

**GUIDELINES ON BEST AVAILABLE  
TECHNIQUES AND PROVISIONAL GUIDANCE  
ON BEST ENVIRONMENTAL PRACTICES**

**relevant to Article 5 and Annex C  
of the Stockholm Convention on  
Persistent Organic Pollutants**

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Thermal processes in the metallurgical industry  
not mentioned in Annex C, Part II



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MAY 2007, GENEVA, SWITZERLAND

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### (i) Secondary lead production

#### ■ Summary

Secondary lead smelting involves the production of lead and lead alloys, primarily from scrap automobile batteries, and also from other used lead sources (pipe, solder, drosses, lead sheathing). Production processes include scrap pretreatment, smelting and refining. Incomplete combustion; high levels of oils, plastics and other organic materials in feed; and temperatures between 250°C and 500°C may all give rise to chemicals listed in Annex C of the Stockholm Convention.

Best available techniques include the use of plastic-free and oil-free feed material, high furnace temperatures above 850°C, effective gas collection, afterburners and rapid quench, activated carbon adsorption, and dedusting fabric filters.

PCDD/PCDF performance levels associated with best available techniques for secondary lead smelters are <0.1 ng I-TEQ/Nm<sup>3</sup> (at operating oxygen concentrations).

### 1. Process description

The following summary of the process is drawn from EPA 1986. Figure 1 summarizes the process in diagrammatic form.

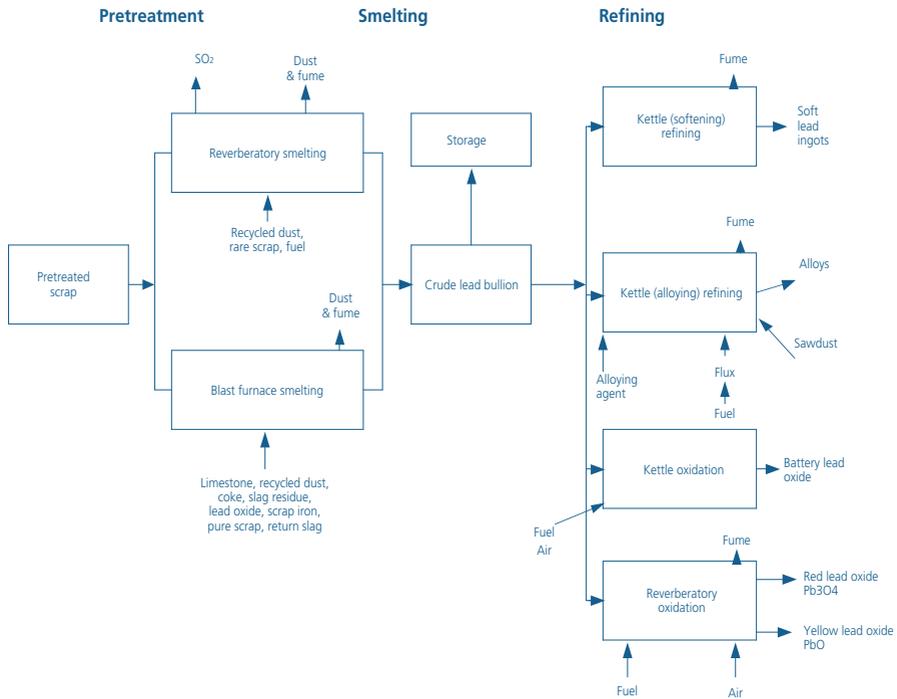
“Secondary lead smelters produce lead and lead alloys from lead-bearing scrap material. More than 60 percent of all secondary lead is derived from scrap automobile batteries. Other raw materials used in secondary lead smelting include wheel balance weights, pipe, solder, drosses, and lead sheathing.

Secondary lead smelting includes 3 major operations: scrap pretreatment, smelting, and refining. Scrap pretreatment is the partial removal of metal and nonmetal contaminants from leadbearing scrap and residue. Processes used for scrap pretreatment 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 pretreated 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.”

■ **Figure 1. Secondary lead smelting**



Source: EPA 1986.

## 2. Sources of chemicals listed in Annex C of the Stockholm Convention

The formation of chemicals listed in Annex C of the Stockholm Convention can result from the presence of unburnt fuels and organic compounds reacting with chlorine-containing compounds in zones where temperatures are in the range 250 – 450°C.

### 2.1 General information on emissions from secondary lead smelters

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<sub>2</sub>), other sulphur compounds and acid mists, nitrogen oxides (NO<sub>x</sub>), metals (especially lead) and their compounds, dusts and traces of polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF). SO<sub>2</sub> is collected and processed into sulphuric acid in acid plants. Fugitive SO<sub>2</sub> emissions can be controlled by good extraction and sealing of furnaces. NO<sub>x</sub> can be reduced using low-NO<sub>x</sub> or oxy-fuel burners. Particulate matter is collected using high-efficiency dust removal methods such as fabric filters and returned to the process (European Commission 2001, p. 359–368).

## 2.2 Emissions of PCDD/PCDF to air

PCDD/PCDF are formed during base metals smelting through reaction of products of incomplete combustion, unburnt organic contaminants and chlorine compounds, usually by de novo synthesis in the cooling zone at temperatures between 250°C and 450°C.

The process is described in European Commission 2001, p. 133:

“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°C 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.”

## 2.3 Releases to other media

The use of wet scrubbing can result in a liquid effluent and solid residue that is likely to contain chemicals listed in Annex C. Dry particulate capture will contain chemicals listed in Annex C. All should be treated or disposed of appropriately.

## 3. Recommended processes

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 best available techniques 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 (European Commission 2001, p. 379).

The submerged electric arc 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 (European Commission 2001, p. 395).

“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” (European Commission 2001, p. 404). This technique minimizes dust emissions during charging and thus reduces the release of PCDD/PCDF through adsorption on particulate matter.

No information is available on alternative processes to smelting for secondary lead processing.

## **4. 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 persistent organic pollutants. Possible measures include:

#### **4.1.1 Presorting of feed material**

Scrap should be sorted and pretreated 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 pretreatment 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 decoating and de-oiling processes. Thermal decoating and de-oiling processes for oil removal should be followed by afterburning to destroy any organic material in the off-gas (European Commission 2001, p. 232).

#### **4.1.2 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/PCDF emissions would be monitored continuously to ensure reduced releases. Continuous emissions sampling of PCDD/PCDF has been demonstrated for some sectors (for example, 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. As installations may differ considerably, variables to be monitored would need to be established on a site-specific basis.

“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” (European Commission 2001, p. 390).

## **4.2 Secondary measures**

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

### **4.2.1 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. Best available techniques 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” (European Commission 2001, p. 397).

### **4.2.2 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 and 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 (European Commission 2001, p. 139–140).

### **4.2.3 Afterburners and quenching**

Afterburners (post-combustion) should be used at a minimum temperature of 950°C to ensure full combustion of organic compounds (Hübner et al. 2000). 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 (European Commission 2001, p. 189).

It has been observed that PCDD/PCDF are formed in the temperature range of 250°C 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 minimize reformation time should be implemented (European Commission 2001, p. 133).

#### **4.2.4 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. Emerging research**

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 can, subject to catalyst selection, be subject to poisoning from trace metals and other exhaust gas contaminants. Validation work would be necessary before use of this process.

Catalytic oxidation processes organic compounds into water, carbon dioxide (CO<sub>2</sub>) and hydrochloric acid using a precious metal catalyst to increase the rate of reaction at 370°C 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 treated for particulate removal 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<sub>2</sub> are released to the air after cooling (Parvesse 2001).

## 6. Summary of measures

Tables 1 and 2 present a summary of the measures discussed in previous sections.

■ **Table 1. Measures for new secondary lead smelters**

Measure	Description	Considerations	Other comments
Recommended processes	Various recommended smelting processes should be considered for new facilities	<p>Processes to consider include:</p> <ul style="list-style-type: none"> <li>• Blast furnace (with good process control), ISA Smelt/Ausmelt furnace, top-blown rotary furnace, electric furnace and rotary furnace</li> <li>• Submerged electric arc furnace (it is a sealed unit for mixed copper and lead materials, cleaner than other processes if the gas extraction system is well designed and sized)</li> <li>• Injection of fine material via the tuyeres of a blast furnace reduces handling of dusty material</li> </ul>	These processes should be applied in combination with good process control, gas collection and abatement systems

**Table 2. Summary of primary and secondary measures for secondary lead smelters**

Measure	Description	Considerations	Other comments
<i>Primary measures</i>			
Presorting of feed material	Scrap should be sorted and pretreated to remove organic compounds and plastics to reduce PCDD/PCDF generation from incomplete combustion or by de novo synthesis. Batteries should be broken prior to charging into the furnace and plastics and other non-lead materials removed rather than being added to the furnace	Processes to consider include: <ul style="list-style-type: none"> <li>• Avoidance of whole battery feed or incomplete separation</li> <li>• Milling and grinding, followed by pneumatic or density separation techniques, to remove plastics</li> <li>• Oil removal conducted through thermal decoating and de-oiling processes</li> </ul>	Thermal decoating 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.  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 minimized

Measure	Description	Considerations	Other comments
<b>Secondary measures</b>			
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 consider include: <ul style="list-style-type: none"> <li>• Furnace-sealing systems to maintain a suitable furnace vacuum that avoids leaks and fugitive emissions</li> <li>• Use of hooding</li> <li>• Hood additions of material, additions via tuyeres or lances and the use of robust rotary valves on feed systems</li> </ul>	Best available techniques 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 consider include: <ul style="list-style-type: none"> <li>• Use of fabric filters, wet/dry scrubbers and ceramic filters</li> </ul>	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: <ul style="list-style-type: none"> <li>• PCDD/PCDF formation between 250°C and 500°C, and destruction &gt;850°C with O<sub>2</sub></li> <li>• Requirement for sufficient O<sub>2</sub> in the upper region of the furnace for complete combustion</li> <li>• Need for proper design of cooling systems to minimize reformation time</li> </ul>	De novo synthesis is still possible as the gases are cooled through the reformation window

Measure	Description	Considerations	Other comments
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 consider include: <ul style="list-style-type: none"> <li>• Treatment with activated carbon using fixed or moving bed reactors</li> <li>• Injection of carbon particulate into the gas stream followed by removal as a filter dust</li> </ul>	Lime/carbon mixtures can also be used

### Emerging research

Catalytic oxidation	Catalytic oxidation is an emerging technology that should be considered due to its high efficiency and lower energy consumption. Catalytic oxidation transforms organic compounds into water, CO <sub>2</sub> and hydrochloric acid using a precious metal catalyst	Considerations include: <ul style="list-style-type: none"> <li>• Process efficiency for the vapour phase of contaminants</li> <li>• Hydrochloric acid treatment using scrubbers while water and CO<sub>2</sub> are released to the air after cooling</li> </ul>	Catalytic oxidation has been shown to destroy PCDD/PCDF with shorter residence times, lower energy consumption and 99% efficiency. Off-gases should be treated for particulate removal prior to catalytic oxidation for optimum efficiency
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## 7. Performance level associated with best available techniques

PCDD/PCDF performance levels associated with best available techniques for secondary lead smelters are <0.1 ng I-TEQ/Nm<sup>3</sup> (at operating oxygen concentrations).

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## (ii) Primary aluminium production

### ■ Summary

Primary aluminium is produced directly from the mined ore, bauxite. The bauxite is refined into alumina through the Bayer process. The alumina is reduced into metallic aluminium by electrolysis through the Hall-Héroult process (either using self-baking anodes – Söderberg anodes – or using prebaked anodes).

Primary aluminium production is generally thought not to be a significant source of chemicals listed in Annex C of the Stockholm Convention. However, contamination with PCDD and PCDF is possible through the graphite-based electrodes used in the electrolytic smelting process.

Possible techniques to reduce the production and release of chemicals listed in Annex C from the primary aluminium sector include improved anode production and control, and using advanced smelting processes. The performance levels associated with best available techniques for air emissions of PCDD/PCDF in the primary aluminium sector are <0.1 ng I-TEQ/Nm<sup>3</sup> (at operating oxygen concentrations).

## 1. 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 aluminium. This section does not cover the secondary aluminium process, which is covered in section V.D (iii) of the present guidelines.

### 1.1 The Bayer process: Refining bauxite to alumina

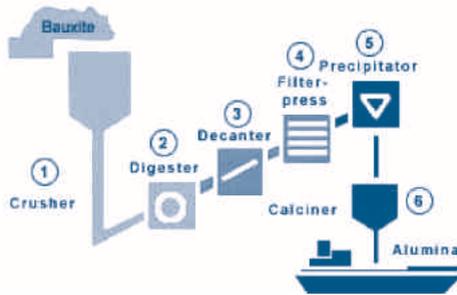
Bauxite is converted to alumina using the Bayer process (Figure 2). The bauxite ore is dried, crushed and ground into a powder and mixed with a solution of caustic soda to extract the alumina at elevated temperatures and pressures in digesters. A slurry is produced which contains dissolved sodium aluminate and a mixture of metal oxides, called red mud, which is removed in thickeners. The red mud is washed to recover the chemicals and is disposed of. 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.

### 1.2 The Hall-Héroult process: Reduction by electrolysis of alumina to aluminium

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

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 . Simplified flow sheet for alumina production**



Source: Aluminium Association of Canada.

### 1.3 Production of aluminium

There are two types of technologies used for the production of aluminium (Figure 3): those using self-baking anodes (Söderberg anodes) and those using prebaked anodes.

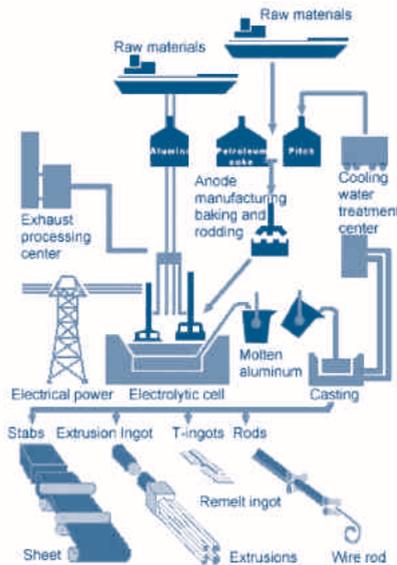
The older Söderberg anodes are made in situ from a paste of calcined petroleum coke and coal tar pitch, and are baked by the heat from the molten electrolytic bath. As the anode is consumed, more paste descends through the anode shell in a process that does not require anode changes. Alumina is added periodically to Söderberg cells through holes made by breaking the crust alumina and frozen electrolyte that covers the molten bath. Depending on the placement of the anode studs, these are known as vertical stud Söderberg or horizontal stud Söderberg cells or pots. Automatic point feeding systems are used in upgraded plants, eliminating the need for regular breaking of the crust.

Prebaked anodes are manufactured in a carbon plant from a mixture of calcined petroleum coke and coal tar pitch, which is formed into a block and baked in an anode furnace. The prebaked anode production plants are often an integrated part of the primary aluminium plant. The prebaked 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 prebake or centre-worked prebake. For side-worked prebake cells, the alumina is fed to the cells after the crust is broken around the perimeter. For centre-worked prebake cells, the alumina is fed to the cells after the crust is broken along the centre line or at selected points on the centre line of the cell.

The cathode typically has to be replaced every five to eight 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 potlining, 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, and sealed containers are used to minimize further oxidation of the dross. Nitrogen and argon blanketing is used. This is followed by removal of 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.

■ **Figure 3. General schematic of the electrolytic process for aluminium production**



Source: Aluminium Association of Canada

## 2. Sources of chemicals listed in Annex C of the Stockholm Convention

Primary aluminium production is unlikely to be a significant source of releases of polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF), although contamination is possible through the graphite-based electrodes (AEA Technology Environment 1999, p. 63). PCDD/PCDF release levels are generally thought to be low and the main interest is in the thermal processing of scrap materials (UNEP 2003, p. 73). This is discussed further in subsection 2.3 below.

## 2.1 Emissions of PCDD/PCDF

There is limited information available on chemicals listed in Annex C of the Stockholm Convention, including PCDD/PCDF formation from primary aluminium processes. Some literature suggests that initial emissions testing indicates that PCDD/PCDF are not considered significant from this sector.

It is reported that it is unlikely that the Söderberg and prebaked processes release significantly different emissions per ton of aluminium produced (AEA Technology Environment 1999, p. 63). Test results on emission sources and abatement units associated with prebaked anode manufacturing indicate that PCDD are not significant from these sources. However, if chlorine compounds or additives are used, emissions will need to be examined (European Commission 2001, p. 669).

Some studies have tested for PCDD 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 PCDD. Results from primary smelter cast houses have shown that releases are significantly below 1 gram per year (European Commission 2001, p. 289). The potential for PCDD/PCDF 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 (European Commission 2001, p. 318).

## 2.2 Releases to land

The production of primary aluminium from ores is not thought to produce significant quantities of PCDD/PCDF (New Zealand Ministry for the Environment 2000). The *Review of Dioxin Releases to Land and Water in the UK* states that there may be the possibility of graphite-based electrodes having some PCDD/PCDF contamination (UK Environment Agency 1997). Swedish data suggest that the spent sludge from the cells may contain 7.8 ng Nordic-TEQ kg<sup>-1</sup>. However, if the cathode is high-purity carbon material and the reduction process does not involve chlorine or chloride materials, it is unlikely that PCDD/PCDF will be present.

Metal reclaim fines may contain PCDD/PCDF 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 PCDD/PCDF from this sector. It has been suggested that primary aluminium production is not considered to be a significant source of releases. One paper reported non-detect levels for dioxin and furan emissions (ESP Environmental Ltd., 2000). However, a 2001 Russian study of the PCDD/PCDF emissions in the city of Krasnoyarsk concluded that the aluminium factory was responsible for 70% of industrial PCDD/PCDF emissions to air and 22% of industrial releases to land (Kucherenko et al. 2001). More studies in this area would be needed in order to show whether or not primary aluminium production is a significant source of dioxins and furans.

## 2.4 General information on releases from primary aluminium plants

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 (SNC-Lavalin Environment 2002, p. 3:14).

“The use of carbon anodes leads to emissions of sulphur dioxide (SO<sub>2</sub>), carbonyl sulphide (COS), polycyclic aromatic hydrocarbons (PAHs) and nitrogen oxides (NO<sub>x</sub>). Most of the sulphur in the carbon anode is released as COS, which is not entirely oxidized to SO<sub>2</sub> before being emitted at the potroom gas scrubber stacks. Sulphur emissions are predominately in the form of SO<sub>2</sub> 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<sub>x</sub> emissions mainly come from the combustion of fuel in the anode baking furnace” (SNC-Lavalin Environment 2002, 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 be 4 to 5 times greater than stack emissions (after the scrubber)” (SNC-Lavalin Environment 2002, p. 3:16).

The “anode effect” results in generation of perfluorocarbons 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, carbon tetrafluoride (CF<sub>4</sub>) and hexafluoroethane (C<sub>2</sub>F<sub>6</sub>) are produced, along with a surge in voltage. The amount of perfluorocarbons generated depends on the efficiency of feed control in the pot. For pots not equipped with proper controls, perfluorocarbon emissions from anode effects can be the largest source, accounting for over 50% of the total smelter emissions (on a CO<sub>2</sub>-equivalent basis). Practically any point-fed, computer-controlled pot can operate at low anode effect frequency. Older technologies, such as horizontal stud and vertical stud Söderberg cells, have higher perfluorocarbon 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 prebaked smelters are such that perfluorocarbon emissions can be reduced to less than 5% of the total greenhouse gas emissions from the smelter. CO<sub>2</sub> emissions from anode consumption are the next largest source for pots without modern controls (SNC-Lavalin Environment 2002, p. 3:10–11).

**Table 3. Emissions, effluents, by-products and solid wastes from primary aluminium production**

Process	Air emissions <sup>a</sup>	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, SO <sub>2</sub> , PCDD/PCDF <sup>b</sup>	Wastewater containing suspended solids, fluorides, and organics	Carbon dust, tar, refractory waste
Aluminium smelting	CO, CO <sub>2</sub> , SO <sub>2</sub> , fluorides (gaseous and particulate), perfluorocarbons (CF <sub>4</sub> , C <sub>2</sub> F <sub>6</sub> ), polycyclic aromatic hydrocarbons, PCDD/PCDF <sup>b</sup>	Wet air pollution control effluents (wet electrostatic precipitator)	Spent potliners, wet air pollution control wastes, sludges

a. Excluding combustion-related emissions.

b. Based on the Krasnoyarsk study (Kucherenko et al. 2001).

Source: Energetics Inc. 1997.

### 3. Alternative processes to primary aluminium smelting (emerging technologies)

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 alternative processes, techniques or practices that have similar usefulness but avoid the formation and release of the identified substances.

There are a number of research initiatives currently under way to produce primary aluminium while concurrently reducing energy consumption and emissions (European Commission 2001, p. 335; SNC-Lavalin Environment 2002; Welch 1999; USGS 2001; BCS Inc. 2003, p. 41–58). These initiatives include:

- Inert anodes: Carbon-free anodes that are inert, dimensionally stable, slowly consumed, and produce oxygen instead of CO<sub>2</sub>. The use of inert anodes eliminates the need for an anode carbon plant (and emissions of polycyclic aromatic hydrocarbons 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 aluminium 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 aluminium using a chemical reaction that takes place within a reactor and requires much less physical space than 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 potliners, and hydrocarbon emissions associated with the baking of consumable carbon anodes;
- Kaolinite reduction technology: The production of aluminium by reduction of aluminium chloride using clays holds appeal because the raw materials are readily available and inexpensive. The thermodynamics also provide high-speed conversion reactions with lower electrical demand and no bauxite residue is produced.

## **4. Primary and secondary measures**

Primary and secondary measures for reducing emissions of PCDD/PCDF 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.

Note that no secondary measures have been developed specifically for primary aluminium smelters to control the unintentional formation of PCDD/PCDF. The following are general measures that may result in lower pollutant emissions at primary aluminium smelters, including releases of PCDD/PCDF.

### **4.1 Primary measures**

Primary measures are understood to be pollution prevention measures that prevent or minimize the formation and release of the identified substances (particulates, fluorides, polycyclic aromatic hydrocarbons, sulphur dioxide, carbon dioxide, carbon monoxide and perfluorocarbons). 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” (see section III.B of the present guidelines). Note that there are no primary measures identified for PCDD/PCDF.

For new smelters, using the prebake technology rather than the Söderberg technology for aluminium smelting is a significant pollution prevention measure (World Bank 1998).

The use of centre-worked prebaked cells with automatic multiple feeding points is considered to be a best available technique for the production of primary aluminium (European Commission 2001, p. 325).

“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” (BCS Inc. 2003, p. 47).

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 remain at their optimal conditions (BCS Inc. 2003).

Primary measures that may assist in reducing the formation and release of the identified substances include (European Commission 2001, p. 326, 675–676):

1. An established system for environmental management, operational control and maintenance;
2. Computer control of the electrolysis process based on active cell databases and monitoring of cell operating parameters to minimize the energy consumption and reduce the number and duration of anode effects;
3. If local, regional or long-range environmental impacts require SO<sub>2</sub> reductions, the use of low-sulphur carbon for the anodes or anode paste if practicable, or an SO<sub>2</sub> scrubbing system.

## 4.2 Secondary measures

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

The following measures have been shown to effectively reduce releases from primary aluminium production and should be considered best available techniques (European Commission 2001, p. 326, 675–676):

1. Feed preparation: Enclosed and extracted grinding and blending of raw materials, fabric filters for abatement;
2. Complete hood coverage of the cells, which is connected to a gas exhaust and filter; use of robust cell covers and adequate extraction rates; sealed anode butt cooling system;

3. Better than 99% fume collection from cells on a long-term basis; minimization of the time taken for opening covers and changing anodes;
4. Gases from the primary smelting process should be treated to remove dust, fluorides and hydrogen fluoride 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;
5. Use of low-NO<sub>x</sub> burners or oxy-fuel firing; control of firing of furnaces to optimize the energy use and reduce polycyclic aromatic hydrocarbons and NO<sub>x</sub> emissions;
6. 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;
7. Destruction of cyanides, tars and hydrocarbons in an afterburner if they have not been removed by other abatement techniques;
8. Use of wet or semi-dry scrubbing to remove SO<sub>2</sub> if necessary;
9. Use of biofilters to remove odorous components if necessary;
10. Use of sealed or indirect cooling systems.

## 5. Summary of measures

Tables 4 and 5 present a summary of the measures discussed in previous sections.

■ **Table 4. Measures for new primary aluminium production plants**

Measure	Description	Considerations	Other comments
Alternative processes	Priority should be given to alternative processes with less environmental impacts than tradition primary aluminium production plants	Examples include: <ul style="list-style-type: none"> <li>• Inert anodes</li> <li>• Wettable cathodes</li> <li>• Vertical electrodes – low-temperature electrolysis</li> <li>• Drained cell technology</li> <li>• Carbothermic technology</li> <li>• Kaolinite reduction technology</li> </ul>	These processes are still in the development phase
Prebake technology	The use of centre-worked prebaked cells with automatic multiple feeding points is considered a best available technique		
Performance levels	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 in Table 5	No performance requirements have been determined for releases of PCDD/PCDF from primary aluminium plants

**Table 5. Summary of primary and secondary measures for primary aluminium production plants**

Measure	Description	Considerations	Other comments
<b>Primary measures</b>			
Environmental management system, operational control and maintenance			
Computer-controlled process and monitoring	To minimize energy consumption and reduce number and duration of anode effects		
Feed selection: Use of low sulphur carbon for anodes or anode paste	To control sulphur dioxide emissions, if necessary	SO <sub>2</sub> scrubbing system may be used	
<b>Secondary measures</b>			
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%. 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 <sub>x</sub> burners or oxy-fuel firing	The firing of the furnace should be optimized to reduce emissions of polycyclic aromatic hydrocarbons and NO <sub>x</sub>		

Measure	Description	Considerations	Other comments
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 polycyclic aromatic hydrocarbons if not removed by other abatement		
Wet or semi-dry scrubbing	To remove SO <sub>2</sub> if necessary		
Biofilters	To remove odorous components if necessary		

## 6. Performance level associated with best available techniques

The performance levels associated with best available techniques for air emissions of PCDD/PCDF in the primary aluminium sector are <0.1 ng I-TEQ/Nm<sup>3</sup> (at operating oxygen concentrations).

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### (iii) Magnesium production

#### ■ Summary

Magnesium is produced either from raw magnesium chloride with molten salt electrolysis, or magnesium oxide reduction with ferrosilicon or aluminium at high temperatures, as well as through secondary magnesium recovery (for example, from asbestos tailings).

The addition of chlorine or chlorides, the presence of carbon anodes and high process temperatures in magnesium production can lead to the formation of chemicals listed in Annex C of the Stockholm Convention and their emission to air and discharge to water.

Alternative techniques may include the elimination of the carbon source by using non-graphite anodes, and the application of activated carbon. However, performance levels associated with best available techniques depend on the type of process and controls utilized for air and water releases.

## 1. 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 converts it to metal through molten salt electrolysis. The second type of process involves reducing magnesium oxide with ferrosilicon 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 and from scrap (VAMI 2004).

### 1.1 Magnesium production process from magnesium oxide resources

The process allows magnesium to be produced from oxide raw materials: magnesite, brucite, serpentine and others. It is also suitable for magnesium production from raw materials containing magnesium sulphate or its mixture with chlorides, including seawater. In all cases chlorine produced by electrolysis is recycled and used for conversion of magnesium oxide or sulphate into magnesium chloride (VAMI 2004).

The process of magnesium production from magnesium oxides consists of the following stages (see Figure 4):

1. Leaching of raw material by hydrochloric acid and purification of the solution produced;
2. Separation of magnesium chloride product in the form of synthetic carnallite or mixture of chlorides from said solution;
3. Dehydration of said product in a fluidized bed by the stream of hot gases, containing hydrogen chloride, with production of solid dehydrated

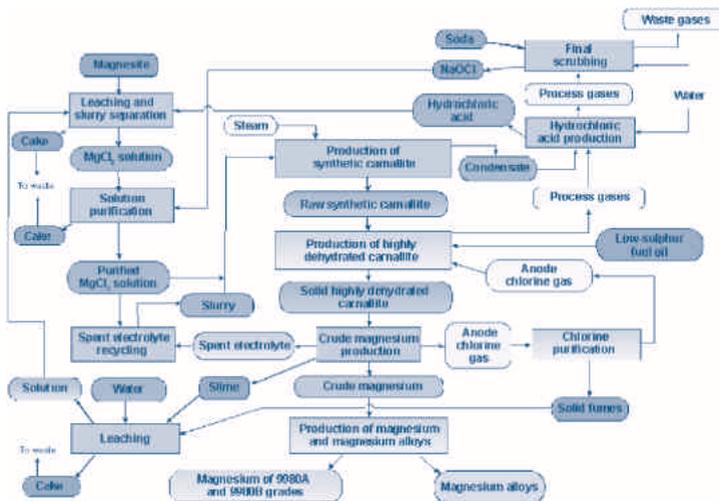
product, containing not more than 0.3 wt.% of magnesium oxide and water each;

- Feeding of said product into electrolyzers or head unit of flow line and its 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 (HCl). Waste gases of the fluidized bed furnaces, containing HCl, are either treated by water to produce hydrochloric acid, which 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 an environmental point of view.

■ **Figure 4. Flow diagram of magnesium production process from magnesium oxide resources**



Source: VAMI 2004.

## 1.2 The Pidgeon process (thermal reduction process)

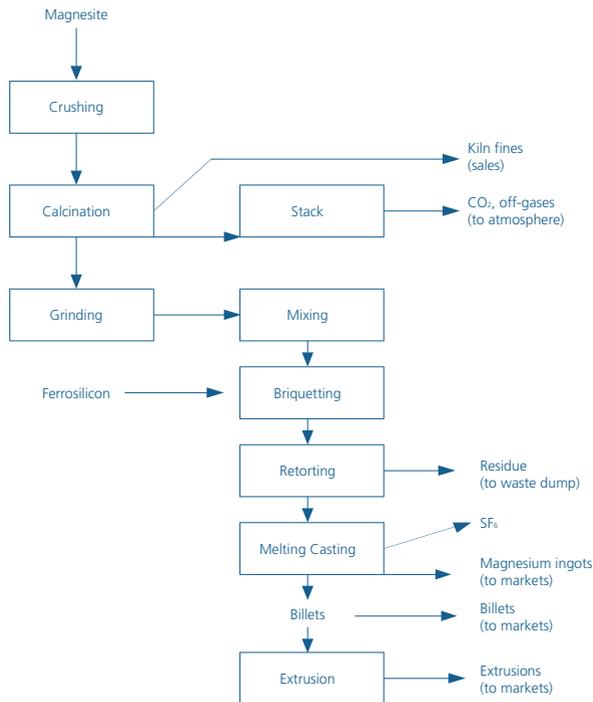
In the Pidgeon process, magnesium is produced from calcined dolomite under vacuum and at high temperatures using silicon as a reducing agent. In the process, the finely crushed dolomite (magnesium/calcium) carbonate is fed to rotary kilns where it is calcined, and where the carbon dioxide is driven off, leaving a product of calcined dolomite. The calcined dolomite is then pulverized in a roller mill 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 (Noranda Magnesium website).

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 the 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.

Figure 5 illustrates the process in diagrammatic form.

■ **Figure 5. Process flow chart: Timminco magnesium plant**



Source: Hatch and Associates 1995.

### 1.3 Various processes and considerations

Various thermal processes for magnesium production are used in a number of countries. These are based around the Pidgeon process developed in Canada in the 1940s. Calcined dolomite (CaO:MgO), is fused with ferrosilicon (FeSi) under vacuum. The magnesium is released from the melt as a vapour and condensed away from the reactor to form a metal deposit that can be removed and recast into ingots for industrial use. The retort is in many cases heated with coal. This can lead to significant emissions of persistent organic pollutants. A waste slag containing iron and calcium silicates together

with a proportion of unreacted magnesium oxide is produced and the ash from the coal combustion must also be disposed of. While cooling water is used this need not be contaminated with process wastes.

The processes will depend on the nature of the raw materials that are available, the size of the proposed facility, the available infrastructure and local conditions. Improved processes are now available that minimize environmental impacts by reducing energy demand. These processes however are only available under licence and so may not be accessible to all. One process that operates almost near continuously has been developed in South Africa, which operates at atmospheric pressure (Mintek process) and is available for licence. Effective control of releases depends on careful specification of the plant and effective operation of the plant to minimize energy use while maximizing conversion of raw materials into product. A range of approaches is available and the choice will be determined by the actual combination of economic and process demands. Suitable air pollution controls would need to be fitted and adequate facilities provided to handle and dispose of solid wastes.

The selection of a process that minimizes energy consumption may minimize the production of persistent organic pollutants. Hence continuous processes tend to be more energy efficient as less heat is required to return the reactor to operating temperature between cycles. One widely used process available for licence is the Magnatherm process, which replaces the coal heating of the retort with electrical induction heating. As a result, no fuel-generated emissions of persistent organic pollutants occur. This also operates semi-continuously and at a lower vacuum than the original Pidgeon process plant. Heating with oil or gas fuels instead of coal can greatly reduce the amount of persistent organic pollutants formed and is recommended where the distribution network for these fuels is reliable.

## **2. Sources of chemicals listed in Annex C of the Stockholm Convention**

### **2.1 Emissions to air**

#### **2.1.1 General information on emission from magnesium production**

Magnesium production facilities generate several types of pollutants, including dust, sulphur dioxide (SO<sub>2</sub>), nitrogen oxides (NO<sub>x</sub>), chlorine (Cl<sub>2</sub>), hydrochloric acid (HCl), and in several cases emission of sulphur hexafluoride (SF<sub>6</sub>) throughout the manufacturing process.

Dust and sulphur dioxide are mainly emitted from the calcinations of dolomite and magnesium oxide (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 the chlorination off-gas treatment system.

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

### 2.1.2 Emissions of PCDD and PCDF

According to tests conducted on an electrolytic process in a magnesium production plant in Norway, the main process causing the formation of polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) was a furnace converting pellets of MgO and coke to magnesium chloride (MgCl<sub>2</sub>) by heating in a Cl<sub>2</sub> atmosphere at 700°C – 800°C (Oehme, Manø and Bjerke 1989; European Commission 2001).

The purification of MgO using HCl and graphite blades (“chlorination”) or electrolysis of MgCl<sub>2</sub> using graphite electrodes are also possible other sources of PCDD/PCDF formation (UNEP 2003).

Timminco Ltd, in Ontario, Canada, which utilizes the thermal reduction Pidgeon process technology, reported PCDD/PCDF release to air of 0.416 g I-TEQ/year (CCME 2003).

Dioxin emission data of a former Norwegian magnesium production plant (Norsk Hydro) in the period 1992–2001 provided by Norway show that emission to air was approximately 0.03–0.25 mg I-TEQ/tonne Mg produced. The emission decreased from approximately 0.3 mg I-TEQ/tonne Mg to below 0.1 mg I-TEQ/tonne Mg after installation of an extra gas cleaning system in the plant.<sup>1</sup>

Table 6 shows emissions to air from different magnesium production processes; note that values provided as representative of Norsk Hydro performance vary from those noted above.

■ **Table 6. PCDD/PCDF emissions to air from different magnesium production processes**

Process type	Source	Emissions <sup>2</sup> (ng TEQ/Nm <sup>3</sup> )	Concentration (µg TEQ/t)
	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

Hydro Magnesium Canada reported a total of 0.456 g I-TEQ/year<sup>3</sup> emissions of PCDD/PCDF to air, broken down as shown in Table 7.

■ **Table 7. Emissions of PCDD/PCDF by source: Hydro Magnesium Canada**

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

## 2.2 Releases to other media

### 2.2.1 Water

The main water pollutants in the magnesium manufacturing process are metal compounds as suspended solids. However, chlorinated hydrocarbons and PCDD/PCDF are also found in wastewater from the magnesium electrolysis process (Table 8).

■ **Table 8. Releases of PCDD/PCDF to water from different magnesium production processes**

Type	ng/m <sup>3</sup>	ug TEQ/t of Mg
Electrolytic	100	13
Thermal	0.08	3
Norsk Hydro process	–	<0.1

Source: Hydro Magnesium Canada.

Emissions data of Norsk Hydro in the period 1992–2001 provided by Norway are as follows (Personal Communication, Norway Member, June 2006) (note that values provided above as representative of Norsk Hydro performance vary from these):

- (1). Dioxin discharges to water: Approximately 0.03–0.09 mg I-TEQ/tonne Mg produced
- (2). Hexachlorobenzene discharges to water: Approximately 0.02–0.2 g I-TEQ/tonne Mg produced.

### 2.2.2 Land

The wet scrubbing process utilized in treatment of gas streams would be expected to generate residues containing PCDD/PCDF. A water treatment system that includes settling of these residues in a lagoon would then constitute a release to land (UNEP 2003).

■ **Table 9. Emission Factors in the magnesium industry: PCDD/PCDF**

Emission factors: µg TEQ/t of Mg					
	Air	Water	Land	Product	Residue
Production using MgO/C thermal treatment in Cl <sub>2</sub> no effluent, limited gas treatment	250	9,000	n.a.	n.a.	0
Production using MgO/C thermal treatment	50	30	n.a.	n.a.	9000
Thermal reduction process	3	n.d.	n.a.	n.a.	n.a.

n.a. Not applicable.

n.d. Not determined.

Source: UNEP 2005.

■ **Table 10. Emission factors in the magnesium industry: Hexachlorobenzene (HCB)**

Emission factors: µg/kg					
	Air	Water	Land	Process generated	Volatilized from land
Norsk Hydro, Posgrunn <sup>a</sup>	700–3,000	n.d.	n.d.	n.d.	n.d.
Norsk Hydro, Bécancour <sup>a</sup>	90–170	2.4	60–120	n.d.	n.d.
Noranda, Asbestos <sup>b</sup>	439	0	8	Not estimated	~6

n.d. Not determined.

a. Source: Bramley 1998.

b. Source: Kemp 2004. Note that facility was operating at only 50% of design capacity and emission factor is believed to be overstated as a result.

### 3. Alternative processes for magnesium production

Although process efficiency and productivity could be the main driving forces in the advancement and development of alternative new technologies, it is expected that environmental aspects will be given due consideration. This means elimination or minimization of the formation of pollutants at source, and the incorporation of effective pollution abatement systems, should be part of the initial design of the project.

#### 3.1 Norsk Hydro dehydration process

Norsk Hydro has developed and successfully implemented a new technology, an MgCl<sub>2</sub> dehydration process, in its plant in Canada (European Commission 2001). Releases of pollutants, especially PCDD/PCDF, generated from this process are significantly lower than from existing processes (Tables 9 and 10).

The plant produces  $\text{MgCl}_2$  brine by dissolving magnesite rock in hydrochloric acid. Impurities such as aluminium, iron and manganese are removed from the leach liquor by purification. The brine is then subjected to evaporation and prilling and drying using the fluidized bed technique. This will result in an anhydrous  $\text{MgCl}_2$  product.

Hydro's electrolysis cells are operated at around 400 kA. The  $\text{MgCl}_2$  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.

### **3.2 Noranda's magnesium recovery from asbestos tailings**

A new technology in use by Noranda<sup>4</sup> involves recovery of magnesium from asbestos tailings (Noranda Inc. website). The process description is as follows:

**Transforming serpentine into high-grade magnesium:** 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. The company's projections for its environmental performance include emission levels of no more than 0.09 g TEQ of PCDD/PCDF to air, using an activated carbon adsorption system.

**Feed preparation:** Noranda's magnesium process starts with crysotile serpentine ( $3\text{MgO}\cdot 2\text{SiO}_2\cdot 2\text{H}_2\text{O}$ ), 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 ( $\text{MgCl}_2$ ). 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 and thereby reconverted into acid, which will be reconverted into gas and reused for the chlorination process.

**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.

### **3.3 Thermal processing and recovery of magnesium from scrap**

Where magnesium is recovered from scrap there will be the potential for formation and release of chemicals listed in Annex C of the Stockholm Convention. A variety of furnace types may be used.

As with other secondary metal processes formation will be enhanced by the presence of incomplete combustion, contaminated feed materials, inadequate process control, inadequate temperature in the furnace and particularly by reactions in the cooling zones (200°C–450°C).

Effective process operation and various secondary measures including afterburning as appropriate, rapid gas cooling, effective dust abatement and possibly injection of carbon will reduce releases. Dusts and effluents may contain elevated levels of chemicals listed in Annex C and will need to be properly treated.

## **4. Primary and secondary measures**

### **4.1 Primary measures**

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

Primary measures that may assist in reducing the formation and release of the identified substances include eliminating the carbon source by substituting the graphite by non-graphite anodes, possibly metal anodes. Replacement of graphite anodes by metal anodes took place in the chlorine industry at the start of the 1970s, and very minor amounts of PCDF were formed (Eurochlor 2001).

The new  $MgCl_2$  dehydrating process has been found to produce much lower levels of PCDD/PCDF (Tables 9 and 10).

It is expected that in the proposed Cogburn magnesium project in British Columbia the STI/VAMI technology will produce less chlorinated hydrocarbons than produced at Magnola due to the absence of chlorinators. See subsection 5 below for additional information.

### **4.2 Secondary measures**

Measures include:

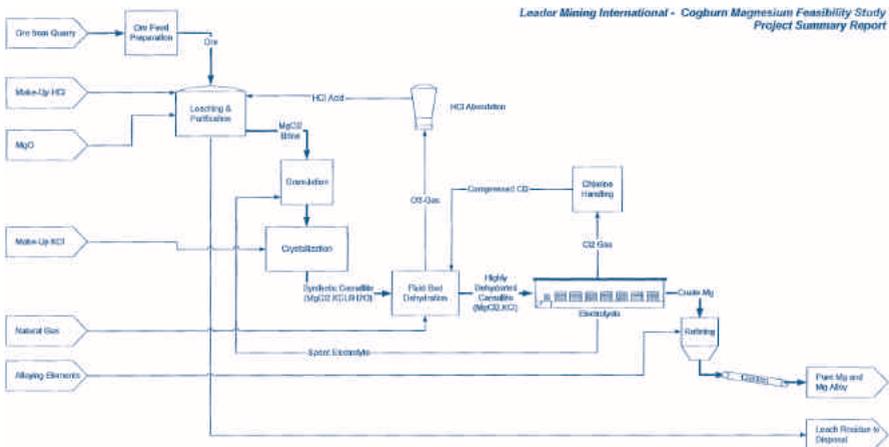
1. Treatment of effluents using techniques such as nanofiltration and use of specially designed containment for solid residues and effluents;

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 activated carbon: In the Cogburn magnesium project, there are two chlorinated hydrocarbon removal systems; both are based on activated carbon removal of chlorinated hydrocarbons in liquid effluents.

## 5. Emerging research

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 (Figure 6). Presently in the magnesium industry, this is done largely in monopolar diaphragmless 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 (Hatch and Associates 2003).

■ **Figure 6 Simplified flow diagram: Cogburn magnesium plant**



Source: Hatch and Associates 2003.

## 6. Summary of measures

Tables 11 and 12 present a summary of the measures discussed in previous sections.

■ **Table 11. Summary of primary measures for magnesium plants**

Measure	Description	Considerations
Alternative processes	Priority consideration should be given to alternative processes with less environmental impacts than traditional magnesium manufacturing processes	Examples include: <ul style="list-style-type: none"> <li>• Norsk Hydro's MgCl<sub>2</sub> brine dehydration process</li> <li>• Elimination of carbon source: replaces graphite with non-graphite anode</li> </ul>
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 scrap, free of contaminants, is used	
Pretreatment techniques	The calcinations of dolomite creates significant amount of dust	Use of gas suspension calciner could reduce it significantly

■ **Table 12. Summary of secondary measures for magnesium plants**

Measure	Description	Considerations
Treatment of off-gases	Off-gases from chlorination furnaces in magnesium plants contain pollutants such as PCDD, PCDF and chlorinated hydrocarbons	Use of wet scrubbers and wet electrostatic precipitators remove aerosols, followed by incineration to destroy PCDD/PCDF and other volatile organic compounds.  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 PCDD/PCDF and chlorinated hydrocarbons	Removal of solids by flocculation, sedimentation and filtration, followed by activated carbon injection to remove contaminants

## 7. Performance levels associated with best available techniques for HCB for Magnesium production process

Performance levels as associated with best available techniques for HCB for different Magnesium production processes are not available.

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## (iv) Secondary steel production

### ■ Summary

Secondary steel is produced through direct smelting of ferrous scrap using electric arc furnaces. The furnace melts and refines a metallic charge of scrap steel to produce carbon, alloy and stainless steels at non-integrated steel mills. Ferrous feed materials may include scrap, such as shredded vehicles and metal turnings, or direct reduced iron. In addition scrap may be added to other melting furnaces in the foundry and primary iron and steel sectors.

Chemicals listed in Annex C of the Stockholm Convention, such as PCDD and PCDF, appear to be most probably formed in the electric arc furnace steel-making process via de novo synthesis by the combustion of non-chlorinated organic matter such as plastics, coal and particulate carbon in the presence of chlorine donors. Many of these substances are contained in trace concentrations in the steel scrap or are process raw materials such as injected carbon.

Primary measures include adequate off-gas handling and appropriate off-gas conditioning to prevent conditions leading to de novo synthesis formation of PCDD/PCDF. This may include post-combustion afterburners, followed by rapid quench of off-gases. Secondary measures include adsorbent injection (for example, activated carbon) and high-level dedusting with fabric filters.

Performance levels for PCDD/PCDF air emissions associated with best available techniques for secondary steel production are  $<0.1 \text{ ng/Nm}^3$  (at operating oxygen concentrations).

## 1. Process description

### 1.1 General process description

The direct smelting of iron-containing materials, such as scrap, is usually performed in electric arc furnaces, which play an important and increasing role in modern steelworks. The furnace melts and refines a metallic charge of scrap steel to produce carbon, alloy and stainless steels at non-integrated (secondary steel) mills.

An electric arc furnace is a cylindrical vessel with a dish-shaped refractory hearth and electrodes that lower from the dome-shaped, removable roof. Refractory bricks form the lining of the furnace. The walls typically contain water-cooled panels, which are covered to minimize heat loss. The electrodes may also be equipped with water-cooling systems.

Electric arc furnace steel making consists of scrap charging, melting, refining, deslagging and tapping. In addition to scrap steel, the charge may include pig iron and alloying elements. As the steel scrap is melted, additional scrap may be added to the furnace. The electric arc furnace generates heat by passing an electric current between electrodes through the charge in the furnace. This energy is supplemented by natural gas, oxygen and other fuels.

Other technologies used to smelt iron-containing materials are cupola furnaces (hot and cold), induction furnaces and blast furnaces.

Cupola furnaces are used for the production of cast iron and cast steel. Cupola furnaces are coke-heated vertical furnaces that are charged batch-wise with raw materials, or sometimes charged continuously using vibrating chutes. The necessary heat for smelting of the charged materials is produced by means of coke combustion and air (hot or cold) blown in through tuyeres at the sides of the furnace. The actual smelting zone is found in the lower third of the vertical furnace. With regard to heat utilization the operation is similar to residential coal-fired stoves. The smelting capacity depends mainly on the air volume blown in for combustion, the amount of fuel and the diameter of the furnace (Quass, Fermann and Bröker 2000).

Induction furnaces are simple crucibles or channels that are heated by an external electrical coil. Channel induction furnaces are mainly used for melting items with large dimensions. Current is induced in the metal that has been charged into the furnace and heat is generated. The furnaces may be equipped with fume extraction hoods and dust abatement that can be used during drossing and pouring operations. Access to an induction furnace for charging and tapping means that a movable hooding system is often used. The hoods are robust so that they can withstand some mechanical impact. Alternatively, efficient fixed or lip extraction is used. The efficiency of this furnace can be low for some materials but can be increased, particularly if the feed material is small. Large items can be cut to improve efficiency and also to allow the fume collection hoods to be deployed properly. Some continuous processes also retain a heel of molten metal in the bottom of the furnace between charges if the operation allows it. They may also be operated under vacuum, for example when melting super alloys, high-alloyed steel or pure metals, and in some cases for metal distillation. The temperature of the furnace can be automatically controlled to minimize the production of fume when melting volatile or oxidizable metals such as zinc or alloys containing zinc. These furnaces are also used to hold molten metal for alloying and casting. The current induced in these furnaces causes the metal to be stirred electromagnetically, which promotes mixing of the charge and any alloying materials that are added (European Commission 2001).

A blast furnace is a vertical furnace using tuyeres to blast heated or cold air into the furnace burden to smelt the contents. Sinter is charged into the top of the blast furnace in alternating layers with coke.

## **1.2 Furnace feedstock**

The major feedstock for the furnace is ferrous scrap, which may include ferrous scrap from inside the steelworks (e.g. offcuts), cut-offs from steel product manufacturers (e.g. vehicle builders) and capital or post-consumer scrap (e.g. end-of-life vehicles and appliances) (European Commission 2000). Additional inputs are fluxes and additions like deoxidants or alloying elements. Direct reduced iron is also increasingly being used as a feedstock, due to both its low gangue content and variable scrap prices (European Commission 2000).

Fluxing materials are added to combine with unwanted materials and form a slag. Slag removes the steel impurities (e.g. silicon, sulphur and phosphorus) from the molten

steel. Oxygen may be added to the furnace to speed up the steel-making process. At the end of a heat, the furnace tips forward and the molten steel is poured off.

### 1.3 The electric arc furnace

Many steel plants increase productivity by using the electric arc furnace for the melting phase and a ladle metallurgy facility for the final refining and alloying phase. In some cases the steel ladle is taken to a vacuum degassing station where the gas content of the molten steel is reduced for quality requirements.

The molten steel from the electric arc furnace or the ladle metallurgical facility is cast in a continuous casting machine to produce cast shapes including slabs, billets or beam blanks. In some processes, the cast shape is torch cut to length and transported hot to the hot rolling mill for further processing. Other steel mills have rehear furnaces. Steel billets are allowed to cool, and are then reheated in a furnace prior to rolling the billets into bars or other shapes.

Production of steel from scrap consumes considerably less energy than production of steel from iron ores (EPRI 1997). Electric arc furnace steel manufacturing is an important recycling activity that contributes to the recovery of steel resources and waste minimization.

The use of electric arc furnaces in the production of steel provides three major benefits: lower capital cost for a steel-making shop; significantly less energy required to produce steel compared to the coke oven, blast furnace and basic oxygen furnace methods of the integrated steel makers; and avoidance of coke ovens.

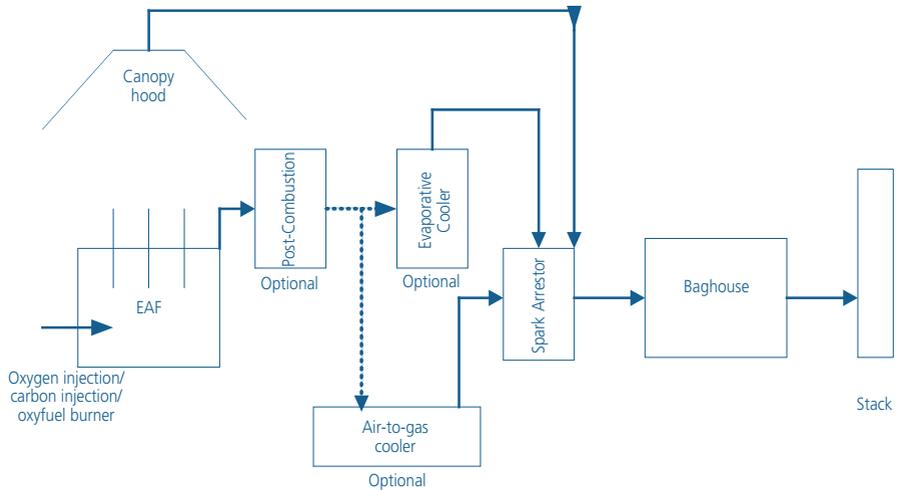
Electric arc furnace steel making is a dynamic batch process with steel tap-to-tap times of one hour or less for a heat, except for stainless and specialty steel producers. The process is constantly changing, from the removal of the furnace roof for charging the steel scrap and the meltdown of the steel scrap (with the resultant emissions from scrap contaminants such as oils and plastics), to the refining period, and finally tapping of the steel. The conditions within the electric arc furnace and the combustion processes vary throughout the heat production cycle.

In recent years, more new and existing electric arc furnaces have been equipped with a system for preheating the scrap in the off-gas in order to recover energy. The so-called shaft technology and the Consteel process are the two proven systems that have been introduced. The shaft system can be designed to reheat 100% of the scrap (European Commission 2000).

Some electric arc furnaces also use a water spray or evaporative cooling system to cool the hot off-gases, and some use heat exchangers ahead of the emission control device. The furnaces may be equipped with dry, semi-wet or wet air pollution controls. Semi-wet and wet gas cleaning systems may be sources of wastewater.

Figure 7 shows the electric arc furnace and a generic fabric filter emission control system.

■ **Figure 7. Generic electric arc furnace emission control system**



Source: William Lemmon and Associates Ltd 2004.

## 2. Sources of chemicals listed in Annex C of the Stockholm Convention

### 2.1 Emissions

#### 2.1.1 PCDD/PCDF formation

Electric arc furnace steel making is a batch process that can result in fluctuating emissions during heating of the charge and from heat to heat. Gas handling systems vary from facility to facility, both in configuration and design. These factors contribute to a varying concentration in process off-gases.

As a high-temperature metallurgical process, particulate matter that contains a fine fume of metal and metal oxides is generated. High-efficiency pollution control systems are required to remove the fine particulate matter in the off-gases.

Aromatic organohalogen compounds, including polychlorinated dibenzo-*p*-dioxins (PCDD), polychlorinated dibenzofurans (PCDF), chlorobenzenes and polychlorinated biphenyls (PCB), may be formed as a consequence of the thermal process and have been detected in electric arc furnace off-gas. The most important members of this group of compounds are PCDD/PCDF. Scrap preheating may result in higher emissions of aromatic organohalogen compounds.

A report entitled *Research on Technical Pollution Prevention Options for Steel Manufacturing Electric Arc Furnaces* (William Lemmon and Associates Ltd 2004), prepared for the Canadian Council of Ministers of the Environment, takes into account

the United Nations Environment Programme (UNEP) document *Formation of PCDD/PCDF: An Overview* (UNEP 2003a), and provides an understanding of the basic formation mechanism of PCDD/PCDF. Information from this report is summarized below.

The processes by which PCDD/PCDF are formed are not completely understood. Most information about these substances in combustion processes has been obtained from laboratory experiments, pilot-scale systems and municipal waste incinerators.

PCDD/PCDF appears to be most probably formed in the electric arc furnace steel-making process via de novo synthesis by the combustion of non-chlorinated organic matter such as plastics, coal and particulate carbon in the presence of chlorine donors. Many of these substances are contained in trace concentrations in the steel scrap or are process raw materials such as injected carbon. The Ohio Valley Aluminium Company (Ovaco) has commented that it is well known that the emission of PCDD/PCDF is very low when using stainless steel scrap as raw material, a fraction only of that of other electric arc furnaces, and speculates that this is possibly due to catalytic effects of metals present in the dusts (Ovaco 2006 communication).

There is an inherent dualism of formation and dechlorination of PCDD/PCDF which occurs in the same temperature range and especially under the conditions present in the electric arc furnace. In general, dechlorination of PCDD/PCDF appears to take place at temperatures above 750°C in the presence of oxygen. As the temperature increases above 750°C, the rate of dechlorination increases and the required residence time decreases.

Increasing the oxygen concentrations results in increasing formation of PCDD/PCDF. It is not known whether this continues at elevated oxygen concentrations (for example, above 10% O<sub>2</sub>). Under pyrolytic conditions (oxygen deficiency) dechlorination of PCDD/PCDF occurs at temperatures above 300°C.

Some metals act as catalysts in the formation of PCDD/PCDF. Copper is a strong catalyst and iron is a weaker one.

Condensation starts in the 125 – 60°C range with the higher-chlorinated PCDD and increases very rapidly as the temperature drops. The lower-chlorinated PCDF are the last to condense, which explains why the tetra and penta PCDF constitute the majority of the PCDF in electric arc furnace emission tests.

Emission test results had higher PCDD/PCDF emission concentrations when the gas temperature exiting the gas conditioning system/gas cooling device was consistently above 225°C, indicating that de novo synthesis had taken place in the gas conditioning system.

PCDF consistently accounted for 60–90% of the PCDD/PCDF concentration in electric arc furnace emission tests.

Two furan congeners, 2,3,7,8-TCDF (tetrachlorodibenzofuran) and 2,3,4,7,8-TCDF, consistently accounted for 60–75% of the PCDD/PCDF I-TEQ concentration in electric arc furnace emission tests. These results are comparable to the theoretical condensation calculations for PCDD/PCDF, as these two congeners would be the last to condense as the gas temperature decreases.

These latter findings indicate that there is a predominant PCDD/PCDF formation mechanism, de novo synthesis, for the electric arc furnace steel-making process. It appears likely that variations in the PCDD/PCDF fingerprint for the process are due to variations in the constituents of the scrap charge, varying conditions in the furnace resulting from changes in operating practices from heat to heat and plant to plant, varying conditions in the gas conditioning and cleaning system, and differences in baghouse collection efficiencies.

Electric induction furnaces require cleaner scrap charges than electric arc furnaces can tolerate, and melt their charge using magnetic fields. While there are some similarities to electric arc furnaces, dioxin and furan generation in such units is expected to be significantly lower than from electric arc furnaces.

With regard to emissions from cupola furnaces employed in cast iron and steel foundries, a German submission to *The European Dioxin Emission Inventory Stage II* (Quass, Fermann and Bröker 2000) summarized the results of a study collecting data on 25 cold blast cupolas located in Germany. Cold blast cupola furnaces (also termed cold air or cold wind cupolas) were identified in UNEP 2003b as having a higher potential than other designs for significant emissions:

“For foundries, there are hardly any data available: testing in Germany (SCEP 1994) showed that hot air cupolas and induction furnaces fitted with fabric filters had low emissions to air, an emission factor of 0.03 g TEQ/t of product should be used. Cold air cupolas showed higher emissions and a factor of 1 g TEQ/t is used for plants with fabric filters.

Limited testing on rotary drum furnaces showed higher levels again and a factor of 4.3 g TEQ/t is applied to plants with fabric filters for gas cleaning. Where cold air cupolas or rotary drum furnaces are used which do not have fabric filters or equivalent for gas cleaning a higher emission factor of 10 g TEQ/t should be used. If poor quality scrap (high contamination) or poorly controlled furnaces with gas cleaning other than effective fabric filters is found this should be noted.”

The more recent work reported for Quass, Fermann and Bröker 2000 focused on well-controlled cold blast cupolas producing iron for castings, equipped with fabric filters for particulate emission control. This study indicates that the range of the 18 individual emission samples obtained was 0.003 to 0.184 ng I-TEQ/Nm<sup>3</sup>, and that the three-run averages for four of the six furnaces tested were below 0.1 ng I-TEQ/Nm<sup>3</sup> (the emission

limit value for municipal waste incinerators). It also concluded that “For all furnaces studied the average emission factor was found to amount to 0.35 g I-TEQ/t of smelted iron in the furnaces with a maximum value reaching 1.45 g I-TEQ/t.” The conclusions of this chapter of Quass, Fermann and Bröker 2000 were:

“Looking at the concentrations found in the waste gases cold-blast cupola furnaces operated in iron and steel foundries cannot be considered as important sources of dioxins and furans due to their emitted total amounts of PCDD and PCDF. Thus, the results of the measurements agree with a few known data that existed before the investigations were started.

Note however, that the emissions for North Rhine-Westphalia were extrapolated from only 6 furnaces. It cannot be said with certainty that these furnaces are representative for all cold-blast cupola furnaces operated in Germany. Within this project one furnace was found having PCDD and PCDF concentrations in the filter-collected dust of up to approximately 12 g I-TEQ/kg. This is considerably higher than from those plants where emissions were measured (highest concentration in the filter-collected dust from these plants was 0.4 g I-TEQ). In addition, a high temporal fluctuation of PCDD and PCDF concentrations in the filter-collected dusts became apparent. Therefore, despite an indication of a positive correlation between the concentrations in the filter-collected dust and the concentrations in the waste gas – obtained from measurement results – it is not allowed to assume that this correlation may be extrapolated on furnaces with higher concentrations in the filter-collected dusts. For clarification, a further study programme would be necessary which, for example, would allow measurements of PCDD and PCDF concentrations in the filter-collected dust of a furnace over a longer period of time.

From the observed interdependence of PCDD and PCDF emissions and the amounts of cast scrap and recycled material applied it can be concluded that the contaminants adhering to the cast scrap (remnants of paint, oils etc.) have an influence on the emissions. In order to reduce dioxin concentrations a decrease of the amount of cast scrap would make sense; however, this would considerably reduce the cost efficiency of foundries. The question arises, whether certain contaminants on the cast scrap play a major role in the development and emission of PCDD and PCDF. If this is so, it would require a selective elimination from the charged input material.”

### **2.1.2 PCDD/PCDF research on electric arc furnaces**

Most of the research on PCDD/PCDF formation and control has been carried out for electric arc furnaces in Europe. The earliest reported work was by Badische Stahlwerke GmbH (BSW) in Kehl/Rheim, Germany, in the early 1990s (Weiss and Karcher 1996). Other European steel companies followed BSW's lead under regulatory pressure from national environmental agencies.

A summary of the electric arc furnace operational findings follows:

- The BSW research project confirmed that a high concentration of hydrocarbon material in the steel scrap significantly increased the emissions of volatile organic compounds and PCDD/PCDF.
- Emission test results from BSW, ProfilARBED, Differdange and Gerdau Ameristeel Cambridge emission-testing programmes had higher PCDD/PCDF emission concentrations when the gas temperature exiting the gas conditioning system or gas cooling device was consistently above 225°C, indicating that de novo synthesis had taken place in the gas conditioning system.
- PCDF consistently accounted for 60–90% of the PCDD/PCDF I-TEQ concentration in the Canadian electric arc furnace emission tests. Similar results have been reported in European emission tests of electric arc furnaces.
- Two PCDF congeners, 2,3,7,8-TCDF and 2,3,4,7,8-TCDF, consistently accounted for 60–75% of the PCDD/PCDF I-TEQ concentration in the Canadian electric arc furnace emission tests. Similar results have been reported in European emission tests of electric arc furnaces. These results are comparable to the theoretical condensation calculations for PCDD/PCDF, as these two congeners would be the last to condense as the gas temperature decreases.
- The congener I-TEQ concentration distributions in the Canadian electric arc furnace emission tests were similar regardless of the total PCDD/PCDF I-TEQ concentrations.
- The findings indicate that de novo synthesis is the predominant PCDD/PCDF formation mechanism for the electric arc furnace steel-making process.
- It appears likely that variations in the PCDD/PCDF emission fingerprint for the electric arc furnace steel-making process are due to variations in the constituents of the scrap charge, varying conditions in the furnace resulting from changes in operating practices from heat to heat and plant to plant, varying conditions in the gas conditioning and cleaning system, and differences in baghouse collection efficiencies. There is insufficient publicly available information to determine the relative importance of these factors.

A report prepared by the Government of Japan studied the implementation of measures specified in the present guidelines to reduce emissions of PCDD/PCDF and coplanar polychlorinated biphenyls from steel-manufacturing electric arc furnaces, targeting 19 factories out of 38 non-integrated steel producers in Japan. The emissions concentration was reduced by between 80% and 87.2% in the factories that implemented a single measure, while reductions of 96% or more were achieved for those implementing two or more measures. The emissions concentration was reduced by 84% on average compared to those not implementing any of the measures. The average concentration was 0.42 ng I-TEQ/Nm<sup>3</sup>. Two factories (10% of all targeted factories) attained the achievable performance level value, which is below 0.1 ng I-TEQ/Nm<sup>3</sup> (Government of Japan 2006).

### 2.1.3 Review of electric arc combustion chemistry and PCDD/PCDF formation

A review of the relationship of electric arc furnace combustion chemistry with PCDD/PCDF formation in the furnace may be summarized as follows:

- PCDD/PCDF can be formed from related chlorinated precursors such as polychlorinated biphenyls, chlorinated phenols and chlorinated benzenes.
- The environment inside a steel-making electric arc furnace is very complex and is constantly varying. The combustion chemistry produces conditions that are amenable to PCDD/PCDF formation. The hydrocarbons entering the furnace in the scrap may be vaporized, cracked, partially combusted or completely combusted, depending on the conditions in the furnace or parts of the furnace during or after charging. Other sources of carbon include injected carbon and the graphite electrodes. The dual processes of PCDD/PCDF formation and dechlorination may be proceeding at the same time if the oxygen concentration and temperature are such that some PCDD or PCDF congeners are being formed while other congeners are being dechlorinated.
- The research on optimization of internal post-combustion indicates that under normal steel-making operations, conditions favourable to PCDD/PCDF formation – oxygen-rich atmosphere, reactive carbon particles and temperatures under 800°C – are present in parts of the furnace during the meltdown phase and possibly for some time afterwards. Given that metals that act as catalysts are present and that trace amounts of chlorine may be present in some of the charge materials and fluxes, the conditions appear to be present for de novo synthesis to occur. Since ideal mixing conditions are not present, it appears that a portion of the PCDD/PCDF that are formed will leave the electric arc furnace in the off-gas without encountering sufficiently high temperatures for dechlorination to take place.
- Most of the research on combustion chemistry and internal post-combustion in electric arc furnace steel making has aimed to increase productivity by taking advantage of fuels within the furnace – such as hydrocarbons, carbon monoxide and hydrogen – to replace electric energy with chemical energy, thus reducing the total energy input, which results in lower production costs per ton of product.
- Scrap preheating may result in elevated emissions of chlorinated aromatic compounds such as PCDD/PCDF, chlorobenzenes, polychlorinated biphenyls, as well as polycyclic aromatic hydrocarbons, and other products of incomplete combustion from scrap contaminated with paints, plastics, lubricants or other organic compounds. The formation of these pollutants may be minimized by post-combustion within the furnace (as opposed to external post-combustion of the off-gas) by additional oxygen burners developed for burning the carbon monoxide and hydrocarbons, which recovers chemical energy. It has been suggested that scrap preheating increases the organic matter in the flue gas and maybe also the formation of chlorinated compounds. What happens to the emissions depends on total heat energy balance of the flue gas system. In

Ovaco's case, scrap preheating decreases the emission of PCDD/PCDF (and most probably increases emission of light organic compounds), due to the fact that scrap preheating acts as an efficient gas cooler; low gas temperature at the filter means that heavy organic compounds are separated with dust.

- Indications are that internal post-combustion may be a more attractive option than external post-combustion for PCDD/PCDF formation prevention.

## **2.2 PCDD/PCDF releases in solid waste and wastewater sources**

Most mills worldwide operate electric arc furnaces with dry off-gas cleaning systems (i.e., fabric filter dust collectors), which produce no process wastewater that would require treatment.

Some existing electric arc furnaces may be equipped with semi-wet air pollution control systems (European Commission 2000). Semi-wet systems apply water to the furnace off-gases in order to partially cool and condition the off-gases prior to particulate removal in an electrostatic precipitator. Sites are able to achieve zero wastewater discharge from semi-wet systems by balancing the applied water with water that evaporates in the conditioning process. Non-contact cooling water is the predominant water source; however, some facilities may use treated process water and plant service water (EPA 2002).

Standards of some jurisdictions identify zero discharge as the best available technique for semi-dry gas cleaning systems.

In some European Union countries wet scrubbers are used to clean the off-gases from electric arc furnaces at some mills. However, no information from these facilities is available on wastewater quantities and methods of treatment (European Commission 2000). Consequently, no findings were concluded as to best available techniques for treating and minimizing PCDD/PCDF releases from wastewater from wet air pollution control systems.

Residues in the form of dust collected by the dry air pollution control system for electric arc furnaces have been found to contain significant levels of PCDD/PCDF.

## **3. Electric arc furnace process improvements and alternative processes for electric steel making**

### **3.1 Process improvements**

The electric arc furnace steel-making process has been undergoing change over the past decades. Research and development for electric arc furnace steel making, especially in Europe, is focused on furnace design improvements to increase productivity and energy efficiency, and to reduce steel-making costs.

There are two major driving forces – reduction of steel-making costs as exemplified by increased productivity, and increased product quality as exemplified by quality demands from the automotive industry. Added to these is a third driving force – environmental

pressures. Productivity improvements have resulted in shorter tap-to-tap times, increased energy efficiency and increased use of chemical energy.

Quality demands have been met through selection of scrap, furnace operating practices and increased use of ancillary processes such as ladle metallurgy and vacuum degassing. Environmental pressures include the requirements for PCDD/PCDF emission reduction and smog precursor reduction of substances such as fine particulate. One option for these producers is to use higher-quality scrap with lower contaminant levels (William Lemmon and Associates Ltd 2004).

A second option is to replace part of the scrap charge by direct reduced iron or similar products that are produced from iron ore and have contaminant concentrations lower than the lower-quality scrap steel grades. Merchant direct reduced iron production is increasing and the international market is growing, so greater availability may mean that some electric arc furnace steel makers have the option of buying direct reduced iron rather than on-site production. There is very limited available information on PCDD/PCDF emissions from the direct reduced iron process but, given the characteristics of the process, PCDD/PCDF emissions are likely to be very small. Information on the formation and emissions of PCDD/PCDF from the use of direct reduced iron in electric arc furnace steel making is not available.

A third option is the use of hot metal in electric arc furnace steel making. This is forecast to increase as steel makers strive for shorter heat cycles and higher productivity (Fruehan 1998). Information on the impact of this option on PCDD/PCDF emissions is not available. With preheating of part of the scrap about 60 kWh/t can be saved; in the case of preheating the total scrap amount up to 100 kWh/t liquid steel can be saved. The applicability of scrap preheating depends on the local circumstances and has to be proved on a plant-by-plant basis.

Advances in the electric arc furnace steel-making process often have collateral benefits, including the reduction of particulate matter and PCDD/PCDF emissions, except for scrap preheating as noted above. Usually the objective of advanced operating practices is improved operational and energy efficiency to increase productivity and thus increase production and reduce operating costs.

### **3.2 Alternative processes**

No alternative steel-making technology would replace the electric arc furnace for the high production operations of steel plants. While other electrode materials have been used for a few furnaces in the past, there are no alternatives to the graphite electrode at the present time.

## **4. Primary and secondary measures**

Primary and secondary measures for reducing emissions of PCDD/PCDF from electric arc furnaces are outlined in the ensuing section. Much of this material has been drawn from William Lemmon and Associates Ltd 2004. Some of these measures also apply to cupola and electric induction furnaces.

The extent of emission reductions possible with implementation of primary measures only is not readily known. Implementation of both primary and secondary measures at existing and new plants is probably necessary to achieve the desired emission levels. A case study of a steelmaking electric arc furnace facility upgrade of pollution prevention and control systems is provided by Finlay and Peng, 2006.

It should be feasible for plants to implement some or all of the pollution prevention practices identified below.

#### **4.1 Primary measures for emissions**

Primary measures, often called pollution prevention techniques, are able to avoid, suppress or minimize the formation of PCDD/PCDF or dechlorinate PCDD/PCDF in the secondary steel-making process.

As a general measure, an integral part of a facility's pollution prevention programme should include best environmental, operating and maintenance practices for all operations and aspects of the electric arc furnace steel-making process.

The following list presents a range of options as primary measures; some may not be applicable to all furnace designs or plants, and some may require further investigation. This list of techniques has been developed based on work done with electric arc furnaces, and while many of the same principles are expected to hold for electric induction and cupola furnaces, they have not been documented for those applications. However, the fact that most of the existing test results for the other furnace types are below 0.1 ng I-TEQ/Nm<sup>3</sup> indicates that a combination of these measures and the secondary measures listed below should be effective to limit emissions.

##### **4.1.1 Raw material quality**

The major raw material used in the secondary steel-making process is iron or steel scrap. Contaminants, including oil, plastics and other hydrocarbons, are often present in the scrap. Pollution prevention practices to prevent or minimize the entry of contaminants into furnaces for iron and steel making include changes in material specifications, improved quality control programmes, changes in the types of raw materials (such as controlling the use of oily scrap or cleaning oily scrap) and programmes to prevent the entry of contaminants.

##### **4.1.2 Furnace operation**

Recent changes in electric arc furnace operational practices that have been adopted to improve operational and energy efficiency appear to have collateral benefits to reduce PCDD/PCDF or, in certain conditions, to dechlorinate PCDD/PCDF. Pollution prevention practices that appear to reduce PCDD/PCDF emissions include minimizing the duration of the roof being open for charging, reduction of air infiltration into the furnace and avoiding or minimizing operational delays. Condensation of PCDD/PCDF increases rapidly at temperatures below 125°C, starting with the higher-chlorinated dioxins.

### **4.1.3 Off-gas conditioning system design**

Off-gas conditioning includes the collection, cooling and ducting of furnace off-gases prior to cleaning in a baghouse. Off-gas conditioning system conditions may be conducive to de novo synthesis formation of PCDD/PCDF unless care is taken to avoid conditions leading to de novo synthesis. Pollution prevention techniques include an adequately sized system, maximization of off-gas mixing, rapid cooling of off-gas to below 200°C and development and implementation of good operating and maintenance practices.

### **4.1.4 Continuous parameter monitoring system**

A continuous parameter monitoring system based on optimizing the appropriate parameters for the operation of the gas conditioning system and documented operating and maintenance procedures should minimize the formation of PCDD/PCDF by de novo synthesis in the gas conditioning system.

## **4.2 Secondary measures for emissions**

Secondary measures, often called pollution control techniques, may be summarized as follows:

### **4.2.1 Off-gas dust collection**

Capturing all of the off-gas, including fugitive emissions, from the electric arc furnace area is an important part of the control system. Dust collection efficiency of primary and secondary emissions from the furnace should be maximized by a combination off-gas and hood system, or doghouse and hood system, or building air evacuation.

### **4.2.2 Fabric filter dust collectors (or baghouses)**

Some of the PCDD/PCDF in the electric arc furnace off-gases adsorb onto fine particulate matter. As the gas temperature decreases through the PCDD/PCDF condensation temperature of the various congeners, more of the PCDD/PCDF either adsorb onto the fine particulate matter or condense and form fine particulate matter. Well designed and operated fabric filters achieve less than 5 mg dust/Nm<sup>3</sup>. Minimizing dust levels also minimizes PCDD/PCDF emissions.

### **4.2.3 External post-combustion system coupled with a rapid water quench**

This technique was the early PCDD/PCDF emission control technique applied to electric arc furnace steel making. External post-combustion systems were originally developed to combust carbon monoxide (CO) and hydrogen (H<sub>2</sub>) in the furnace off-gas in a refractory lined combustion chamber, usually with supplementary fuel. Subsequently a number of European electric arc furnace steel-making plants adopted the external post-combustion technology to dechlorinate PCDD/PCDF emissions by maintaining the post-combustion temperature above 800°C. This emission control technique is not able to consistently meet the Canada-wide standard of 100 pg I-TEQ/Nm<sup>3</sup> (0.1 ng I-TEQ/Nm<sup>3</sup>). It may not be feasible for some plants to install external post-combustion and

improvements to gas conditioning systems due to site-specific space considerations. For some furnaces, internal post combustion within the furnace may be effective in helping prevent PCDD/PCDF emissions.

#### **4.2.4 Adsorbent injection**

This control technique was originally developed to control PCDD/PCDF emissions from waste incinerators. Sized lignite coke (activated carbon is a similar adsorbent) injection technology is used in a number of European electric arc furnace steel-making plants to supplement the fabric filter baghouse technology to achieve low PCDD/PCDF emission concentrations consistently. This technique also reduces emissions of mercury. Reported emission test results from electric arc furnace steel-making plants in Europe indicate that this technique, in combination with a high-efficiency fabric filter baghouse, consistently achieves PCDD/PCDF emission concentrations of less than 0.1 ng I-TEQ/Nm<sup>3</sup> <sup>5</sup>. However other techniques may also be effective in reducing emissions to these levels.

The sized lignite coke is injected into the off-gas upstream of the baghouse. The coke (or activated carbon) adsorbs the PCDD/PCDF in the off-gas. Good mixing of the coke with the off-gas, and appropriate sizing of the coke (to a size similar to particles in the gas stream), are essential for optimum PCDD/PCDF removal.

Sized lignite coke production and activated carbon do not release captured PCDD/PCDF at normal product storage and landfill temperatures, and are resistant to leaching. Use of sized lignite coke as an adsorbent increases baghouse dust volume by 2%.

Activated carbon or sized coke injection systems should be considered for use at steel plants to reduce emissions of PCDD/PCDF. Site-specific considerations, such as lack of available space, configuration of existing emission control systems and cost impacts may influence the feasibility of using this technique.

### **4.3 Primary and secondary measures for solid wastes and wastewater**

The measures in this section generally apply for electric arc, electric induction and cupola furnaces. With respect to solid wastes, electric furnace slag and filter dusts from any furnace should be recycled to the maximum extent possible. Filter dust from high-alloy steel production, where possible, may be treated to recover valuable metals. Excess solid waste should be disposed of in an environmentally sound manner.

Ovaco has commented that the landfilling of electric arc furnace dust is no longer allowed in most industrial countries. The standard method is recovery of valuable metals in a separate treatment process or processes outside the steelworks. If stainless steel scrap is used as raw material, chromium, nickel, zinc and lead are recovered, otherwise (for the main part of dust) zinc and lead are separated only. The measured dioxin content of Ovaco's dust is around 1,300 pg I-TEQ/g and it represents 96% of the total amount synthesized in their process. Consequently electric arc furnace dust may be a significant reservoir of PCDD/PCDF and should be managed appropriately as a waste with respect to containments and disposal.

With respect to wastewater, closed-loop water-cooling systems for electric furnace components avoid wastewater being generated, or ensure it is recycled to the maximum extent possible to minimize waste volume for treatment.

Semi-dry emission control systems may be used at some plants. While replacement with dry dust collectors would be the desirable option, semi-dry systems can be designed to avoid the generation of wastewater.

Wastewater may originate at facilities that use wet scrubbing systems. The desired approach is the replacement of existing systems with dry dust collectors. If replacement of existing emission control systems is not feasible, the wastewater would need treatment. However, standards for treated wastewater quality concerning PCDD/PCDF discharge levels or other parameters were not found.

## 5. Summary of measures

Tables 13 and 14 present a summary of the measures discussed in previous sections.

■ **Table 13. Measures for new electric arc furnaces**

Measure	Description	Considerations	Other comments
Process design	Priority consideration should be given to the latest proven process designs based on process and emissions performance	An example is internal post-combustion design for a new electric arc furnace	
Performance requirements	Arc furnaces should be required by the applicable jurisdiction to achieve stringent performance and reporting levels	Consideration should be given to the primary and secondary measures listed in Table 14, in particular appropriate sizing of ventilation systems and use and appropriate maintenance of high efficiency fabric filters.	Achievable emission limits expected are: <0.1 ng I-TEQ/Nm <sup>3</sup> for PCDD/PCDF

■ **Table 14. Measures for new and existing electric arc furnaces**

Measure	Description	Considerations	Other comments
<i>Primary measures</i>			
General operating practices	An integral part of a facility's pollution prevention programme should include best environmental, operating and maintenance practices for all operations and aspects of the electric arc furnace steel-making process	Generally applicable; part of an integrated concept for pollution prevention	
Raw material quality	A review of feed materials and identification of alternative inputs and/or procedures to minimize unwanted inputs should be conducted. Documented procedures should be developed and implemented to carry out the appropriate changes	Generally applicable. Measures include changes in material specifications, improved quality control programmes, changes in the types of raw materials (such as controlling the use of oily scrap) and programmes to prevent the entry of contaminants	
Electric arc furnace operation	Minimizing the duration of the roof being open for charging, reduction of air infiltration into the furnace, and avoiding or minimizing operational delays	Collateral benefit is reduced PCDD/PCDF	Other pollutants are reduced, including aromatic organohalogen compounds, carbon monoxide, hydrocarbons and greenhouse gases

Measure	Description	Considerations	Other comments
Off-gas conditioning	<p>Design and installation of an adequately sized gas conditioning system based on optimum system parameters should prevent or minimize formation of PCDD/PCDF in the gas conditioning system.</p> <p>Development and implementation of documented operating and maintenance procedures should be developed to assist in optimizing the operation of the gas conditioning system</p>	<p>A reduction in de novo synthesis in the gas conditioning system has been linked to the rapid cooling of the furnace off-gases to below a range of 225°C to 200°C</p>	
Continuous parameter monitoring	<p>A continuous parameter monitoring system such as Continuous Opacity Monitors (COMs) or Bag Leak Detection (BLD) systems should be employed to ensure optimum operation.</p> <p>Operators should prepare a site-specific monitoring plan for the continuous parameter monitoring system and keep records that document conformance with the plan</p>	<p>Correlations between parameter values and stack emissions (stable operation) should be established. Parameters are then continuously monitored in comparison to optimum values</p>	<p>System can be alarmed and corrective action taken when significant deviations occur</p>

## Secondary measures

The following secondary measures can effectively reduce releases of PCDD/PCDF and serve as examples of best available techniques

Measure	Description	Considerations	Other comments
Off-gas collection	Dust collection efficiency of primary and secondary emissions from the electric arc furnace should be maximized by a combination off-gas and hood system, or doghouse and hood system, or building air evacuation	Ventilation systems in the EAF melt shop should be appropriately sized to ensure capture of process emissions within the building and conveyance to the air pollution control system.	98% efficiency or more of dust collection is achievable
Fabric filters	<p>Well-designed fabric filters achieve low dust emissions.</p> <p>Procedures should be developed for the operation and maintenance of the fabric filter dust collector to optimize and improve collection performance, including optimization of fabric bag cleaning cycles, improved fabric bag material and preventive maintenance practices.</p> <p>A continuous temperature monitoring and alarm system should be provided to monitor the off-gas inlet temperature to the emission control device.</p> <p>A bag leak detection system should be provided with documented operating and maintenance procedures for responding to monitoring system alarms</p>	<p>There are correlations between PCDD/PCDF emissions and dust emissions. At various flue gas temperatures, PCDD/PCDF will be absorbed and adsorbed on the dust captured in the fabric filter. Modern baghouses that are appropriately sized, operated, maintained and monitored are capable of dust emissions &lt;5 mg/Nm<sup>3</sup>.</p>	<p>Maintaining the off-gases in the baghouse to below 60°C will reduce PCDD/PCDF evaporation and increase capture of PCDD/PCDF associated with the dust. The collected dust should be appropriately managed, considering the pollutants contained in the dust.</p> <p>Enclosing the filter dust collection areas and transfer points minimizes fugitive dust</p> <p>The use of appropriately sized and operated ventilation systems will reduce facility workers to occupational exposure of pollutants.</p>

Mesure	Description	Considérations	Autres commentaires
Post-combustion of off-gas	<p>PCDD/PCDF formation may be minimized by post-combustion within the off-gas duct system or in a separate post-combustion chamber.</p> <p>Indications are that internal post-combustion may be a more attractive option than external post-combustion for PCDD/PCDF formation prevention</p>		<p>PCDD/PCDF that have been formed in the process undergo dechlorination reactions as the off-gas is burnt by the additional oxygen burners.</p> <p>This technique with a rapid water quench has been an early PCDD/PCDF emission control technique applied to electric arc furnace steel making</p>
Adsorbent injection	<p>Injection of activated carbon or similar adsorptive material into the off-gas upstream of high-efficiency fabric filters in electric arc furnaces at European steel-making plants has consistently achieved low levels of PCDD/PCDF emissions, according to data from demonstration projects</p>		

Mesure	Description	Considérations	Autres commentaires
Minimize solid waste generation	<p>Electric arc furnace slag and filter dust should be recycled to the extent possible.</p> <p>Filter dust from high-alloy steel production, where possible, may be treated to recover valuable metals.</p> <p>Best management practices should be developed and implemented for hauling and handling dust-generating solid wastes.</p> <p>Excess solid waste should be disposed of in an environmentally sound manner</p>		
Minimize wastewater	<p>Closed-loop water-cooling systems for electric arc furnace components avoid wastewater being generated.</p> <p>Recycle wastewater to the maximum extent possible.</p> <p>Residual wastewater should be treated.</p> <p>Semi-dry air pollution control systems can be designed to have zero discharge of excess wastewater.</p> <p>Wastewater from wet gas cleaning systems should be treated before discharging to the environment</p>	<p>These measures would be primarily associated with general pollution prevention and control practices rather than being applied specifically, or only, for the purpose of PCDD/PCDF</p>	<p>No standards were found on PCDD/PCDF limits for treated wastewater discharged as final effluent from wet off-gas cleaning systems</p>

## 6. Performance level associated with best available techniques

A performance level associated with best available techniques for air emissions of PCDD/PCDF from secondary steel-making plants and iron and steel foundries is <0.1 ng I-TEQ/Nm<sup>3</sup>. (at operating oxygen concentrations)

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## (v) Primary base metals smelting

### ■ Summary

Primary base metals smelting involves the extraction and refining of nickel, lead, copper, zinc and cobalt. Generally, primary base metals smelting facilities process ore concentrates. Most primary smelters have the technical capability to supplement primary concentrate feed with secondary materials (e.g. recyclables).

Production techniques may include pyrometallurgical or hydrometallurgical processes. Chemicals listed in Annex C of the Stockholm Convention are thought to originate through high-temperature thermal metallurgical processes; hydrometallurgical processes are therefore not considered in this section on best available techniques for primary base metals smelting.

Available information on emissions of PCDD and PCDF from a variety of source sectors (e.g. incinerators, steel electric arc furnaces, iron sintering plants) suggests that process technologies and techniques, and associated off-gas conditioning, can influence the formation and subsequent release of PCDD/PCDF. Consideration should be given to hydrometallurgical processes, where technically and economically feasible, as alternatives to pyrometallurgical processes when considering proposals for the construction and commissioning of new base metals smelting facilities or processes.

Primary measures include the use of hydrometallurgical processes, quality control of feed materials and scrap to minimize contaminants leading to PCDD/PCDF formation, effective process control to avoid conditions leading to PCDD/PCDF formation, and use of flash smelting technology. Identified secondary measures include high-efficiency gas cleaning and conversion of sulphur dioxide to sulphuric acid, effective fume and gas collection and high-efficiency dust removal.

PCDD/PCDF performance levels in air emissions associated with best available techniques for base metals smelters are  $<0.1 \text{ ng I-TEQ/Nm}^3$  (at operating oxygen concentrations).

## 1. Process description

The technical processes involved in the extraction and refining of base metals (nickel, lead, copper, zinc and cobalt) generally proceed as shown in Figure 8. Key metal recovery technologies that are used to produce refined metals can be categorized as follows:

1. Pyrometallurgical technologies use heat to separate desired metals from unwanted materials. These processes exploit the differences between constituent oxidation potential, melting point, vapour pressure, density and miscibility when melted;
2. Hydrometallurgical technologies use differences between constituent's solubility and electrochemical properties while in aqueous acid solutions to separate desired metals from unwanted materials;

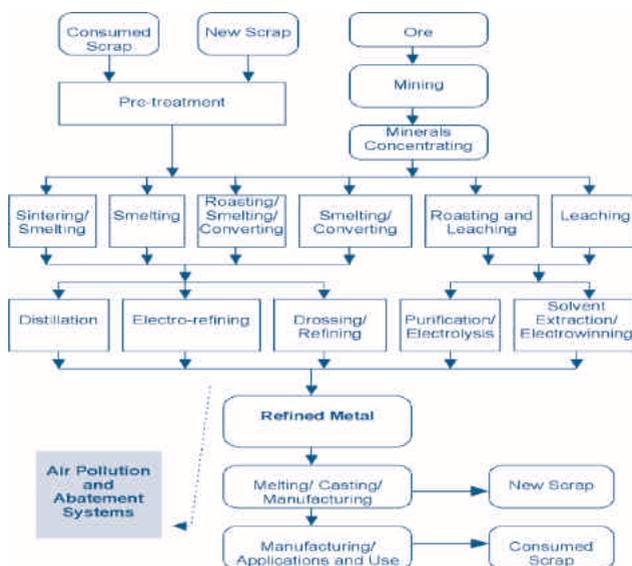
- Vapometallurgical technologies apply to the Inco carbonyl process whereby nickel alloys are treated with carbon monoxide gas to form nickel carbonyl.

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

Figure 8 provides a generic flow sheet showing the main production processes associated with primary smelting and refining.

Chemicals listed in Annex C of the Stockholm Convention are thought to originate through high-temperature thermal metallurgical processes; hydrometallurgical processes are therefore not considered in this section on best available techniques for primary base metals smelting.

**Figure 8. Generic flow sheet for primary base metals smelting**



Artisanal and small enterprise metal recovery activities are sometimes used in developing countries and countries with economies in transition. These artisanal processes may be significant sources of pollution and of adverse human health impacts. Metals that are known to be produced by artisanal and small enterprise metal recovery activities include aluminium, antimony, copper, gold, iron, lead, manganese, mercury, tin, tungsten, silver and zinc. These activities usually do not have any pollution controls and may be sources of chemicals listed in Annex C.

While artisanal metal recovery activities are not considered best available techniques or best environmental practices, it is recommended that, as a minimum, appropriate

ventilation and material handling should be carried out to minimize human exposure to pollutants from these activities.

## **2. Sources of chemicals listed in Annex C of the Stockholm Convention**

Primary base metals smelters can be sources of chemicals listed in Annex C. The formation and release of such chemicals from primary smelters are not well understood, and it has been shown that emissions of polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) can range significantly between operations using similar processes.

### **2.1 Releases to air**

#### **2.1.1 General information on emissions from base metals smelting**

“The main environmental issues for the production of most non-ferrous metals from primary raw materials are the potential emission to air of dust and metals/metal compounds and of sulphur dioxide if roasting and smelting sulphide concentrates or using sulphur containing fuels or other materials. The capture of sulphur and its conversion or removal is therefore an important factor in the production of non-ferrous metals. The pyrometallurgical processes are potential sources of dust, fugitive fumes and metals from furnaces, reactors and from the launders and ladles during the transfer of molten metal” (European Commission 2001).

#### **2.1.2 Emissions of PCDD and PCDF**

“There is limited published information on dioxin/furan mechanisms of formation for the base metals smelting sector, most of which is based on European experience for secondary base metal smelters. There are a few general statements that dioxins and furans might be present in some of the raw materials for secondary base metals smelting and that oils and organic materials are present in many of these raw materials. The presence of oils and other organic materials in scrap or other sources of carbon (partially burnt fuels and reductants such as coke) can produce fine carbon particles or gaseous precursors which react with inorganic chlorides or organically bound chlorine in the temperature range of 250°C to 500°C to produce dioxins and furans. This process is known as *de novo* synthesis which is dependent on catalysts such as copper and iron. Although dioxins and furans are destroyed at high temperature (above 850°C) in the presence of oxygen, the process of *de novo* synthesis is still possible as the gases are cooled” (Charles E. Napier Co. Ltd 2002).

Available information on emissions of PCDD and PCDF from a variety of source sectors (e.g. incinerators, steel electric arc furnaces, iron sintering plants) suggests that process technologies and techniques, and associated off-gas conditioning, can influence the formation and subsequent release of PCDD/PCDF.

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

Smelting facilities in Canada generally process sulphide concentrates and, at some facilities, also process some secondary materials. Off-gas conditioning varies from extensive cleaning (e.g. high-efficiency dedusting) and conversion to sulphuric acid, to dedusting by fabric filters, to dedusting by electrostatic precipitator. These facilities produce nickel, copper, lead, zinc and co-product metals. There were 11 participating facilities in the Canadian test programme, conducting approximately 20 emission tests on 16 different sources. No two facilities had the same combination and configuration of production processes and off-gas conditioning systems, further complicating any possible analysis. As such, the observations noted below are general in nature.

Where off-gases were cleaned (i.e., dedusted, scrubbed) and processed through an acid plant for conversion of off-gases rich in sulphur dioxide (SO<sub>2</sub>) to sulphuric acid, emission test results showed concentrations below 5 pg (0.005 ng) I-TEQ/m<sup>3</sup>.<sup>6</sup>

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

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

## 2.2 Releases to other media

No information was found on releases of chemicals listed in Annex C from primary base metals smelters to media other than air. However, they are likely to be present in some liquid effluents from wet scrubbers and in some dusts and scrubber residues collected in air pollution abatement systems.

## 3. Alternative processes for base metals smelting

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

As indicated in Figure 8, there is a wide range of processes used in the primary production of base metals smelting. The processes used to produce crude or refined base metals from primary sources will depend to a large extent on the available ore or concentrate (e.g. laterite ore or sulphide ore), and other considerations (e.g. properties of the desired metal(s), properties of the feed materials, available fuel and energy sources, capacity and economic considerations).

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

## **4. Primary and secondary measures**

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

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

### **4.1 Primary measures**

Primary measures are regarded as pollution prevention measures that will prevent or minimize the formation and release of the identified substances, namely PCDD, PCDF, hexachlorobenzene (HCB) and polychlorinated biphenyls (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” (See section III.B of the present guidelines).

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

#### **4.1.1 Use of hydrometallurgical processes**

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

#### **4.1.2 Quality control of (scrap) feed material**

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

Methods to be considered are (European Commission 2001, p. 232):

1. Sufficient blending of material to provide a homogeneous feed in order to promote steady-state conditions
2. Oil removal from feed (e.g. thermal decoating and de-oiling processes followed by afterburning to destroy any organic material in the off-gas);
3. 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;
4. Elimination of plastic by stripping cable insulation (e.g. possible cryogenic techniques to make plastics friable and easily separable).

#### **4.1.3 Effective process control**

Process control systems should be utilized to maintain process stability and ensure operation 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/PCDF 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.

#### **4.1.4 Use of flash smelting technology**

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

#### **4.1.5 Maximization of SO<sub>2</sub> content for sulphur fixation**

A general measure involves operation of processes in a manner that maximizes the concentration of the SO<sub>2</sub> in the off-gas (when processing sulphide ores or concentrates). It is important, therefore, that a process be selected that uses oxygen-enriched air (or pure oxygen) to raise the SO<sub>2</sub> content of the process gas stream and reduce the total volume of the stream, thus permitting efficient fixation of SO<sub>2</sub>.

### **4.2 Secondary measures**

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

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

#### **4.2.1 High-efficiency gas cleaning and conversion of SO<sub>2</sub> to sulphuric acid**

For SO<sub>2</sub>-rich off-gases (typically 5% or greater) generated by pyrometallurgical processing of sulphide ores or concentrates, high-efficiency precleaning of off-gases followed by conversion of SO<sub>2</sub> to sulphuric acid are together considered best available techniques for this type of source. Emission concentrations of PCDD/PCDF with use of this combination of techniques are <0.005 ng I-TEQ/m<sup>3</sup>.

For conversion to sulphuric acid, a double-contact, double-absorption process is considered a best available technique. A double-contact, double-absorption plant should emit no more than 0.2 kg of SO<sub>2</sub> per ton of sulphuric acid produced (based on a conversion efficiency of 99.7%) (World Bank 1998).

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

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

Other techniques for sulphur fixation, which may require precleaning of off-gases prior to conversion or recovery, may potentially contribute to the minimization of PCDD/PCDF emissions (World Bank 1998). These techniques include:

1. Recovery as liquid sulphur dioxide (absorption of clean, dry off-gas in water or chemical absorption by ammonium bisulphite or dimethyl aniline);
2. Recovery as elemental sulphur, using reductants such as hydrocarbons, carbon or hydrogen sulphide. Normally the sulphur content in the gas is still higher than acceptable when using this technique. The reduction conditions are also favourable for dioxins formation. Thus, after the recovery, the gas should be post-combusted and cleaned using techniques such as scrubbing.

#### **4.2.2 Fume and gas collection**

Air emissions should be controlled at all stages of the process, including 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 (European Commission 2001, p. 187–188).

The use of reverberatory furnaces is steadily decreasing because of the difficulty of controlling emissions and the high costs involved. It is difficult to imagine that further reverberatory furnaces will be built.

(Personal Communication, February 2006)

### **4.2.3 High-efficiency dust removal**

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

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

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

## **5. Emerging research**

Selective catalytic reduction has been used for controlling emissions of nitrogen oxides ( $\text{NO}_x$ ) from a number of industrial processes. Modified selective catalytic reduction technology (i.e., increased reactive area) and select catalytic processes have been shown to decompose PCDD and PCDF contained in off-gases, probably through catalytic oxidation reactions. This may be considered as an evolving technique with potential for effectively reducing emissions of persistent organic pollutants from base metals smelting operations and other applications. However, catalytic oxidation can, subject to catalyst selection, be subject to poisoning from trace metals and other exhaust gas contaminants. Validation work would be necessary before use of this process.

## 6. Summary of measures

Tables 15 and 16 present a summary of the measures discussed in previous sections.

■ **Table 15. Measures for new primary base metals smelting operations**

Measure	Description	Considerations	Other comments
Alternative processes	Priority consideration should be given to alternative processes with potentially less environmental impacts than pyrometallurgical base metals smelting	Hydrometallurgical processes are a significant means of preventing emissions. It has been commented that direct atmospheric leaching of sulphide concentrations (Fex to Zn concentrates) should be considered. (Finnish representative, 2006) Closed-loop electrolysis plants will contribute to prevention of pollution	
Performance requirements	New primary base metals smelting operations should be permitted to achieve stringent performance and reporting levels associated with best available techniques	Consideration should be given to the primary and secondary measures listed in Table 16	Performance requirements for achievement should take into consideration achievable emission levels of PCDD/PCDF identified in subsection 7 below

■ **Table 16. Summary of primary and secondary measures for primary base metals smelting operations**

Measure	Description	Considerations	Other comments
<i>Primary measures</i>			
Use of hydrometallurgical processes	Use of hydrometallurgical processes rather than pyrometallurgical processes where possible, as a significant means of preventing emissions. Closed-loop electrolysis plants will contribute to prevention of pollution	Use of hydrometallurgical processes will depend in large part on the ore and concentrate to be processed (e.g. laterite or sulphide). The combination of hydrometallurgy and pyrometallurgy, emerging for metals such as nickel and copper, may offer potential for zinc smelting (Finnish representative, 2006)	

Measure	Description	Considerations	Other comments
Quality control of (scrap) feed material	Selection and sorting to prevent the addition of material that is contaminated with organic matter or precursors can reduce the potential for PCDD/PCDF formation	<p>Methods to be considered are:</p> <ul style="list-style-type: none"> <li>• Oil removal from feed (e.g. thermal deoiling and de-oiling processes followed by afterburning to destroy any organic material in the off-gas)</li> <li>• Use of milling and grinding techniques with good dust extraction and abatement. The resulting particles can be treated to recover valuable metals using density or pneumatic separation</li> <li>• Elimination of plastic by stripping cable insulation (e.g. possible cryogenic techniques to make plastics friable and easily separable)</li> <li>• Sufficient blending of material to provide a homogeneous feed in order to promote steady-state conditions is possibly the first priority</li> </ul> <p>(Finnish representative, 2006)</p>	

Measure	Description	Considerations	Other comments
Effective process control	Process control systems should be utilized to maintain process stability and operate at parameter levels that will contribute to the minimization of PCDD/PCDF generation. In the absence of continuous PCDD/PCDF monitoring, other variables such as temperature, residence time, gas components and fume collection damper controls should be continuously monitored and maintained to establish optimum operating conditions for the reduction of PCDD/PCDF	For example, furnace temperatures should be maintained above 850°C to destroy PCDD/PCDF	
Use flash smelting technology	Where pyrometallurgical techniques are used, use of flash smelting technology rather than older technologies (e.g. roasters, blast furnace) is a significant means of reducing energy use and reducing emissions	Flash smelting will also result in high concentration of SO <sub>2</sub> in the off-gas stream, which would permit the efficient fixation or recovery of SO <sub>2</sub> prior to off-gas venting	

Measure	Description	Considerations	Other comments
Maximize SO <sub>2</sub> content for sulphur fixation	This general measure involves operation of processes in a manner that maximizes the concentration of the SO <sub>2</sub> in the off-gas (where processing sulphide ores or concentrates), to enable recovery or fixation of the sulphur. Preference should be given to processes that use oxygen-enriched air (or pure oxygen) to raise the SO <sub>2</sub> content of the process gas stream and reduce the total volume of the stream		

### **Secondary measures**

The following secondary measures can effectively reduce emissions of PCDD/PCDF and should be considered as examples of best available techniques

High-efficiency gas cleaning and conversion of SO <sub>2</sub> to sulphuric acid	SO <sub>2</sub> -rich off-gases, high-efficiency precleaning of off-gases followed by conversion of SO <sub>2</sub> to sulphuric acid should be employed, and are together considered best available techniques	This combination of techniques has the co-benefit of controlling dust and SO <sub>2</sub> emissions, in addition to PCDD/PCDF	Emission concentrations of PCDD/PCDF with use of high-efficiency gas cleaning and conversion of SO <sub>2</sub> to sulphuric acid are <0.005 ng I-TEQ/m <sup>3</sup>
Fume and gas collection	Air emissions should be controlled at all stages of the process, including material handling, smelting and material transfer points, to control the emission of PCDD/PCDF		

Measure	Description	Considerations	Other comments
High-efficiency dust removal	<p>Dusts and metal compounds should be removed to reduce PCDD/PCDF emissions. Very high-efficiency dust removal techniques should be employed, e.g. ceramic filters, high-efficiency fabric filters or the gas-cleaning train prior to a sulphuric acid plant.</p> <p>Dust from dust control equipment should be returned to the process. Returned/collected dust should be treated in high-temperature furnaces to destroy PCDD/PCDF and recover metals.</p> <p>Fabric filter operations should be constantly monitored by devices to detect bag failure</p>	<p>Preference should be given to fabric filters over wet scrubbers, wet electrostatic precipitators, or hot electrostatic precipitators for dust control.</p> <p>Dust that is captured but not recycled will need to be disposed of in a secure landfill or other acceptable manner</p>	

## 7. Performance level associated with best available techniques

PCDD/PCDF performance levels in air emissions associated with best available techniques for base metals smelters are  $<0.1 \text{ ng I-TEQ/Nm}^3$  (at operating oxygen concentrations).

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- <sup>1</sup> Personal Communication, Norway Member, June 2006.
- <sup>2</sup> 1 ng (nanogram) =  $1 \times 10^{-12}$  kilogram ( $1 \times 10^{-9}$  gram); Nm<sup>3</sup> = normal cubic metre, dry gas volume measured at 0°C and 101.3 kPa. For information on toxicity measurement see section I.C, subsection 3 of the present guidelines.
- <sup>3</sup> Hydro Magnesium Canada presentation at Electrolytic Magnesium Industry Bi-national Informative Meeting, Montreal, 12 December 2000, by Jean Laperriere, Environment Chief.
- <sup>4</sup> In April 2003 this plant was shut down for an indefinite time due to market conditions.
- <sup>5</sup> 1 ng (nanogram) =  $1 \times 10^{-12}$  kilogram ( $1 \times 10^{-9}$  gram); Nm<sup>3</sup> = normal cubic metre, dry gas volume measured at 0°C and 101.3 kPa. For information on toxicity measurement see section I.C, subsection 3 of the present guidelines. The operating oxygen concentration conditions of exhaust gases are used for metallurgical sources.
- <sup>6</sup> 1 pg (picogram) =  $1 \times 10^{-15}$  kilogram ( $1 \times 10^{-12}$  gram); 1 ng (nanogram) =  $1 \times 10^{-12}$  kilogram ( $1 \times 10^{-9}$  gram), for information on toxicity measurement see section I.C, subsection 3 of the present guidelines. The operating oxygen concentration conditions of exhaust gases are used for metallurgical sources.



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