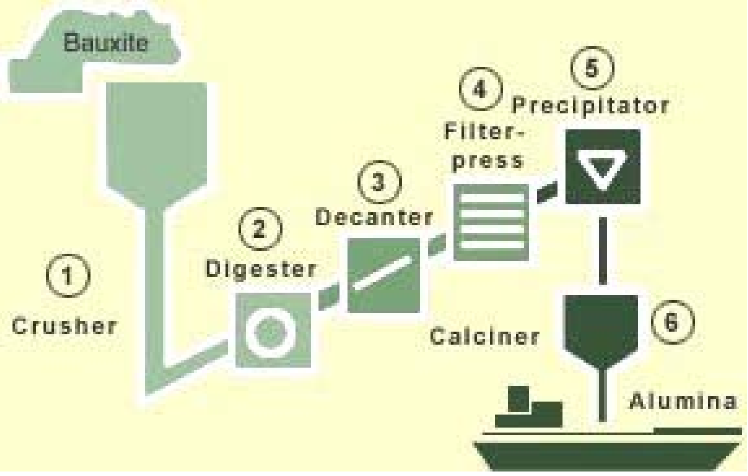

**Figure 1: Simplified Flow Sheet for Alumina Production**[1]

### The Hall-Héroult Process: Reduction by Electrolysis of Alumina to Aluminum

Aluminium is produced from alumina by electrolysis in a process known as the Hall-Héroult Process. The alumina is dissolved in an electrolytic bath of molten cryolite (sodium aluminium fluoride). An electric current is passed through the electrolyte and flows between the anode and cathode. Molten aluminium is produced, deposited at the bottom of the electrolytic cell, or "pot", and periodically siphoned off and transferred to a

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[1] **Aluminium Association of Canada, http://aac.aluminium.qc.ca/anglais/production/index.html**

reverberatory holding furnace. There it is alloyed, fluxed and degassed to remove trace impurities. Finally, the aluminium is cast or transported to the fabricating plants.

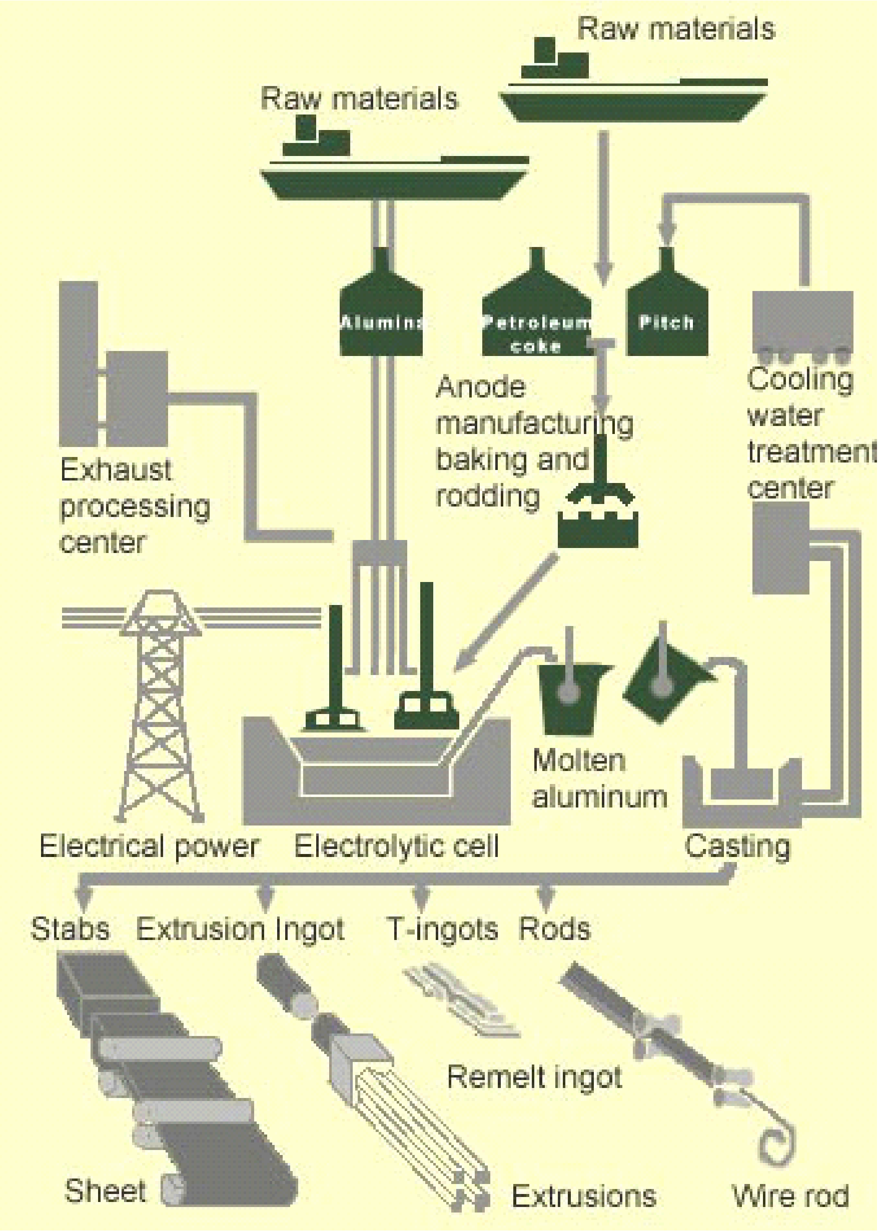

**Figure 2: General Schematic of the Electrolytic Process**[2]

There are two types of technologies used for the production of aluminium, those using self-baking anodes (Söderberg anodes) and those using pre-baked anodes.

The older Söderberg anodes are made in-situ from a paste of calcined petroleum coke and coal tar pitch, and are baked by the heat from the molten electrolytic bath. As the

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[2] **Aluminium Association of Canada, http://aac.aluminium.qc.ca/anglais/production/index.html**

anode is consumed, more paste descends through the anode shell in a process that does not require anode changes. Alumina is added periodically to Söderberg cells through holes made by breaking the crust alumina and frozen electrolyte which covers the molten bath. Depending on the placement of the anode studs, these are known as Vertical Stud Söderberg (VSS) or Horizontal Stud Söderberg (HSS) cells or pots. Automatic point feeding systems are used in upgraded plants, eliminating the need for regular braking of the crust.

Pre-bake anodes are manufactured in a carbon plant from a mixture of calcined petroleum coke and coal tar pitch that is formed into a block and baked in an anode furnace. The pre-bake anode production plants are often an integrated part of the primary aluminium plant. The pre-baked anodes are gradually lowered into the pots as they are consumed, and need to be replaced before the entire block has been consumed. The anode remnants, known as anode “butts”, are cleaned and returned to the carbon plant for recycling. Depending on the method of feeding the alumina into the electrolytic cells, the cells are called Side-Worked Pre-Bake (SWPB) or Center-Worked Pre-Bake (CWPB). For SWPB cells, the alumina is fed to the cells after the crust is broken around the perimeter. For CWPB cells, the alumina is fed to the cells after the crust is broken along the centreline or at selected points on the centreline of the cell.

The cathode typically has to be replaced every 5 to 8 years because of deterioration which can allow the molten electrolyte and aluminium to penetrate the cathode conductor bar and steel shell. The spent cathode, known as spent pot lining, contains hazardous and toxic substances such as cyanides and fluorides which must be disposed of properly.

Molten alumina is periodically withdrawn from the cells by vacuum siphon and is transferred to crucibles. The crucibles containing liquid metal are transported to the casting plant where the aluminium is transferred to the holding furnaces. Alloying elements are added in these furnaces. Dross (“skimmings”) formed by the oxidation of molten aluminium is skimmed off, sealed containers are used to minimize further oxidation of the dross, nitrogen and argon blanketing is used. This is followed by removal sodium, magnesium, calcium and hydrogen. The treatment gas used varies depending on the impurities, argon or nitrogen is used to remove hydrogen; mixtures of chlorine with nitrogen or argon are used to remove metallic impurities.

## *Sources of Unintentionally Produced POPs*

Primary aluminium production is unlikely to be a significant source of dioxin and furan releases although contamination is possible through the graphite-based electrodes[3].

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[3] AEA Technology Environment, *Releases of Dioxins and Furans to Land and Water in Europe*, prepared for Landesumweltamt Nordrhein-Westfalen, Germany, on behalf of European Commission DG Environment, September 1999, p. 63

However, release levels are generally thought to be low and the main interest is in the thermal processing of scrap materials[4].

## 2.1 Emissions of Dioxins and Furans

There is limited information available on dioxins and furans formation from primary aluminium processes. No emission factors have been developed for the industry and available literature suggests that initial emissions testing indicate that dioxins and furans are not considered significant from this sector.

It is unlikely that the Söderberg and pre-baked processes release significantly different emissions per tonne of aluminium produced[5]. Test results on emission sources and abatement units associated with pre-bake anode manufacturing indicate that dioxins are not significant from these sources. However, if chlorine compounds or additives are used, emissions will need to be examined.[6]

Some studies have tested for dioxins in fume from the casting process because the use of chlorine for degassing and the presence of carbon from the combustion gases may lead to the formation of dioxins. Results from primary smelter cast houses have shown that releases are significantly below 1 gram per year.[7] The potential for dioxin formation during the refining processes for both primary and secondary aluminium production has not been fully investigated. It has been recommended that this source be quantified.[8]

## 2.2 Releases to Land[9]

The production of primary aluminium from ores is not thought to produce significant quantities of dioxins and furans. The UK Review of Dioxin Releases to Land and Water states that there may be the possibility of graphite-based electrodes having some dioxin and furan contamination. Swedish data suggests the spent sludge from the cells may contain 7.8 ng Nordic-TEQ $kg^{-1}$. However, if the cathode is high purity carbon material

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[4] UNEP Chemicals, *Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases*, 1st Edition, Geneva, Switzerland, May 2003, p. 73.

[5] AEA Technology Environment, *Releases of Dioxins and Furans to Land and Water in Europe*, prepared for Landesumweltamt Nordrhein-Westfalen, Germany, on behalf of European Commission DG Environment, September 1999, p. 63.

[6] European Integrated Pollution Prevention and Control Bureau (EIPPCB), *Reference Document on Best Available Techniques in the Non-Ferrous Metals Industries*, Seville, Spain, 2001, p.669.

[7] Ibid., p. 289.

[8] Ibid., p. 318.

[9] New Zealand Ministry for the Environment, *New Zealand inventory of dioxin emissions to air, land and water, and reservoir sources*, March 2000, p. 80 (url: http://www.mfe.govt.nz/publications/hazardous/dioxin-emissions-inventory-mar00.pdf). And references within to the UK Environment Agency report: *A Review of Dioxin Releases to Land and Water in the UK*, Research and Development Publication 3. Environment Agency, Bristol, United Kingdom, 1997.

and the reduction process does not involve chlorine or chloride materials, it is unlikely that dioxins and furans will be present.

Metal reclaim fines may contain dioxins and furans because chlorine or chlorine based products are used to degas the fraction of the aluminium that is poured into the extrusion billets.

## 2.3 Research Findings of Interest

Limited information exists on the unintentional formation of dioxins and furans from this sector. It is not considered to be a significant source of releases.

## 2.4 General Information on Releases from Primary Aluminium Plants[10]

Greenhouse gases are a major pollutant from aluminium production and result from fossil fuel combustion, carbon anode consumption, and perfluorocarbons from anode effects. In addition to greenhouse gases, aluminium smelters also discharge other atmospheric emissions, as well as some solid wastes (spent potliners) and liquid effluents. (p. 3-14)

*The use of carbon anodes leads to emissions of sulphur dioxide ($SO_2$), carbonyl sulphide (COS), polycyclic aromatic hydrocarbons (PAHs) and nitrogen oxides ($NO_x$). Most of the sulphur in the carbon anode is released as COS, which is not entirely oxidized to $SO_2$ before being emitted at the potroom gas scrubber stacks. Sulphur emissions are predominately in the form of $SO_2$ with a minor component of COS. The emission of sulphur gases from aluminium reduction is expected to rise with the increasing sulphur content of petroleum cokes used for anode manufacture. PAHs are the result of incomplete combustion of hydrocarbons found in certain pitch used to form the anodes. The use of prebake anodes has virtually eliminated the emissions of PAHs, mainly associated with Söderberg anodes. The $NO_x$ emissions mainly come from the combustion of fuel in the anode baking furnace.* [p. 3-14]

*The electrolysis of alumina also leads to the emission of fluorides (particulate fluorides and gaseous HF) and other particulates. The removal of fluorides from the cell gases in modern alumina injection dry scrubber systems is now greater than 99% efficient and the final fluoride emissions from modern prebake smelters are significantly lower. Anode changing and cooling of spent anode butts are the most important sources of fugitive fluoride emissions from an aluminium smelter and these are estimated to 4 to 5 times greater than stack emissions (after the scrubber).* [p. 3-16]

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[10] SNC-Lavalin Environment, *Evaluation of Feasibility and Roadmap for Implementing Aluminium Production Technologies that Reduce/Eliminate Greenhouse Gases and Other Emissions*, prepared for Environment Canada, November 2002. pp. 3-14 to 3-16.

The “anode effect” results in generation of perfluorocarbons (PFC) in smelting pots when the concentration of alumina falls below a certain level due to the lack of fresh feed. The carbon anode preferentially reacts with the fluorine in the cryolite solution because there is insufficient oxygen available from the alumina. When this event occurs, $CF_4$ and $C_2F_6$ are produced along with a surge in voltage. The amount of PFCs generated depends on the efficiency of feed control in the pot. For pots not equipped with proper controls, PFC emissions from anode effects can be the largest source, accounting for over 50% of the total smelter emissions (on a $CO_2$-equivalent basis). Practically any point-fed, computer-controlled pot can operate at low anode effect frequency. Older technologies such as HSS and VSS have higher PFC generation rates. These technologies typically do not have individual pot sensing systems and the feed is usually a non-automated bulk system. The process control techniques in modern pre-baked smelters are such that the PFC emissions can be reduced to less than 5% of the total GHG emissions from the smelter. $CO_2$ emissions from anode consumption are the next largest source for pots without modern controls. [p. 3-10 to 11]

**Table 1: Emissions, Effluents, By-products and Solid Wastes from Primary Aluminium Production**[11]

| Process | Air Emissions [a] | Effluents | By-products and Solid Wastes |
|---|---|---|---|
| Alumina Refining | Particulate | Wastewater containing starch, sand, and caustic | Red mud, sodium oxalate |
| Anode Production | Particulates, fluorides, polycyclic aromatic hydrocarbons (PAH), $SO_2$ | Wastewater containing suspended solids, fluorides, and organics | Carbon dust, tar, refractory waste |
| Aluminum Smelting | CO, $CO_2$, $SO_2$, fluorides (gaseous and particulate), perfluorocarbons ($CF_4$, $C_2F_6$), PAH | Wet air pollution control effluents (wet ESP) | Spent potliners, wet air pollution control wastes, sludges |

[a] Excluding combustion-related emissions.

## *3.0 New Primary Aluminium Plants*

The Stockholm Convention states that when consideration is being given to proposals for construction of a new primary aluminium plant, 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. [Text taken from Draft Guidelines on BAT for Iron Sintering].

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[11] Energetics Inc., *Energy and Environmental Profile of the U.S. Aluminum Industry*, prepared by Energetics, for the U.S. Dept of Energy, Office of Industrial Technologies, Maryland, U.S., July 1997. (url: http://www.oit.doe.gov/aluminum/pdfs/alprofile.pdf)

## 3.1 Alternate Processes to Primary Aluminium Smelting (Emerging Technologies)

There are a number of research initiatives currently underway to produce primary aluminium while concurrently reducing energy consumption and emissions. These include[12, 13, 14, 15, 16]:

- Inert Anodes: Carbon-free anodes that are inert, dimensionally stable, that are slowly consumed, produce oxygen instead of $CO_2$. The use of inert anodes eliminates the need for an anode carbon plant (and PAH emissions from the process).
- Wettable Cathodes: New cathode materials or coatings for existing cathode materials that allow for better energy efficiency.
- Vertical Electrodes – Low Temperature Electrolysis (“VELTE”): The process uses a non-consumable metal alloy anode, a wetted cathode and an electrolytic bath, which is kept saturated with alumina at the relatively low temperature of 750°C by means of free alumina particles suspended in the bath. This technology could produce primary aluminium metal with lower energy consumption, lower cost, and lower environmental degradation than the conventional Hall-Héroult process.
- Drained Cell Technology: features the coating of aluminum cell cathodes with titanium dibromide and eliminating the metal pad, which reduces the distance between anode and cathode, thereby lowering the required cell voltage and reducing heat loss.
- Carbothermic Technology: Carbothermic reduction produces aluminum using a chemical reaction that takes place within a reactor and requires much less physical space than with the Hall-Héroult reaction. This process would result in significantly reduced electrical consumption, and the elimination of perfluorocarbon emissions resulting from carbon anode effects, hazardous spent pot liners, and hydrocarbon emissions associated with the baking of consumable carbon anodes.
- Kaolinite Reduction Technology: The production of aluminum by reduction of aluminum chloride using clays holds appeal because the raw materials are readily available and inexpensive. The thermodynamics also provide high-speed

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[12] European Integrated Pollution Prevention and Control Bureau (EIPPCB), *Reference Document on Best Available Techniques in the Non-Ferrous Metals Industries*, Seville, Spain, 2001, p. 335.

[13] SNC-Lavalin Environment, *Evaluation of Feasibility and Roadmap for Implementing Aluminium Production Technologies that Reduce/Eliminate Greenhouse Gases and Other Emissions*, prepared for Environment Canada, November 2002.

[14] Welsh, Barry J., “Aluminum Production Paths in the New Millennium” in JOM, 51 (5) (1999), pp. 24–28. (url: http://www.tms.org/pubs/journals/JOM/9905/Welch-9905.html)

[15] USGS, APPENDIX 2 -- ALUMINUM CASE STUDY from: Technological Advancement -- A Factor in Increasing Resource Use, Open-File Report 01-197, Online version 1.02 (url: http://pubs.usgs.gov/of/of01-197/html/app2.htm)

[16] BCS Inc., *U.S. Energy Requirements for Aluminum Production: Historical Perspectives, Theoretical Limits and New Opportunities*, prepared under contract for the U.S. Department of Energy, Energy Efficiency and Renewable Energy, February 2003. p. 41-58.

conversion reactions with lower electrical demand and no bauxite residue is produced.

## 3.2 Performance Requirements for New Primary Aluminium Plants

** The author has found no references on which to base a recommended standard for the releases of dioxins and furans from primary aluminium plants.

# *4.0 Primary and Secondary Measures*

*Primary and secondary measures for reducing emissions of dioxins and furans from primary aluminium production processes are outlined below.*

*The extent of emission reduction possible with the 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 at existing plants [**from Guidelines on BAT for Iron Sintering**].*

Note that no specific secondary measures have been developed specifically for the primary aluminium smelters to control the unintentional formation of dioxins and furans. The following measures identified below constitute general measures which may result in lower pollutant emissions at primary aluminium smelters, including releases of dioxins and furans.

## 4.1 Primary Measures

(Process integrated, holistic measures, primary Pollution Prevention)

Primary measures are understood to be pollution prevention measures that will prevent or minimize the formation and release of the identified substances (particulates, fluorides, polycyclic aromatic hydrocarbons, sulphur dioxide, carbon dioxide, carbon monoxide, and perfluorocarbons – Note that there are no primary measures identified for dioxins and furans). 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*. [**Taken from the Iron Sintering BAT Guidelines**]

For new smelters, using the prebake technology rather than the Söderberg technology for aluminium smelting is a significant pollution prevention measure.[17] The use of

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[17] World Bank, *Pollution Prevention and Abatement Handbook 1998*, Industry Sector Guidelines – Aluminum Manufacturing, Washington, D.C., 1999.

centre-worked prebaked cells with automatic multiple feeding points is considered to be BAT for the production of primary aluminium.[18]

*Point feeders enable more precise, incremental feeding for better cell operation. They are generally located at the centre of the cell and thereby cut down on the diffusion required to move dissolved alumina to the anodic reaction sites. The controlled addition of discrete amounts of alumina enhances the dissolution process, which aids in improving cell stability and control, minimizing anode effects, and decreasing the formation of undissolved sludge on the cathode. In the jargon of modern commerce, point feeders enable "just-in-time alumina supply" to permit optimum cell operation. Point feeder improvements continue to be made as more accurate cell controllers become available.*[19]

Advanced process controllers are also being adopted by industry to reduce the frequency of anode effects and control operational variables, particularly bath chemistry and alumina saturation, so that cells to remain at their optimal conditions.[20]

Primary measures which may assist in reducing the formation and release of the identified substances include:[21]

- An established system for environmental management, operational control and maintenance.
- Computer control of the electrolysis process based on active cell databases and monitoring of cell operating parameters to minimise the energy consumption and reduce the number and duration of anode effects.
- If local, regional or long-range environmental impacts require $SO_2$ reductions, the use of low sulphur carbon for the anodes or anode paste if practicable or a $SO_2$ scrubbing system.

## 4.2 Secondary Measures

(End of pipe measures)

Secondary measures are understood to be pollution control technologies or techniques, sometimes described as 'end-of-pipe' treatments. <u>Note that the following are not considered secondary measures specific to minimization of dioxins and furans releases, but for pollutant releases generally.</u>

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[18] European Integrated Pollution Prevention and Control Bureau (EIPPCB), *Reference Document on Best Available Techniques in the Non-Ferrous Metals Industries*, Seville, Spain, 2001, p. 325.

[19] BCS Inc., *U.S. Energy Requirements for Aluminum Production: Historical Perspectives, Theoretical Limits and New Opportunities*, prepared under contract for the U.S. Department of Energy, Energy Efficiency and Renewable Energy, February 2003. p. 47

[20] Ibid.

[21] European Integrated Pollution Prevention and Control Bureau (EIPPCB), *Reference Document on Best Available Techniques in the Non-Ferrous Metals Industries*, Seville, Spain, 2001. p. 326, 675-676.

The following measures have been shown to effectively reduce releases from primary aluminium production and should be considered at BAT:[22]

- Feed preparation: Enclosed and extracted grinding and blending of raw materials, fabric filters for abatement.
- Complete hood coverage of the cells, which is connected to a gas exhaust and filter. The use of robust cell covers and adequate extraction rates. Sealed anode butt cooling system.
- Better than 99% fume collection from cells on a long term basis. Minimization of the time taken for opening covers and changing anodes.
- Gases from the primary smelting process should be treated to remove dust, fluorides and HF using an alumina scrubber and fabric filter. The scrubbing efficiency for total fluoride should be >99.8%, and the collected alumina used in the electrolytic cells.
- Use of low-$NO_x$ burners or oxy-fuel firing. Control of firing of furnaces to optimize the energy use and reduce PAH and $NO_x$ emissions.
- If there is an integrated anode plant the process gases should be treated in an alumina scrubber and fabric filter system and the collected alumina used in the electrolytic cells. Tars from mixing and forming processes can be treated in a coke filter.
- Destruction of cyanides, tars and hydrocarbons in an afterburner if they have not been removed by other abatement techniques.
- Use of wet or semi-dry scrubbing to remove $SO_2$ if necessary.
- Use of bio-filters to remove odorous components if necessary.
- Use of sealed or indirect cooling systems.

## *5.0 Summary of Measures*

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

**Table 2: Measures for New Primary Aluminium Production Plants**

| Measure | Description | Considerations | Other Comments |
|---|---|---|---|
| **Alternate Processes** | Priority should be given to alternate processes with less environmental impacts than tradition primary aluminium production plants. | Examples include:<br>○ Inert anodes<br>○ Wettable cathodes<br>○ Vertical Electrodes – Low Temperature Electrolysis<br>○ Drained Cell Technology<br>○ Carbothermic Technology | These processes are still in the development phase. |

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[22] Ibid. p. 326 and 675-676.

| | | | |
|---|---|---|---|
| | | ○ Kaolinite Reduction Technology | |
| **Prebake technology** | The use of centre-worked prebaked cells with automatic multiple feeding points is considered BAT. | | |
| **Performance Requirements** | New primary aluminium production plants should be required to achieve stringent performance and reporting requirements associated with best available technologies and techniques. | ○ Consideration should be given to the primary and secondary measures listed below in the following table. | No performance requirements have been determined for releases of dioxins and furans from primary aluminium plants. |

**Table 3: Summary of Primary and Secondary Measures for Primary Aluminium Production Plants**

| Measure | Description | Considerations | Other Comments |
|---|---|---|---|
| ***Primary Measures*** | | | |
| **Environmental management system, operational control and maintenance** | | | |
| **Computer controlled process and monitoring** | To minimise energy consumption and reduce number and duration of anode effects. | ○ | |
| **Feed selection:** Use of low sulphur carbon for anodes or anode paste. Use of | To control sulphur dioxide emissions, if necessary. | ○ $SO_2$ scrubbing system may be used. | |
| ***Secondary Measures*** | | | |
| **Feed preparation:** Enclosed grinding and blending of raw materials. Use of fabric filters. | To prevent the releases of particulates. | | |
| **Complete hood coverage of cells** | The use of hoods that completely cover cells to collect gases to the exhaust and filter. | | |
| **Fume collection and treatment** | Fume collection efficiency should be greater than 99%.<br>Gases should be treated to remove dust, fluorides and HF using an alumina scrubber and fabric filter. | | The time taken for opening the covers and changing the anodes should be minimized. |
| **Low $NO_x$ burners Oxy-fuel firing** | The firing of the furnace should be optimized to reduce PAH and $NO_x$ emissions. | | |
| **Alumina scrubber** | Process gases from anode plant should be treated in an alumina scrubber and fabric filter system. | | The alumina should be used in the electrolytic cells. Tars can be treated in a |

| | | | |
|---|---|---|---|
| | | | coke filter |
| **Afterburner** | To destroy cyanides, tars and PAHs if not removed by other abatement. | | |
| **Wet or semi-dry scrubbing** | To remove $SO_2$ if necessary. | | |
| **Bio-filters** | To remove odorous components if necessary. | | |

## *6.0 Performance Standards*

***I have found no existing performance standards or timelines for the release of dioxins and furans from primary aluminium plants.***

## *7.0 Performance Reporting*

The recommended performance reporting for dioxins and furans should be similar to that of other existing sectors.

# Attachment 7

# Draft Guidelines on Best Available Techniques (BAT) for Magnesium Production

## MAGNESIUM

### 1.0 Process Description

There are two major process routes utilized for production of magnesium metal. The first process recovers magnesium chloride from the raw materials and coverts it to metal through molten salt electrolysis. The second type of process involves reducing magnesium oxide with ferro-silicon or aluminium at high temperatures. Examples of the two types of processes are described below.

Magnesium can also be recovered and produced from a variety of magnesium containing secondary raw materials ( e.g see reference 1).

### 1.1Magnesium production process from magnesium oxide resources[1]

The process allows producing magnesium from oxide raw materials: magnesite, brusite, serpentine and other. It is also suitable for magnesium production from raw materials, containing magnesium sulphate or its mixture with chlorides, including seas water. In all the cases chlorine produced by electrolysis is recycle which is used for conversion of magnesium oxide or sulphate into magnesium chloride.

The process consists of the following stages (see flow sheet):

- leaching of raw material by hydrochloric acid and purification of the solution produced
- separation of magnesium chloride product in the form of synthetic carnallite or mixture of chlorides from said solution,
- dehydration of said product in fluidized bed by the stream of hot gases, containing hydrogen chloride, with production of solid dehydrated product, containing not more than 0,3 wt.% of magnesium oxide and water each,
- feeding of said product into electrolyzers or head unit of flow line and its

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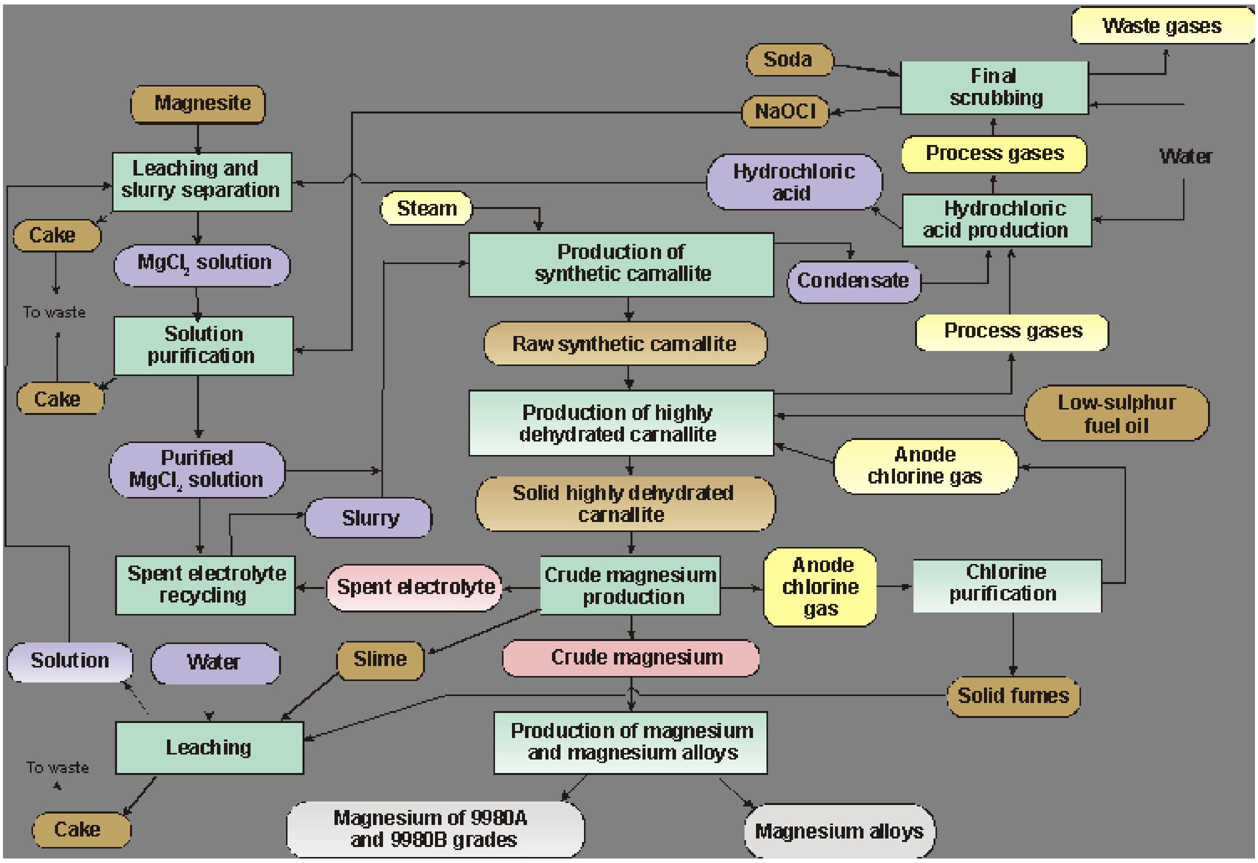
[1] http://www.vami.ru/processes/magnesium/sposob_proizvod_magnia_is_oksidnogo_siria.htm

electrolysis with production of magnesium and chlorine.

Chlorine produced by electrolysis is fed into the burners of fluidized bed furnaces, where it is converted into hydrogen chloride. Waste gases of FB furnaces, containing HCl, are either treated by water to produce hydrochloric acid that is used for raw material leaching, or neutralized by aqueous suspension of magnesium oxide to produce magnesium chloride solution.

Spent electrolyte forming in the course of electrolysis is used for synthetic carnallite production.All the waste products containing chlorine are utilized with the production of neutral oxides. It is a significant advantage of the process from environmental point of view.



## 1.2 The Pidgeon Process – The thermal reduction process[2]

In the Pidgeon Process, magnesium is produced from calcined dolomite under vacuum and at high temperatures using silicon as a reducing agent. In the

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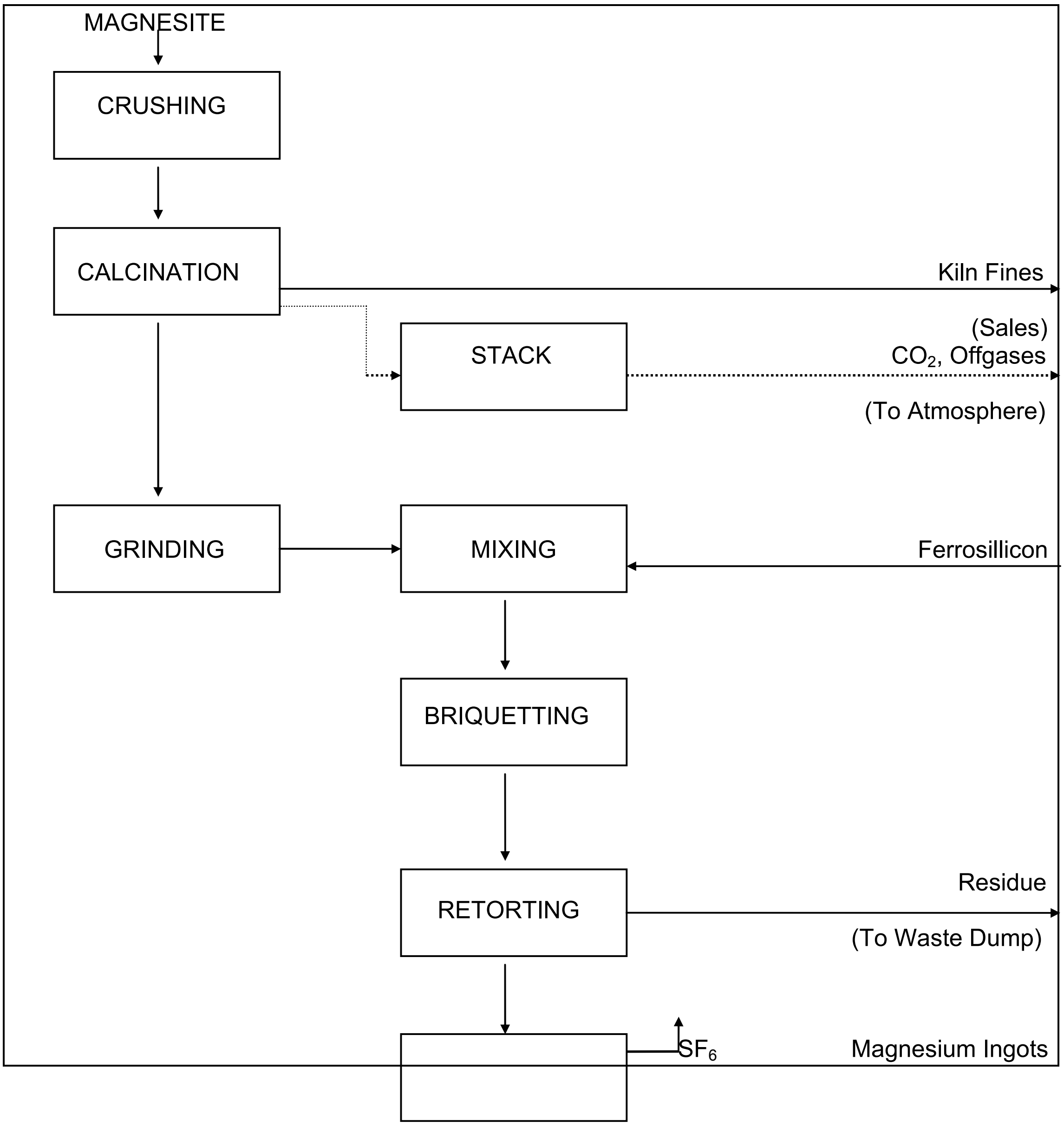
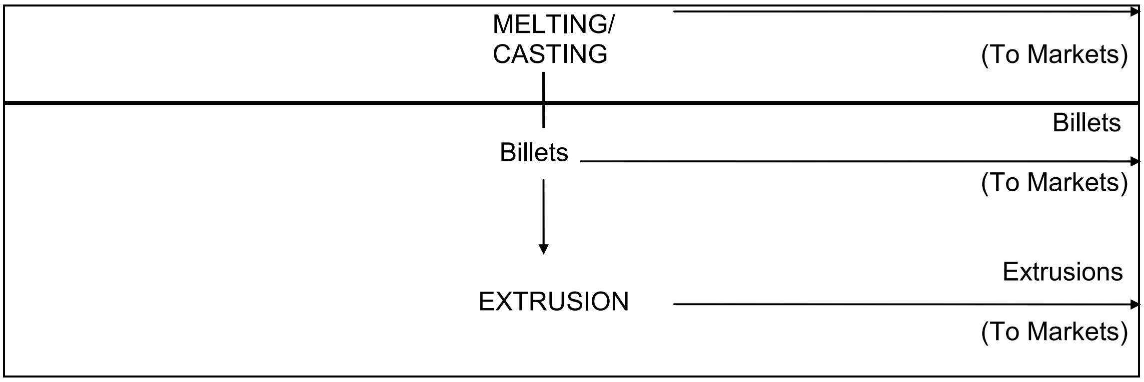
[2] http://www.norandamagnesium.com/

process, the finely crushed dolomite (magnesium/calcium) carbonate is fed to rotary kilns where it is calcined, and where the carbon dioxide is driven off leaving a product of calcined dolomite. The calcined dolomite is then pulverized n a roller mil prior to mixing with finely ground ferrosilicon and fluorspar. The fine calcined dolomite, ferrosilicon, and fluorspar are weighed in batch lots and mixed in a rotary blender. This mixture is then briquetted in briquetting presses. Briquettes are then conveyed to the reduction furnaces. The reduction operation is a batch process releasing magnesium in vapour form, which condenses in the water cooled section of the retort outside furnace wall. After removal from the furnace, the magnesium "crown" is pressed from the sleeve in a hydraulic press. The residue from the reduction charge is removed from the retort and sent to a waste dump.

**Process Flow Chart - Timminco Magnesium Plant**





Source: Hatch and Associates, Addendum to Primary NonFerrous Smelting and Refining Sector in Canada - Magnesium, October 1995

## 2.0 Sources of Unintentionally Produced POPs

According to tests conducted in an electrolytic process of magnesium production plant in Norway, the main process causing the formation of PCDD/PCDF was a furnace converting pellets of MgO and coke to $MgCl_2$ by heating in a $Cl_2$ atmosphere at 700-800 $^0$ C (Oehme et al. 1989). The purification of MgO using HCl and graphite blades ("chlorination) or electrolysis of $MgCl_2$ using graphite electrodes are also possible other sources of PCDD/PCDF formation.[3]

## 2.1 Emissions of Dioxins and Furans[4]

| **Process Type** | **Source** | **Emissions ($ng/Nm^3$)** | **Unit Mass/t (ug/t TEQ)** |
|---|---|---|---|
| Electrolytic | From Chlorination of off gas treatment. | 0.8 | 12 |
| | From Chlorination vent gas | 0.8 | 28 |
| | From electrolysis/chlorination | | 13 |
| Thermal | Reduction, refining and melting | 0.08 | 3 |
| Norsk Hydro Process | | | <1.0 |

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[3] UNEP- http://www.pops.int/documents/guidance/Toolkit_2003.pdf

[4] Integrated Pollution prevention and Control (IPPC), Reference Document on Best Available Techniques in the Non-Ferrous Metal Industries, May 2000

- Emissions of Dioxins and Furans to water (IPPC Bref)[5]

| ***Type*** | ***ng/Nm³*** | ***Unit mass/t of Mg*** |
|---|---|---|
| Electrolytic | 100 | 13 |
| | | |
| Thermal | 0.08 | 3 |
| | | |
| Norsk Hydro Process | | <0.1 |

**Canada**

There are three magnesium production facilities in Canada, two in Quebec and one in Ontario.

Timminco Ltd, in Ontario, which utilizes the "Thermal Reduction" Pidgeon process technology, reported dioxins and furans release to the air of 0.416 g TEQ/y. (*Dioxins and Furans CWS status report*, *pg 25)*

Hydro Magnesium Canada (HMC) reported a total of 0.456 g/year (1998 data??)[6] emissions of dioxins and furans to air. Broken down as follows:

| **Source** | **g/year** |
|---|---|
| Dissolving | 0.001 |
| Dehydration | 0.112 |
| Electrolysis | 0.277 |
| Foundry | 0.025 |
| HCl synthesis | 0.0003 |
| Mg remelting | 0.050 |

In the 2001 NPRI, magnesium producing facilities reported the following:

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[5] ibid

[6] *HMC presentation at "Electrolytic Magnesium Industry Bi-national Informative Meeting", Montreal, Dec.12, 2000 by Jean Laperriere, Environment Chief*)

| Facility | On-site Release | Transfer for Disposal | Transfer for Recycling | Units gTEQ |
|---|---|---|---|---|
| HMC- *Becancour* | 0.24 | 0.46 | 0.0 | |
| Noranda-*Murdocville* | 0.10 | 0.00 | 0.0 | |
| Timminco – *Haley* | 0.17 | 0.00 | 0.0 | |

## Emission Factors in the Magnesium Industry[7] (UNEP)

### PCDD/PCDFs

| Classification | Emission factors – ug TEQ/t of Mg | | | | |
|---|---|---|---|---|---|
| | **AIR** | **Water** | **Land** | **Product** | **Residue** |
| 1. Production using MgO/C thermal treatment in $Cl_2$ no effluent, limited gas treatment. | 250 | 9000 | NA | NA | 0 |
| 2. Production using MgO/C thermal treatment. | 50 | 30 | NA | NA | NA |
| 3. Thermal reduction process | 3 | ND | NA | NA | NA |

**HCBs**

**Emission factors – (ug/Kg)[8]**

| | **AIR** | **Water** | **Land** | **Process Generated** | **Volatilzed from Land** |
|---|---|---|---|---|---|
| Norsk Hydro, Posgrum | 700-3000 | - | unknown | unknown | unknown |
| Norsk Hydro, Beconcour | 90-170 | 2.4 | 60-120 | unknown | unknown |
| Noranda, Asbestos | 300 | nil | 800-3000 | 84,000 | 600-2400 |

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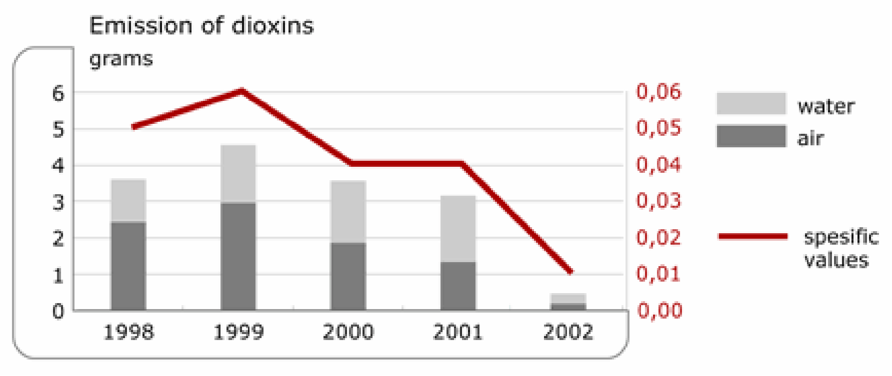
[7] http://www.pops.int/documents/guidance/Toolkit_2003.pdf

[8] Dioxin and Hexachlorobenzene Release from Magnesium Production in North America: Lessons from Noranda's Magnola Project in Asbestos, Quebec; Mathew J. Bramley, Ph.D., Greenpeace, Canada (June 5, 1998)

The figure below shows emissions and discharges of dioxins from Norsk Hydro's magnesium production. The graph for specific values shows grams dioxin per 1000 tonnes magnesium. The reduction in 2002 is mainly due to the closure of the magnesium plant in Porsgrunn[9].



## 2.3 General Information Magnesium production facilities.

Magnesium production facilities generate several types of pollutants that include dust, $SO_2$ , $NO_x$, $Cl_2$ , HCl, and in several cases emission of sulphur hexafluoride ($SF_6$) throughout the manufacturing process.
Dust and sulphur dioxide are mainly emitted from the calcinations of dolomite and MgO, from pellet drying as well as from chlorination off-gas treatment.
The source of nitrogen oxides emissions are dolomite and MgO calcinations and pellet drying. Chlorine and hydrochloric acid are released from electrolysis and chlorination processes, and chlorination off-gas treatment system.

While carbon dioxide is emitted from the whole manufacturing process, the source of sulphur hexafluoride ($SF_6$) discharges is the cast-house.

## 3.0 New Technology[10]

Norsk Hydro has developed and successfully implemented a $MgCl_2$ Dehydration process in its plant in Canada.

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[9] profile Nordsk Hydro.htm

[10] *Integrated Pollution prevention and Control (IPPC), Reference Document on Best Available Techniques in the Non-Ferrous Metal Industries, May 2000.*

The plant produces $MgCl_2$ brine by dissolving magnesite rock in hydrochloric acid. Impurities such as aluminium, iron, manganese etc are removed from the leach liquor by purification. The brine is the subjected to evaporation and prilling and drying by fluidised bed technique. This will result in an anhydrous $MgCl_2$ product.

Hydro's electrolysis cells are operated at around 400 kA. The $MgCl_2$ prills are fed continuously from the dehydration plant into the electrolysis cells. This operation produces magnesium metal and chlorine gas. The chlorine gas is reacted with hydrogen to produce hydrochloric acid which is recycled to the magnesite dissolving stage. The molten magnesium is cast under controlled conditions. The final products are pure metal and alloys in the form of ingots and grinding slabs.

## 3.1 Alternative Process

### 3.1.1 Magnétherm Process[11]

The Magnétherm process is very similar to the Pidgeon process but somewhat more efficient. The process uses dolomite as the magnesium source and reduces it at high temperature using silicon in the form of ferrosilicon.

A variation of the Pidgeon process was developed by Pechiney Inc and is known as the Magnatherm process. Essentially the same raw materials are utilized but a resistance furnace and condenser assembly are used in place of the retort. This adaptation allows higher temperature operation and thus the operating pressure, although still a vacuum is much higher. These changes enable the process to become semi-continuous and greatly reduce the requirement for manpower. The addition of magnesite and aluminium to the feed increases the productivity of the Magnatherm process and is termed the Aluminothermic process[12].

Considerable efficiency improvements are within reach to this technology by applying a dc exposed arc as the heat source to the furnace, where sufficient heat is generated to allow the furnace and condenser to operate near atmospheric pressure. This enables the system to be accessed for slag and metal tapping without interruption of the reduction process. In addition to the process being converted from a batch to continuous process, the resulting metal purity is enhanced compared to the magnetherm product.

### 3.1.2 Noranda's Magnesium Recovery from Asbestos Tailings.

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[11] *http://www.norandamagnesium.com/*

[12] *http://www.newworldalloys.com/magnesium.html*

A new technology in use by Noranda* involves recovery of magnesium from asbestos tailings. The process description is as follows:

* Note: *This plant was shutdown for an indefinite time due to market conditions – april 2003)*

## TRANSFORMING SERPENTINE INTO HIGH-GRADE MAGNESIUM[13]

In Noranda's proprietary magnesium process, serpentine undergoes a series of chemical processes and filtration steps to produce a very pure anhydrous magnesium chloride. This is electrolytically reduced in state-of-the-art high efficiency cells into magnesium and chlorine. The chlorine is completely captured and recycled.

### Feed Preparation

Noranda's magnesium process starts with crysotile serpentine ($3MgO \bullet 2SiO_2 \bullet 2H_2O$), a mining residue containing 23% magnesium. The material is already mined and above ground, adjacent to the plant. Serpentine is crushed, screened, and magnetically separated.

The material is then leached with hydrochloric acid to create magnesium chloride brine, along with a silica and iron residue.

### Brine Purification

To purify the magnesium chloride solution, the brine goes through further purification steps to remove major impurities such as boron. The impurities are extracted from the brine by precipitation.

### Fluid Bed Drying

High purity brine is dried to produce granular magnesium chloride. This yields partially dehydrated magnesium chloride ($MgCl_2$). HCl is recycled for use in the Leaching phase.

### Melt Chlorinator

The magnesium chloride granules are melted in an electrolyte and treated by a chlorination process involving the injection of gaseous HCl. The acid and water are recovered in the process for use in the Leaching phase.

### Electrolytic Cell

Metallic magnesium is produced through electrolysis by sending a strong electrical current through the electrolyte. The chlorine gas that is produced during the electrolysis phase is washed and combined with hydrogen thereby reconverted into acid, which will be reconverted into gas and re-used for the chlorination process.

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[13] *http://my.noranda.com/Noranda/magnesium/Introducing+Noranda+Magnesium/A+Production+Breakthrough/_A+Production+Breakthrough.htm*

### Casting

The metallic magnesium is tapped and then cast in ingots.

### Purification of Emissions

The production facility is equipped with gas scrubbers throughout the process to purify the process and ventilation emissions. The chlorine is completely captured, recycled, and returned to the process. Emissions are washed to extract particles and other contaminants before being released into the atmosphere. The process releases no water effluent to the environment.

## 3.13 Emerging Technology

VAMI and Titanium Institute in cooperation with other companies are engaged in Feasibility studies for magnesium plants in Russia, Iceland, Australia, Canada and other countries. Magnesium works in Congo (Kouilou Project) using the VAMI's technology will have the lowest operating costs in the world[14].

## The Cogburn Magnesium Project[15]

A Cogburn magnesium project in British Columbia is expected to utilize the STI/VAMI electrolytic cell technology for the decomposition of $MgCl_2$ to magnesium metal and chlorine gas. Presently in the magnesium industry, this is done largely in mono-polar diaphragm-less electrolytic cells. The STI/VAMI technology is based on a flow through design in which all the cells in the cell hall are linked together. Each cell is fed individually. The magnesium and electrolyte flow from one cell to the next via a system of enclosed launders. The magnesium is collected at the end of the flow line in a separator cell, and is siphoned out for casting at the cast house. This system is currently utilized at the Dead Sea Magnesium plant in Israel.

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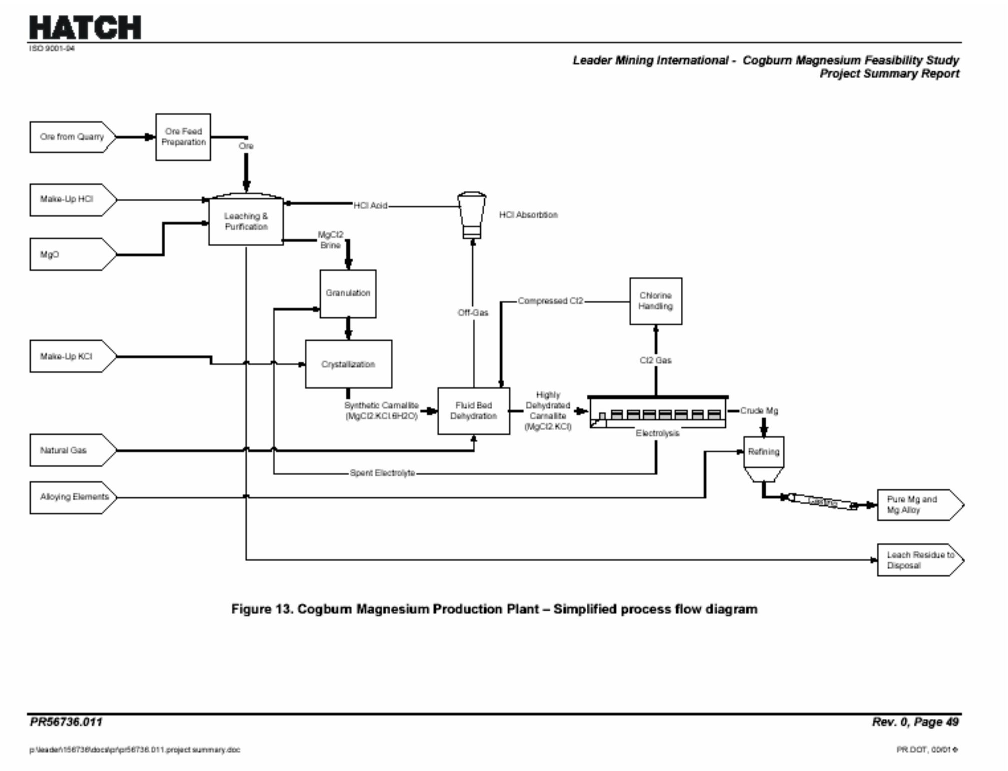
[14] \Poluchenie_magnia.htm

[15] (*http://www.leadermining.com/Binder_No1_Project_Summary.pdf)*



**HATCH**

ISO 9001-94

***Leader Mining International - Cogburn Magnesium Feasibility Study***
***Project Summary Report***

**Figure 13. Cogburn Magnesium Production Plant – Simplified process flow diagram**

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## 3.2 Performance requirements for New Magnesium Plants.

None identified- Information gap ???

## 4.0 Primary and Secondary Measures.

### 4.1 Primary Measures

The electrolysis process is of the most interest from the PCDD/PCDF point of view because of the presence of carbon and of chlorine in the process and the high temperature conditions.

Primary measures which may assist in reducing the formation and release of the identified substances include eliminating the carbon source, by substituting the graphite by a non-grahite anode.

The new $MgCl_{2\ \mathrm{dehydrating}}$ process has been found to produce much lower levels of dioxins and Furans (see tables above).

It is expected that in the proposed Cogburn Magensium Project, in British Columbia, that the STI/VAMI technology will produce less CHC's than produced at Magnola due to the absence of chlorinators.

### 4.2 Secondary Measures

Measures include:

1. Treatment of effluents using techniques such as nanofiltration and use of specially designed containment for solid residues and effluents.
2. Treatment of off-gases by cleaning of the off-gas from the chlorinators in a series of wet scrubbers and wet electrostatic precipitators before incineration, and using bag filters to clean and remove entrained salts from the magnesium electrolysis process.
3. Use of Acitvated Carbon: In the Cogburn Magnesium Project, there are two CHC removal systems; both are based on activated carbon removal of CHC's in liquid effluents.

## *5.0 Summary of Measures*

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

### Measures for New Magnesium Plants

| Measure | Description | Considerations | Other comments |
|---|---|---|---|
| ***New Magnesium Plants-Primary Measures*** | | | |
| **Alternate Processes** | Priority consideration should be given to alternate processes with less environmental impacts than traditional magnesium manufacturing process. | Examples include:<br>- Norsk Hydro's $Mgcl_{2\ brine}$ Dehydration Process.<br>- Elimination of carbon source-replaces graphite with non-graphite anode. | |
| **Feed Quality** | Increasing availability of magnesium scrap and other magnesium containing raw materials would make it attractive for smelters to use it in their process. | Smelter should ensure that only high grade and free from contaminants scrap be used. | |
| **Pre-treatment Techniques** | The calcinations of dolomite creates significant amount of dust | Use of Gas Suspension Calciner could reduce it significantly. | |

| Measure | Description | Considerations | Other comments |
|---|---|---|---|
| ***Magnesium Plants-Secondary Measures*** | | | |
| **Treatment of the off-gases** | Off-gases from chlorination furnaces in magnesium plants contain pollutants such as dioxins/ and furans, CHCs, and others. | Use of wet scrubbers and wet electrostatic precipitators remove aerosols, followed by incineration to destroy dioxins/furans and other VOCs.<br>Activated carbon is also used to absorb pollutants. | |
| **Treatment of effluent** | Wastewater collected from the various parts of the magnesium plant such as the scrubbing effluent from the chlorination stage contain dioxins and furans and other CHCs. | Removal of solids by flocculation, sedimentation and filtration. followed by activated carbon injection to remove contaminants. | |

## 6. Performance Standards

None identified – Information gap????

## 7. Performance Reporting.

- Comprehensive program of monitoring and measurement of emissions and transfers of PCDD/PCDF, HCB and other chlorinated POPs must be implemented at all facilities. Measurements should cover emissions to air, water, land including landfill, fugitive emissions, volatilisation from land, and transfer off-site as waste or commercial product.