

Section V

**Guidance/guidelines by source category:
Source categories in Part II of Annex C**

**Part II Source category (d):
Thermal processes in the metallurgical industry**

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V.D Thermal processes in the metallurgical industry

(i) Secondary copper production

Summary

Secondary copper smelting involves copper production from sources that may include copper scrap, sludge, computer and electronic scrap, and drosses from refineries. Processes involved in copper production are feed pretreatment, smelting, alloying and casting. Factors that may give rise to chemicals listed in Annex C of the Stockholm Convention include the presence of catalytic metals (of which copper is a highly effective example); organic materials in feed such as oils, plastics and coatings; incomplete combustion of fuel; and temperatures between 250 °C and 500 °C.

Best available techniques include presorting, cleaning feed materials, maintaining temperatures above 850 °C, utilizing afterburners with rapid quenching, activated carbon adsorption and fabric filter dedusting.

PCDD/PCDF performance levels in air emissions associated with best available techniques and best environmental practices for secondary copper smelters are $< 0.5 \text{ ng I-TEQ/Nm}^3$ (at operating oxygen concentrations).

1. Process description

Secondary copper smelting involves pyrometallurgical processes dependent on the copper content of the feed material, size distribution and other constituents. Feed sources are copper scrap, sludge, computer scrap, drosses from refineries and semi-finished products. These materials may contain organic materials like coatings or oil, and installations take this into account by using de-oiling and decoating methods or by correct design of the furnace and abatement system (European Commission 2001, p. 201–202). Copper can be infinitely recycled without loss of its intrinsic properties.

The quoted material that follows is from *Secondary Copper Smelting, Refining and Alloying*, a report of the Environmental Protection Agency of the United States of America (EPA 1995).

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

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

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

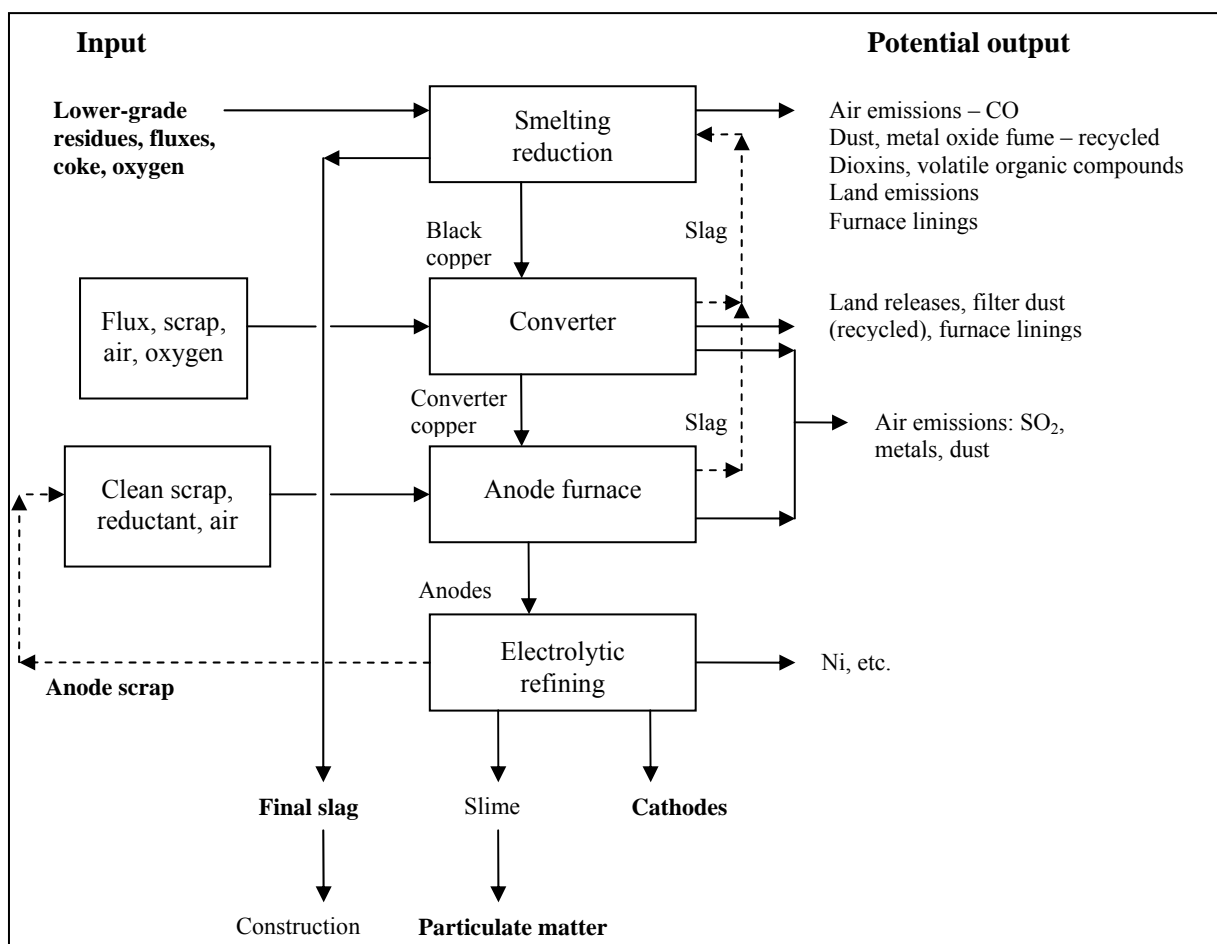
These impurities are then removed as slag. Then, by reducing the furnace atmosphere, cuprous oxide (CuO) is converted to copper. Fire-refined copper is cast into anodes, which are used during electrolysis. The anodes are submerged in a sulphuric acid solution containing copper sulphate. As copper is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

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

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

Figure 1 presents the process in diagrammatic form.

Figure 1. Secondary copper smelting



Source: European Commission 2001, p. 217.

Artisanal and small enterprise metal recovery activities may be significant, particularly in developing countries and countries with economies in transition. These activities may contribute significantly to

pollution and have negative health impacts. For example, artisanal zinc smelting is an important atmospheric mercury emission source. The technique used to smelt both zinc and mercury is simple; the ores are heated in a furnace for a few hours, and zinc metal and liquid mercury are produced. In many cases there are no pollution control devices employed at all during the melting process. Other metals that are known to be produced by artisanal and small enterprise metal recovery activities include antimony, iron, lead, manganese, tin, tungsten, gold, silver, copper and aluminium.

These are not considered best available techniques or best environmental practices. However, as a minimum, appropriate ventilation and material handling should be carried out.

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

The formation of polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) is probably due to the presence of carbon, oxygen, chlorine precursors (from feeds and fuels) and highly potent copper catalyst from plastics and trace oils in the feed material in a system that can provide ideal formation conditions of temperatures between 200 °C – 450 °C, high levels of particulate and long residence times. As copper is the most efficient metal to catalyse PCDD/PCDF formation, copper smelting is a particular concern.

2.1 General information on emissions from secondary copper smelters

Airborne pollutant emissions include nitrogen oxides (NO_x), carbon monoxide (CO), dust and metal compounds, organic carbon compounds and persistent organic pollutants. Off-gases usually contain little or no sulphur dioxide (SO₂), provided sulphidic material is avoided. Scrap treatment and smelting generate the largest quantity of atmospheric emissions. Dust and metal compounds are emitted from most stages of the process and are more prone to fugitive emissions during charging and tapping cycles. Particulate matter may be removed from collected and cooled combustion gases by electrostatic precipitators or fabric filters. Fume collection hoods are used during the conversion and refining stages due to the batch process, which prevents a sealed atmosphere. NO_x is minimized in low-NO_x burners, while CO is burnt in hydrocarbon afterburners. Burner control systems are monitored to minimize CO generation during smelting (European Commission 2001, p. 218–229).

2.2 Emissions of PCDD/PCDF to air

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

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 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 minimize the residence time in the window is practised to prevent de novo synthesis.”

2.3 Releases to other media

Process, surface and cooling water can be contaminated by suspended solids, metal compounds and oils, as well as by chemicals listed in Annex C of the Stockholm Convention. Most process and cooling water is recycled. Wastewater treatment methods should be used before discharge. By-products and residues are often recycled in the process as these contain recoverable quantities of copper and other non-ferrous metals. Waste material generally consists of acid slimes, which are disposed of on site. Care must be taken to ensure the proper disposal of slimes and pollution control residues in order to minimize exposure of the environment to copper and dioxins. Any transfer to another process should be carefully evaluated for the need to abate and control releases of chemicals listed in Annex C.

3. Recommended processes

Process design and configuration is influenced by the variation in feed material and quality control. Processes considered as best available techniques for smelting and reduction include the blast furnace, the mini-smelter (totally enclosed), the top-blown rotary furnace, the sealed submerged electric arc furnace, and ISA smelt. The top-blown rotary furnace (totally enclosed) and Pierce-Smith converter are best available techniques for converting. The submerged electric arc furnace is sealed and is cleaner than other designs if the gas extraction system is adequately designed and sized.

The use of blast furnaces for scrap melting is becoming less common due to difficulties in economically preventing pollution, and shaft furnaces without a coal/coke feed are increasingly being used instead.

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

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

4. Primary and secondary measures

Primary and secondary measures for 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

The presence of oils, plastics and chlorine compounds in the feed material should be avoided to reduce the generation of chemicals listed in Annex C during incomplete combustion or by de novo synthesis. Feed material should be classified according to composition and possible contaminants. Storage, handling and pretreatment techniques will be determined by feed size distribution and contamination.

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

- Oil removal from feed (for example, thermal decoating and de-oiling processes followed by afterburning to destroy any organic material in the off-gas);
- Use of milling and grinding techniques with good dust extraction and abatement. The resulting particles can be treated to recover valuable metals using density or pneumatic separation;
- Elimination of plastic by stripping cable insulation (for example, possible cryogenic techniques to make plastics friable and easily separable);

- Sufficient blending of material to provide a homogeneous feed in order to promote steady-state conditions.

Additional techniques for oil removal are solvent use and caustic scrubbing. Cryogenic stripping can be used to remove cable coatings.

Washing with an aqueous solution of detergents is a potential additional technique for oil removal. In this way, contaminating oil can also be recovered.

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 (e.g. waste incineration), but research is still ongoing for applications to other sources. In the absence of continuous PCDD/PCDF monitoring, other variables such as temperature, residence time, gas composition and fume collection damper controls should be continuously monitored and maintained to establish optimum operating conditions for the reduction of PCDD/PCDF emissions.

4.2 Secondary measures

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

4.2.1 Fume and gas collection

Air emissions should be controlled at all stages of the process, from material handling, smelting and material transfer points, to limit potential emissions of chemicals listed in Annex C. 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, reducing fan sizes and associated 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).

4.2.2 High-efficiency dust removal

The smelting process generates large quantities of particulate matter with high surface area on which chemicals listed in Annex C can form and adsorb. These dusts with their associated metal compounds should be removed to reduce emissions of chemicals listed in Annex C. Fabric filters are the most effective technique, although wet or dry scrubbers and ceramic filters can also be considered. Collected dust must be treated in high-temperature furnaces to destroy PCDD/PCDF and recover metals.

Fabric filter operations should be constantly monitored by devices to detect bag failure. Other relevant technology developments include online cleaning methods and use of catalytic coatings to destroy PCDD/PCDF (European Commission 2001, p. 139–140).

4.2.3 Afterburners and quenching

Afterburners (used post-combustion) should be operated 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 also promote complete combustion (European Commission 2001, p. 189). Further information on optimal temperature is provided in Section I.

It has been observed that PCDD/PCDF are formed, on a net basis, in the temperature range of 250 °C to 500 °C. They are destroyed above 850 °C in the presence of oxygen. However, de novo synthesis remains possible as the gases are cooled through the reformation window present in abatement systems and cooler areas of the furnace if the necessary precursors and metal catalysts are still present. Proper operation of cooling systems to minimize the time during which exhaust gases are within the de novo synthesis temperature range should be implemented (European Commission 2001, p. 133).

4.2.4 Adsorption on activated carbon

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

5. Emerging research

Catalytic oxidation is an emerging technology used in waste incinerators to reduce 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. However, catalytic oxidation can 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 (CO₂) 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. Particulate matter should be removed from exhaust gases 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 CO₂ are released to the air after cooling (Parvesse 2001).

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

6. Summary of measures

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

Table 1. Measures for recommended processes for new secondary copper smelters

Measure	Description	Considerations	Other comments
Recommended processes	Various recommended smelting processes should be considered for new facilities	Processes to consider include: <ul style="list-style-type: none"> Blast furnace, mini-smelter, top-blown rotary furnace, sealed submerged electric arc furnace, ISA smelt, and the Pierce-Smith converter Reverberatory hearth furnace, hearth shaft furnace and Contimelt process to treat clean copper scrap devoid of organic contamination 	These are considered to be best available techniques in configuration with suitable gas collection and abatement. The submerged electric arc furnace is sealed and can be cleaner than other designs if the gas extraction system is adequately designed and sized

Table 2. Summary of primary and secondary measures for secondary copper smelters

Measure	Description	Considerations	Other comments
<i>Primary measures</i>			
Presorting of feed material	The presence of oils, plastics, organic materials and chlorine compounds in the feed material should be avoided to reduce the generation of PCDD/PCDF during incomplete combustion or by de novo synthesis	Processes to consider include: <ul style="list-style-type: none"> • Strict control over materials sources • Oil removal from feed material • Use of milling and grinding techniques with good dust extraction and abatement • Elimination of plastic by stripping cable insulation 	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	Good combustion. Process control systems should be utilized to maintain process stability and operate at parameter levels that will contribute to minimizing generation of chemicals listed in Annex C	PCDD/PCDF emissions may be minimized by controlling other variables such as temperature, residence time, gas composition 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 (for example, waste incineration), but research is still ongoing for applications to other sources
<i>Secondary measures</i>			
Fume and gas collection	Effective fume and off-gas collection should be implemented in all stages of the smelting process to capture PCDD/PCDF emissions	Processes to consider include: <ul style="list-style-type: none"> • Sealed furnaces to contain fugitive emissions while permitting heat recovery and collecting off-gases. Furnace or reactor enclosures may be necessary • Proper design of hooding and ductwork to trap fumes 	Roofline collection of fume is to be avoided due to high energy requirements
High-efficiency dust removal	Dusts and metal compounds should be removed as this material possesses high surface area on which PCDD/PCDF easily adsorb. Removal of these dusts would contribute to the reduction of PCDD/PCDF emissions	Processes to consider include: <ul style="list-style-type: none"> • Fabric filters (most effective method) • Wet/dry scrubbers and ceramic filters 	Dust removal is to be followed by afterburners and quenching. Collected dust must be treated in high-temperature furnaces to destroy PCDD/PCDF and recover metals
Afterburners and quenching	Afterburners should be used at temperatures > 950 °C to ensure full combustion of organic compounds, followed by rapid quenching of hot	Considerations include: <ul style="list-style-type: none"> • PCDD/PCDF formation at 250–500 °C, and destruction > 850 °C with O₂ • Requirement for sufficient O₂ 	De novo synthesis is still possible as the gases are cooled through the reformation window

Measure	Description	Considerations	Other comments
	gases to temperatures below 250 °C	<p>in the upper region of the furnace for complete combustion</p> <ul style="list-style-type: none"> • Need for proper design of cooling systems to minimize reformation time 	
Adsorption on activated carbon	Activated carbon treatment should be considered as this material possesses large surface area on which PCDD/PCDF can be adsorbed from smelter off-gases	<p>Processes to consider include:</p> <ul style="list-style-type: none"> • Treatment with activated carbon using fixed or moving bed reactors • Injection of powdered carbon into the gas stream followed by removal as a filter dust 	Lime/carbon mixtures can also be used
<i>Emerging research</i>			
Catalytic oxidation	Catalytic oxidation is an emerging technology for sources in this sector (demonstrated technology for incinerator applications) which should be considered due to its high efficiency and lower energy consumption. Catalytic oxidation transforms organic compounds into water, CO ₂ and hydrochloric acid using a precious metal catalyst	<p>Considerations include:</p> <ul style="list-style-type: none"> • Process efficiency for the vapour phase of contaminants • Hydrochloric acid treatment using scrubbers while water and CO₂ are released to the air after cooling • Complexity, sensitivity to flue gas conditions and high cost 	<p>Catalytic oxidation has been shown to destroy PCDD/PCDF with shorter residence times, lower energy consumption and > 99% efficiency.</p> <p>Particulate matter should be removed from exhaust gases prior to catalytic oxidation for optimum efficiency</p>

7. Performance levels associated with best available techniques and best environmental practices

PCDD/PCDF performance levels in air emissions associated with best available techniques and best environmental practices for secondary copper smelters are < 0.5 ng I-TEQ/Nm³ (at operating oxygen concentrations).

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(ii) Sinter plants in the iron and steel industry

Summary

Sinter plants in the iron and steel industry are a pretreatment step in the production of iron whereby fine particles of iron ores and, in some plants, secondary iron oxide wastes (collected dusts, mill scale) are agglomerated by combustion. Sintering involves the heating of fine iron ore with flux and coke fines or coal to produce a semi-molten mass that solidifies into porous pieces of sinter with the size and strength characteristics necessary for feeding into the blast furnace.

Chemicals listed in Annex C appear to be formed in the iron sintering process mainly via de novo synthesis. PCDF generally dominate in the waste gas from sinter plants. The PCDD/PCDF formation mechanism appears to start in the upper regions of the sinter bed shortly after ignition, and then the dioxins, furans and other compounds condense on cooler burden beneath as the sinter layer advances along the sinter strand towards the burn-through point.

Primary measures identified to prevent or minimize the formation of PCDD/PCDF during iron sintering include the stable and consistent operation of the sinter plant, continuous parameter monitoring, recirculation of waste gases, minimization of feed materials contaminated with persistent organic pollutants or contaminants leading to formation of such pollutants, and feed material preparation.

Secondary measures identified to control or reduce releases of PCDD/PCDF from iron sintering include adsorption/absorption (for example, activated carbon injection), suppression of formation using urea addition, and high-efficiency dedusting, as well as fine wet scrubbing of waste gases combined with effective treatment of the scrubber wastewaters and disposal of wastewater sludge in a secure landfill.

PCDD/PCDF performance levels in air emissions associated with best available techniques and best environmental practices for an iron sintering plant are $< 0.2 \text{ ng I-TEQ/Nm}^3$ (at operating oxygen concentrations).

1. Process description

Iron sintering plants may be used in the manufacture of iron and steel, often in integrated steel mills. The sintering process is a pretreatment step in the production of iron whereby fine particles of iron ores and, in some plants, secondary iron oxide wastes (collected dusts, mill scale) are agglomerated by combustion. The sinter feed materials and rations, as well as the amount of sinter that is used in a blast furnace, vary; typically a greater proportion of the furnace feed would be sinter in Europe compared to North American practice. Agglomeration of the fines is necessary to enable the passage of hot gases during the subsequent blast furnace operation (UNEP 2003, p. 60).

Sintering involves the heating of fine iron ore with flux and coke fines or coal to produce a semi-molten mass that solidifies into porous pieces of sinter with the size and strength characteristics necessary for feeding into the blast furnace. Moistened feed is delivered as a layer onto a continuously moving grate or strand. The surface is ignited with gas burners at the start of the strand and air is drawn through the moving bed, causing the fuel to burn. Strand velocity and gas flow are controlled to ensure that burn-through (i.e., the point at which the burning fuel layer reaches the base of the strand) occurs just prior to the sinter being discharged. The solidified sinter is then broken into pieces in a crusher and is air cooled. Product outside the required size range is screened out, oversize material is recrushed, and undersize material is recycled back to the process. Sinter plants that are located in a steel plant recycle iron ore fines from the raw material storage and handling operations and from waste iron oxides from steel plant operations and environmental control systems. Iron ore may also be processed in on-site sinter plants (Environment Canada 2001, p. 18).

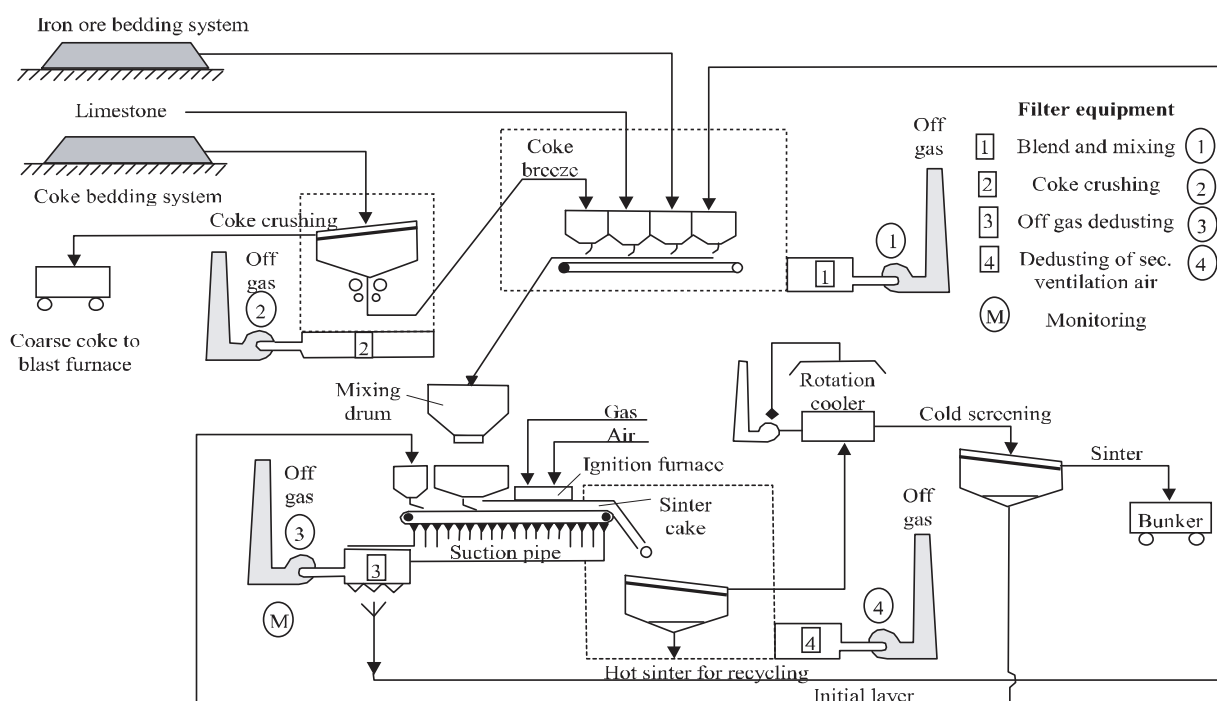
A blast furnace is a vertical furnace using tuyeres to blast heated or cold air into the furnace burden to smelt the contents. Sinter is charged into the top of the blast furnace in alternating layers with coke.

The flexibility of the sintering process permits conversion of a variety of materials, including iron ore fines, captured dusts, ore concentrates, and other iron-bearing materials of small particle size (e.g. mill scale) into a clinker-like agglomerate (Lankford et al. 1985, p. 305–306). The types and amounts of materials that are recycled can vary widely; this may be a significant factor in determining formation and release of chemicals listed in Annex C of the Stockholm Convention.

Waste gases are usually treated for dust removal in electrostatic precipitators; more recently, fabric filters and (less commonly) wet scrubbers have been used. Any of these may be preceded by a cyclone or other inertial removal device in order to reduce the loading to the final particulate collection device.

Figure 1 provides a schematic of an iron sintering plant

Figure 1. Process diagram of a sinter plant



Source: United Kingdom Environment Agency, 2001.

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

As regards emissions of chemicals listed in Annex C of the Stockholm Convention, iron sintering has been identified as a source of polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF). The formation and release of hexachlorobenzene (HCB) and polychlorinated biphenyls (PCB) have yet to be fully assessed.

2.1 Releases to air

2.1.1 General information on emissions from iron sintering plants

The following information is drawn from Environment Canada 2001, p. 23–25.

“Emissions from the sintering process arise primarily from materials-handling operations, which result in airborne dust, and from the combustion reaction on the strand. Combustion gases from the latter source contain dust entrained directly from the strand along with products of combustion such as CO, CO₂, SO_x, NO_x, and particulate matter. The concentrations of these substances vary with the quality of the fuel and raw materials used and combustion conditions. Atmospheric emissions also include volatile organic compounds (VOCs) formed from volatile material in the coke breeze, oily mill scale, etc., and dioxins and furans, formed from organic material under certain operating conditions. Metals are volatilized from the raw materials used, and acid vapours are formed from the halides present in the raw materials.

Combustion gases are most often cleaned in electrostatic precipitators (ESPs), which significantly reduce dust emissions but have minimal effect on the gaseous emissions. Water scrubbers, which are sometimes used for sinter plants, may have lower particulate collection efficiency than ESPs but higher collection efficiency for gaseous emissions. Significant amounts of oil in the raw material feed may create explosive conditions in the ESP. Sinter crushing and screening emissions are usually controlled by ESPs or fabric filters. Wastewater discharges, including runoff from the materials storage areas, are treated in a wastewater treatment plant that may also be used to treat blast furnace wastewater.

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

2.1.2 Emissions of PCDD and PCDF

The processes by which PCDD/PCDF are formed are complex. PCDD/PCDF appear to be formed in the iron sintering process via de novo synthesis. PCDF generally dominate in the waste gas from sinter plants (William Lemmon and Associates Ltd. 2004, p. 20–21).

The PCDD/PCDF formation mechanism appears to start in the upper regions of the sinter bed shortly after ignition, and then the dioxin/furan and other compounds condense on cooler burden beneath as the sinter layer advances along the sinter strand towards the burn-through point. The process of volatilization and condensation continues until the temperature of the cooler burden beneath rises sufficiently to prevent condensation and the PCDD/PCDF exit with the flue gas. This appears to increase rapidly and peak just before burn-through and then decrease rapidly to a minimum. This is supported by the dioxin/furan profile compared to the temperature profile along the sinter strand in several studies.

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

2.1.3 Research findings of interest

It appears that the composition of the feed mixture has an impact on the formation of PCDD/PCDF, i.e., increased chlorine content can result in increased PCDD/PCDF formation and the form of the carbon source appears to be more significant than simply the amount of carbon. The replacement of coke as a fuel with anthracite coal appears to reduce PCDD/PCDF concentration.

The form of the solid fuel (another potential carbon source) has also been noted to impact furan emissions. Changing between coal, graphite, and activated coke in a Japanese laboratory research programme reduced pentachlorinated dibenzofuran emissions by approximately 90%.

The operating parameters of the sintering process appear to have an impact on the formation of PCDD/PCDF (William Lemmon and Associates Ltd. 2004).

2.2 Releases to other media

No information has been identified on releases of chemicals listed in Annex C from iron sintering operations to other media such as through wastewater or collected dusts.

3. Alternatives

In accordance with the Stockholm Convention, when consideration is being given to proposals for construction of a new iron sintering plant, consideration should be given to alternative processes, techniques or practices that have similar usefulness but avoid the formation and release of chemicals listed in Annex C. With respect to iron sintering, careful consideration should be given to the benefits of sintering in recycling iron wastes and the need for sintering in traditional iron and steel making processes using coke and blast furnaces, and the various stages of existing steel production and product mixes. For any alternative processes the environmental advantages and disadvantages of these alternatives should also be carefully assessed. A comprehensive review of alternative ironmaking processes is provided by Lockheed Martin Energy Systems, 2000 and Augerman, 2004.

Alternative processes to iron sintering include:

3.1 Direct reduction

This technique, also known as direct reduction iron or hot briquetted iron, processes iron ore to produce a direct reduced iron product that can be used as a feed material to steel-manufacturing electric arc furnaces, iron-making blast furnaces, or steel-making basic oxygen furnaces. Natural gas is reformed to make hydrogen and carbon dioxide, where hydrogen is the reductant used to produce the direct reduced iron. The availability and cost of natural gas will impact the feasibility of using this technique.

Two new direct reduction processes for iron ore fines, Circored® and Circofer®, are available. Both processes use a two-stage configuration, combining a circulating fluidized bed with a bubbling fluidized bed. The Circored process uses hydrogen as reductant. The first-of-its-kind Circored plant was built in Trinidad for the production of 500,000 tons per year of hot briquetted iron and commissioned in 1999. In the Circofer process, coal is used as reductant. In some direct reduction process systems (e.g. Fastmet®), various carbon sources can be used as the reductant. Examples of carbon sources that may be used include coal, coke breeze and carbon-bearing steel mill wastes (blast furnace dust, sludge, basic oxygen furnace dust, mill scale, electric arc furnace dust, sinter dust). These processes convert iron oxide pellet feed, oxide fines or steel mill wastes into metallic iron, and produces a direct reduced iron product suitable for use in a blast furnace.

An innovative air-based direct smelting technology, called the HIsmelt iron-making process, has been developed recently. The process takes place under pressure within a vertical smelt reduction vessel that has a refractory lined hearth and a water-cooled topspace. The biggest advantage of the process to iron makers is that it produces hot metal without the need for coke ovens and sinter plants.

Other patented technologies such as Tecnored® are reported by Lockheed Martin Energy Systems, 2000.

3.2 Direct smelting

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

4. Primary and secondary measures

Primary and secondary measures for reducing emissions of PCDD and PCDF from iron sintering processes are outlined below. Much of this material has been drawn from William Lemmon and Associates Ltd. 2004.

The extent of emission reduction possible with implementation of primary measures only is not fully understood and may well be plant specific.

A review of experiences of sinter plant waste gas cleaning by European industry is presented by the Nordic Council et al., June 2006. A review of experiences by Nordic facilities is included in a general best available techniques review by Norden 2006.

4.1 Primary measures

Primary measures are understood to be pollution prevention measures that will prevent or minimize the formation and release of chemicals listed in Annex C. 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 have been identified that may assist in preventing and minimizing the formation and release of chemicals listed in Annex C. Plant-specific emission reductions associated with implementation of the following primary measures only are not known and would need to be assessed. It is recommended that the following measures be implemented together with appropriate secondary measures to ensure the greatest minimization and reduction of emissions possible. Identified primary measures include the following:

4.1.1 Stable and consistent operation of the sinter strand

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

Sinter strands should be operated to maintain consistent and stable process conditions (i.e., steady-state operations, minimization of process upsets) in order to minimize the formation and release of PCDD, PCDF and other pollutants. Operating conditions requiring consistent management include strand speed, bed composition (consistent blending of revert materials, minimization of chloride input), bed height, use of additives (for example, addition of burnt lime may help reduce PCDD/PCDF formation), minimization of oil content in mill scale, minimization of air in-leakage through the strand, ductwork and off-gas conditioning systems, and minimization of strand stoppages. This approach will also result in beneficial operating performance improvements (e.g. productivity, sinter quality, energy efficiency) (European Commission 2000, p. 47; IPPC 2001, p. 39).

4.1.2 Continuous parameter monitoring

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

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

Operators of iron sintering plants should prepare a site-specific monitoring plan for the continuous parameter monitoring system that addresses installation, performance, operation and maintenance,

quality assurance and record keeping, and reporting procedures. Operators should keep records documenting conformance with the identified monitoring requirements and the operation and maintenance plan (EPA 2003).

4.1.3 Recirculation of off-gases

Recycling of sinter off-gas (waste gas) has been shown to minimize pollutant emissions, and reduce the amount of off-gas requiring end-of-pipe treatment. Recirculation of part of the off-gas from the entire sinter strand, or sectional recirculation of off-gas, can minimize formation and release of pollutants. For further information on this technique see ECSC 2003 and European Commission 2000, p. 56–62.

Recycling of iron sintering off-gases can reduce emissions of PCDD/PCDF, NO_x and SO₂. However, this option can also lead to reduced production, can affect sinter quality and may result in increased workplace dust exposure and maintenance requirements. Any such measure needs to be carefully implemented taking into account its potential to impact other aspects of plant operation.

4.1.4 Feed material selection

Unwanted substances should be minimized in the feed to the sinter strand. Unwanted substances include persistent organic pollutants and other substances associated with the formation of PCDD/PCDF, HCB and PCB (e.g. chlorine/chlorides, carbon, precursors and oils). Poor control over inputs can also affect the operation of the blast furnace.

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

- Removal of the contaminant from the material (e.g. de-oiling of mill scales);
- Substitution of the material (e.g. replacement of coke breeze with anthracite);
- Avoidance of the use of the contaminated material (e.g. avoid processing electrostatic precipitator sinter dusts, which have been shown to increase PCDD/PCDF formation and release) (Kasai et al. 2001);
- Specification of limits on permissible concentrations of unwanted substances (e.g. oil content in feed should be limited to less than 0.02%) (EPA 2003).

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

4.1.5 Feed material preparation

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

4.1.6 Urea injection

Tests using urea injection to suppress formation of dioxins and furans have been conducted at an iron sintering plant in the United Kingdom. Controlled quantities of urea prills were added to the sinter strand. This technique is thought to prevent or reduce both PCDD/PCDF and sulphur dioxide emissions. The trials indicated that PCDD/PCDF formation was reduced by approximately 50%. It is estimated that a 50% reduction in PCDD/PCDF would achieve a 0.5 ng I-TEQ/m³ emission concentration. Capital costs are estimated at UK£0.5 million to £1 million per plant (approximately US\$0.9 million to \$1.8 million) (Entec UK Ltd. 2003, p. D10–D20).

A number of European sinter facilities have tested urea addition and reported that PCDD/PDF emission could be reduced by 50% by addition of small quantities of urea into the sinter mix (Hartig, Steden and Lin, 2005). However it was also reported that there were additional emissions of dust,

NO_x and NH₃ in the cleaned waste gases (presumably using the existing air pollution prevention and control systems). Also, while significant reductions of SO₂ were found in some facilities, other facilities indicated that ammonia compounds may adulterate SO₂ results by using conventional measurement methods. It was not reported, however, if these trials tried to optimize and modify air pollution prevention and control systems for various pollutants. As of December 2005 it was reported that no member of the European industry association was using urea addition in their current operations at that time

At Canada's only sinter plant, operated by Stelco Inc. in Hamilton, Ontario, trials have been completed using a new similar process in order to reduce dioxin emissions. Stelco found that sealing the furnace to reduce the amount of oxygen and adding a small amount of urea interfered with the chemical reaction that produces dioxins, resulting in reduced emissions. This new process configuration, combined with air-scrubbing systems, released 177 pg/m³ of dioxins in a test. This result surpasses the 2005 Canada-wide standard limit of 500 pg/Rm³ and is below the 200 pg/Rm³ limit for 2010. It also represents a 93% reduction from the 1998 measured levels of 2,700 pg/Rm³. The improvement clearly does not depend on scrubbing dioxins out of the stack gases, but is thought to result from "true pollution prevention", as chlorine is needed to produce dioxins and the urea releases ammonia, which captures chlorides in the dust, reducing its availability for dioxin formation (*Hamilton Spectator* 1 March 2006).

4.2 Secondary measures

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

Primary measures identified earlier should be implemented together with appropriate secondary measures to ensure the greatest minimization and reduction of emissions possible. Measures that have been shown to effectively minimize and reduce PCDD and PCDF emissions include:

4.2.1 Removal techniques

4.2.1.1 Adsorption/absorption and high-efficiency dedusting

This technique involves sorption of PCDD/PCDF to a material such as activated carbon, together with effective particulate matter (dedusting) control.

For regenerative activated carbon technology an electrostatic precipitator is used to reduce dust concentration in the off-gases prior to entry to the activated carbon unit (William Lemmon and Associates Ltd. 2004). The waste gas passes through a slowly moving bed of char granules, which acts as a filter/adsorption medium. The used char is discharged and transferred to a regenerator, where it is heated to elevated temperatures. PCDD/PCDF adsorbed to the char are decomposed and destroyed within the inert atmosphere of the regenerator. This technique has been shown to reduce emissions to 0.1 to < 0.3 ng I-TEQ/m³.

Another sorption technique is the use of lignite or activated carbon injection, together with a fabric filter. PCDD/PCDF are sorbed onto the injected material, and the material is collected in the fabric filter. Along with good operation of the sinter strand, this technique is associated with PCDD/PCDF emission concentrations ranging from 0.1 to 0.5 ng I-TEQ/m³ (IPPC 2001, p. 135).

In principle it should be possible to inject carbon into the gas stream ahead of existing dust collectors such as electrostatic precipitators and fabric filters in the same manner that some incinerators control emissions of persistent organic pollutants, and there has been some success with this technique for iron sintering in Belgium. Capital costs for adding carbon to existing equipment would be much less than for adding a regenerative active carbon system.

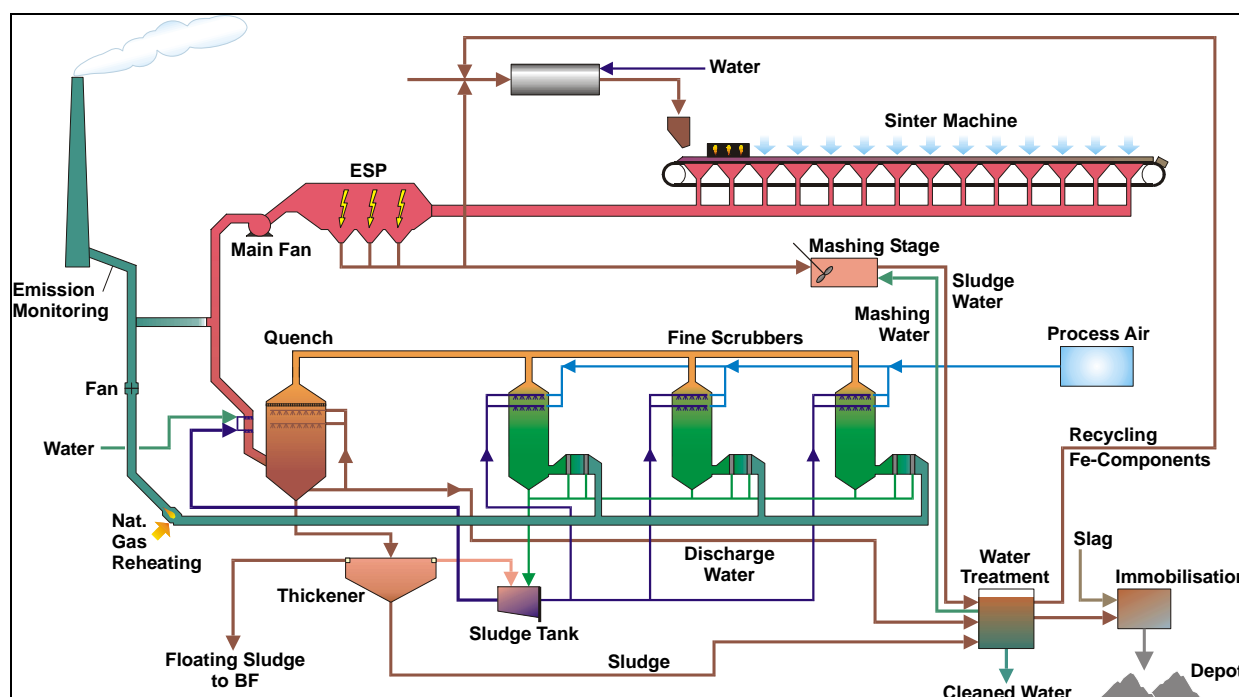
4.2.1.2 Fine wet scrubbing system

The Airfine scrubbing system, shown in Figure 2, developed by Voest Alpine Industries (Austria), has been shown to effectively reduce emission concentrations to 0.2 to 0.4 ng I-TEQ/m³. The scrubbing system uses a countercurrent flow of water against the rising waste gas to scrub out coarse particles

and gaseous components (for example, sulphur dioxide (SO₂)), and to quench the waste gas. (An electrostatic precipitator may also be used upstream for preliminary dedusting.) Caustic soda may be added to improve SO₂ absorption. A fine scrubber, the main feature of the system, follows, employing high-pressure mist jet co-current with the gas flow to remove impurities. Dual flow nozzles eject water and compressed air (creating microscopic droplets) to remove fine dust particles, PCDD and PCDF (William Lemmon and Associates Ltd. 2004, p. 29–30; European Commission 2000, p. 72–74).

This technique should be combined with effective treatment of the scrubber wastewaters and wastewater sludge should be disposed of in a secure landfill (European Commission 2000). The application of this technique should be considered cautiously with respect to its suitability for each site.

Figure 2. Process diagram of a sinter plant using a wet scrubbing system



Source: Hofstadler et al. 2003.

4.2.2 General measures

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

4.2.2.1 Removal of particulate matter from sinter off-gases

It has been suggested that effective removal of dust can help reduce emissions of PCDD and PCDF. Fine particles in the sinter off-gas have an extremely large surface area for adsorption and condensation of gaseous pollutants, including PCDD and PCDF (Hofstadler et al. 2003). The best available technique for removal of particulate matter is the use of fabric filters. Fabric filters used at sinter plants are associated with particulate matter emission concentrations of < 10 to < 30 mg/m³ (UNECE 1998; IPPC 2001, p. 131).

Other particulate control options that are commonly used for sinter plant off-gases include electrostatic precipitators and occasionally wet scrubbers, though their particulate removal efficiencies are not as high as for fabric filters. Good performance of electrostatic precipitators and high-efficiency wet gas scrubbers is associated with particulate matter concentrations of < 30 to 50 mg/m³ (IPPC 2001; William Lemmon and Associates Ltd. 2004, p. 26; UNECE 1998).

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

Fabric filters can also be fitted downstream of electrostatic precipitators, allowing separate collection and use of the dusts they collect.

4.2.2.2 *Hooding of the sinter strand*

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

5. Emerging research

Selective catalytic reduction has been used for controlling NO_x emissions from a number of industrial processes, including iron sintering. 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 an emerging technique with potential for reducing emissions of persistent organic pollutants from iron sintering plants and other applications.

A study investigating stack emissions from four sinter plants noted lower concentrations of PCDD/PCDF (0.995–2.06 ng I-TEQ/Nm³) in the stack gases of sinter plants with selective catalytic reduction than a sinter plant without (3.10 ng I-TEQ/Nm³), and that the PCDD/PCDF degree of chlorination was lower for plants with selective catalytic reduction. It was concluded that selective catalytic reduction did indeed decompose PCDD/PCDF, but would not necessarily be sufficient as a stand-alone PCDD/PCDF destruction technology to meet stringent emission limits. Add-on techniques (for example, activated carbon injection) may be required (Wang et al. 2003, p. 1123–1129).

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

6. Summary of measures

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

Table 1. Alternatives and requirements for new iron sintering plants

Measure	Description	Considerations	Other comments
Alternative processes	Priority consideration should be given to alternative processes with potentially less environmental impacts than traditional iron sintering	Examples include: <ul style="list-style-type: none"> • Pelletization plants • Direct reduction of iron (Fastmet®, Circored® and Circofer®) • Direct smelting 	
Performance requirements	New iron sintering plants should be permitted to achieve stringent performance and reporting requirements associated with best available techniques	Consideration should be given to the primary and secondary measures listed in Table 2 below	Performance levels associated with BAT and BEP are: < 0.2 ng I-TEQ/Nm ³ for PCDD/PCDF and may be as low as <0.1 ng I-TEQ/Nm ³

Table 2. Summary of primary and secondary measures for iron sintering plants

Measure	Description	Considerations	Other comments
<i>Primary measures</i>			
Stable and consistent operation of the sinter plant	The sinter strand should be operated to maintain stable consistent operating conditions (steady-state conditions, minimization of process upsets) to minimize formation of PCDD, PCDF and other pollutants	Conditions to optimize operation of the strand include: <ul style="list-style-type: none"> • Minimization of stoppages • Consistent strand speed • Bed composition • Bed height • Additives (e.g. burnt lime) • Minimization of oil content • Minimization of air in-leakage 	This approach will have co-benefits such as increased productivity, increased sinter quality and improved energy efficiency. Impact on chemicals listed in Annex C would need to be assessed on a plant-specific basis
Continuous parameter monitoring	A continuous parameter monitoring system should be employed to ensure optimum operation of the sinter strand and off-gas conditioning systems. Operators should prepare a site-specific monitoring plan for the continuous parameter monitoring system and keep records that document conformance with the plan	Correlations between parameter values and stack emissions (stable operation) should be established. Parameters are then continuously monitored in comparison to optimum values. System can be alarmed and corrective action taken when significant deviations occur	
Recirculation of waste gases	Waste gases may be recycled back to the sinter strand to minimize pollutant emissions and reduce the amount of off-gas requiring end-of-pipe treatment	Recirculation of the waste gases can entail recycling of part of the off-gas from the entire sinter strand, or sectional recirculation of off-gas	This technique will result in only a modest reduction of PCDD/PCDF but can have significant impacts on other operational parameters and should be carefully assessed
Feed material selection: Minimization of feed materials contaminated with persistent organic pollutants or leading to their formation	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	Examples include: <ul style="list-style-type: none"> • Removal of the contaminant from the material (e.g. de-oiling of mill scales) • Substitution of the material (e.g. replacement of coke breeze with anthracite) • Avoid use of the material (e.g. collected sinter) 	Plant-specific assessment may be needed

Measure	Description	Considerations	Other comments
		electrostatic precipitator dust) <ul style="list-style-type: none"> • Specification of limits on permissible concentrations of unwanted substances (e.g. oil content in feed should be limited to less than 0.02%) 	
Feed material preparation	Fine material (e.g. collected dusts) should be agglomerated before being placed on the sinter strand. Feed materials should be intimately mixed before placement on the sinter strand		These measures will help reduce entrainment of pollutants in the waste gas, and minimize fugitive emissions
Urea addition	Controlled quantities of urea prills are added to feed mix on the sinter strand; this technique is thought to prevent or reduce both PCDD/PCDF and sulphur dioxide emissions	Need to seal the strand to reduce the amount of oxygen (ammonia acts as a reducing agent; excess oxygen as an oxidant). Recommended for use combined with air-scrubbing systems to remove nitrogenous gaseous emissions	
Secondary measures			
The following secondary measures can effectively reduce emissions of PCDD/PCDF and should be considered as examples of best available techniques:			
Adsorption/absorption and high-efficiency dedusting	Use of this technique should include an adsorption stage together with high-efficiency particulate control as key components of the off-gas conditioning system	The following adsorption techniques have been demonstrated: <ul style="list-style-type: none"> • Injection of carbon with collection on electrostatic precipitators • Regenerative activated carbon technology whereby off-gases are first cleaned by electrostatic precipitator, and passed through moving adsorption bed (char) to both adsorb PCDD/PCDF and to filter particulates. Adsorptive material is then regenerated • Injection of activated carbon, lignite or other similar adsorptive 	These techniques are associated with the following emission concentration levels: < 0.3 ng I-TEQ/m ³ ; 0.1 to 0.5 ng I-TEQ/m ³ . Cost-effectiveness of different carbon-based adsorption systems needs to be assessed carefully; in-flight injection would probably be much less expensive than regenerative carbon bed systems

Measure	Description	Considerations	Other comments
		material into the gas stream followed by fabric filter dedusting	
Fine wet scrubbing of waste gases	Use of this technique should include a preliminary countercurrent wet scrubber to quench gases and remove larger particles, followed by a fine scrubber using high pressure mist jet co-current with off-gases to remove fine particles and impurities		The fine wet scrubbing system under the trade name Airfine®, as developed by Voest Alpine Industries, has been shown to reduce emission concentrations to 0.2 to 0.4 ng I-TEQ/m ³ . However application should be considered cautiously for each site.
The following secondary measures should not be considered best available techniques on their own. For effective minimization and reduction of PCDD, PCDF and other persistent organic pollutants, these measures should be employed in concert with other identified measures:			
Removal of particulate matter from waste gases	Waste gases should be treated using high-efficiency techniques, as this can help minimize PCDD/PCDF emissions. A recommended best available technique for particulate control is the use of fabric filters. Feed and discharge ends of the sinter strand should be adequately hooded and controlled to capture and mitigate fugitive emissions	Fabric filters have been shown to reduce sinter off-gas particulate emissions to < 10 to < 30 mg/m ³	Other particulate control techniques used include electrostatic precipitators and high-efficiency scrubbers. Good performance of these technologies is associated with particulate concentrations of < 30 to 50 mg/m ³ . Lower particulate emissions (and associated Dioxins and Furans) may be achieved with fabric filters <5 to 20 mg/m ³
Hooding of the sinter strand	The sinter strand should be hooded to minimize fugitive process emissions		Hooding of the strand will enable use of other measures, such as waste gas recirculation

7. Performance levels associated with BAT and BEP

PCDD/PCDF performance levels in air emissions associated with best available techniques and best environmental practices for an iron sintering plant are < 0.2 ng I-TEQ/Nm³ (at operating oxygen concentrations).

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(iii) Secondary aluminium production

Summary

Secondary aluminium smelting involves the production of aluminium from used aluminium products or process waste to recover metals by pretreatment, smelting and refining.

Fuels, fluxes and alloys are used, while magnesium removal is practised by the addition of chlorine, aluminium chloride or chlorinated organics. Chemicals listed in Annex C of the Stockholm Convention probably result from demagging additions, incomplete combustion, organics in the feed, chlorine compounds and formation in the system at temperatures between 250 °C and 500 °C.

Best available techniques include high-temperature advanced furnaces, oil- and chlorine-free feeds (if alternatives are available), afterburners with rapid quench, activated carbon adsorption and dedusting fabric filters, as well as avoiding the use of hexachloroethane for the removal of magnesium from the melt (demagging) and maintaining careful control over demagging in general.

PCDD/PCDF performance levels in air emissions associated with best available techniques and best environmental practices for secondary aluminium smelters are < 0.5 ng I-TEQ/Nm³ (at operating oxygen concentrations).

1. Process description

Processes used in secondary aluminium smelting are dependent on feed material. Pretreatment, furnace type and fluxes used will vary with each installation. Production processes involve scrap pretreatment and smelting/refining. Pretreatment methods include mechanical, pyrometallurgical and hydrometallurgical cleaning. Smelting is conducted using reverberatory or rotary furnaces. Induction furnaces may also be used to smelt the cleaner aluminium feed materials.

Reverberatory furnaces consist of two sections: a smelting chamber heated by a heavy oil burner and an open well where aluminium scraps of various sizes are supplied. Rotary furnaces consist of a horizontal cylindrical shell mounted on rollers and lined with refractory material. The furnace is fired from one end, usually using gas or oil as the fuel.

Feed consists of process scrap, used beverage cans, foils, extrusions, commercial scraps, turnings and old rolled or cast metal. Skimmings from the secondary smelting process are also recycled as feed. Presorting of scrap into desired alloy groups can reduce processing time. Scrap is often contaminated with oil or coatings, which must be removed to reduce emissions and improve melting rate (European Commission 2001, p. 279). Salt slag is treated to recover the salt, which is reutilized as flux in rotary furnaces. The residue from the salt slag treatment has a high aluminium oxide (Al₂O₃) content and can be recycled using the Bayer process or used as an additive in the cement industry.

The following summary of the process is drawn from EPA 1994:

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

Smelting and refining operations can involve the following steps: charging, melting, fluxing, demagging, degassing, alloying, skimming, and pouring. Charging consists of placing pretreated aluminium scrap into a melted aluminium pool (heel) that is maintained in melting furnaces. The scrap, mixed with flux material, is normally placed into the furnace charging well, where heat from the molten aluminium surrounding the scrap causes it to melt by conduction. Flux materials combine with contaminants and float to the surface of the

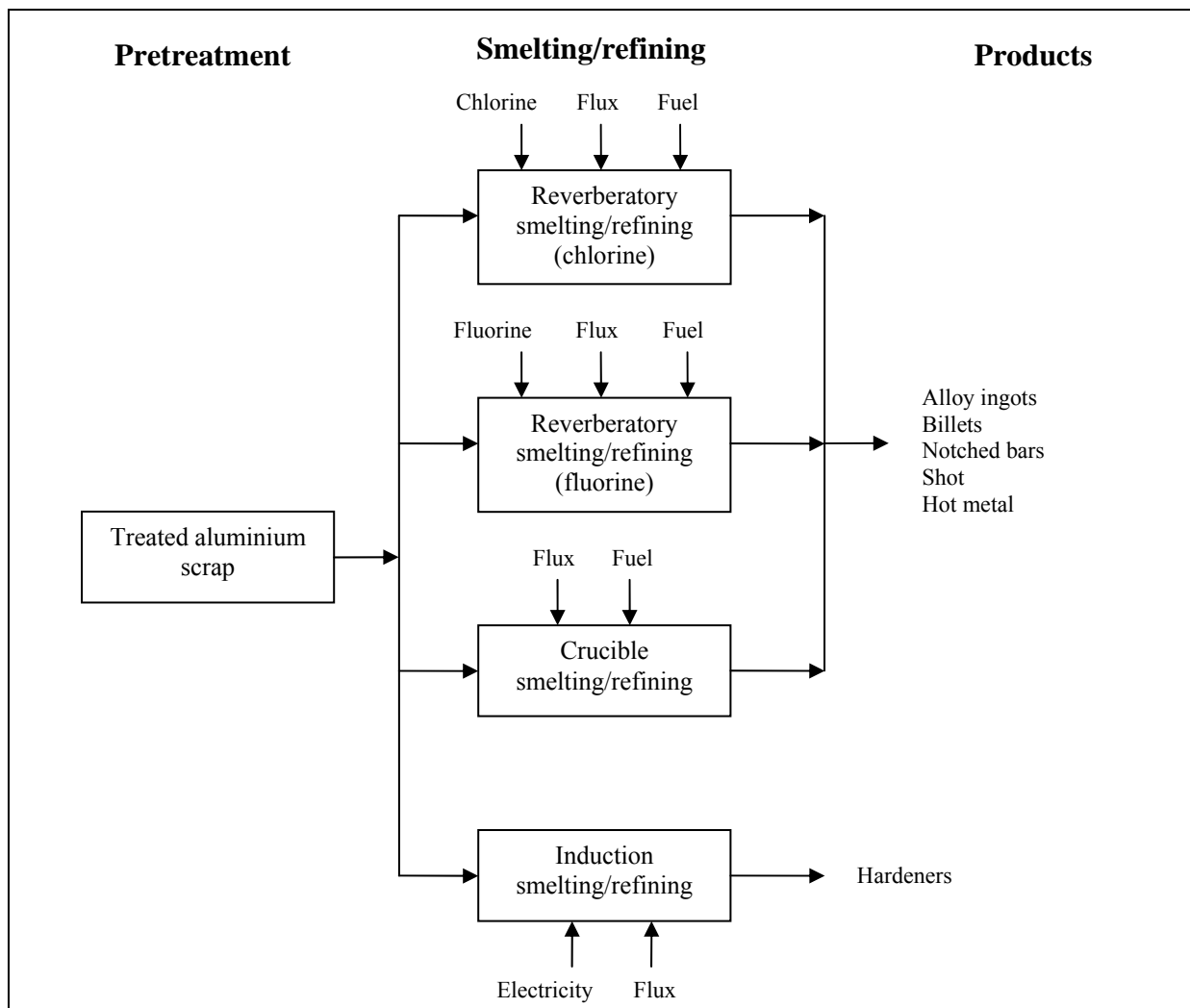
aluminium, trapping impurities and providing a barrier (up to 6 inches thick) that reduces oxidation of the melted aluminium. To minimize aluminium oxidation (melt loss), mechanical methods are used to submerge scrap into the heel as quickly as possible.

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

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

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

Figure 1. Secondary aluminium smelting



Source: EPA 1994.

Artisanal and other small-scale aluminium recovery processes are used in a number of countries. Achievable performance limits are not applicable to artisanal and small-scale aluminium recovery processes as the processes used cannot be considered best available techniques or best environmental practices and ideally would not be practised at all. Sometimes largely unsorted scrap is melted in a small crucible or furnace housed in a building or a roofed space, most often inadequately ventilated. This device may be fired with charcoal, oil, waste oil or coal, depending on economic factors and the local fuel supply situation. In larger furnaces, the melt may be treated with fluxes and degasifying chemicals to improve the quality of the molten metal. Artisanal and other small-scale aluminium recovery processes may release many chemicals into the environment, including persistent organic pollutants. These processes should be discouraged in favour of using the proper air pollution controls on larger-scale secondary aluminium smelting operations.

However, where artisanal and other small-scale aluminium recovery processes are practised, certain measures can be put in place in order to reduce the amount of pollutants released into the environment. Measures to reduce emissions of persistent organic pollutants and other pollutants from artisanal processes include presorting of scrap material, selecting a better fuel supply (oil or gas fuels instead of coal), adequate ventilation, filtration of exhaust gases, proper management of wastes and proper choice of degasifiers. These measures can be achieved by education and outreach programmes working with craft groups and town authorities.

Effective presorting can lead to significant reductions in releases of persistent organic pollutants. Manual scrap sorting, rather than mechanical sorting, is feasible in some economies, depending on the balance between labour costs and capital availability. Proper training and supervision can make manual scrap sorting highly effective, and has the potential to lead to improvements in energy consumption and product quality and a reduction in the amount of slag to be disposed of. The drying of feed materials and prewarming of refractories, while using more fuel, reduces hydrogen production in the melt and so can improve product quality without use of chemicals.

Adequate ventilation of the workplace will reduce workplace exposure. Extraction of fumes and off-gases through a chimney and hood enclosure around the crucible by providing natural draught will aid ventilation and provide some dispersion but will not reduce emissions except by improving the quality of combustion. Heating with oil or gas fuels reduces the amount of persistent organic pollutants formed.

In larger facilities, ducting exhaust gases and fitting pollution controls may be feasible. Filters, dry scrubbers or wet scrubbers for particle abatement can be effective at pollution control but require a reliable electricity supply to power the fans. Wet scrubbers require appropriate arrangements for the collection, treatment and safe disposal of effluent. All pollution control systems require appropriate residue handling arrangements and disposal routes to be in place before installation. If effluent treatment is not in place then dry air pollution control devices should be preferred. However, storage of fine particulate matter is demanding in many environments and appropriate storage and waste arrangements are required for the captured material until a safe disposal route is identified. Co-location of facilities and regional cooperation to manage and dispose of wastes would be beneficial.

The use of hexachloroethane as a degasifier for reducing melts has been thought to lead to significant release of persistent organic pollutants. The use of potassium fluoride or potassium aluminium fluoride as a degassing agent has proved successful in some larger plants. Other large plants have successfully used chlorine as a degasifier. At these locations appropriate handling and safety arrangements are in place, including appropriately trained staff.

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

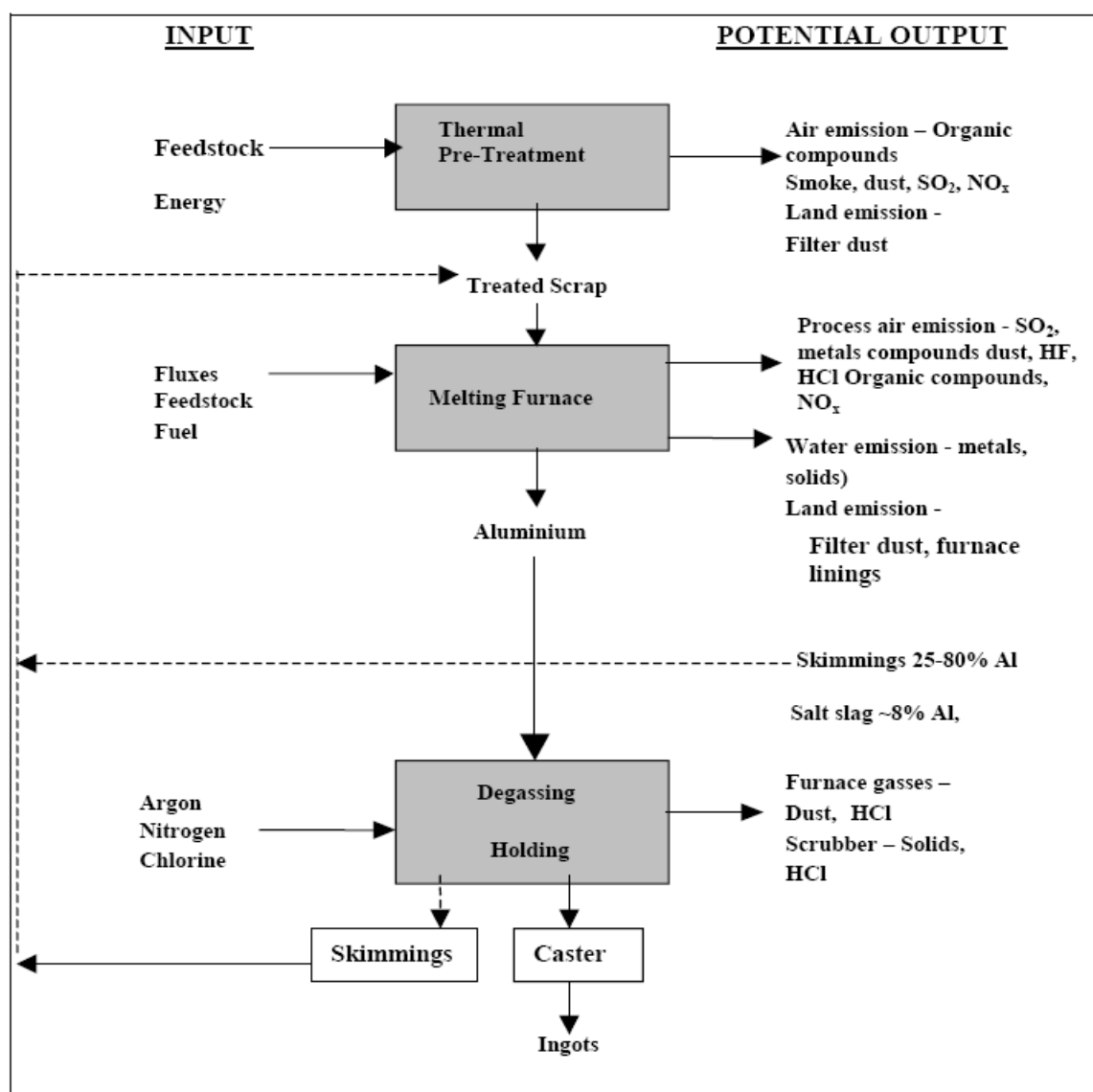
The generation of chemicals listed in Annex C of the Stockholm Convention is probable due to incomplete combustion and addition of contaminants in the feed, and from chemical additions for demagging combined with process conditions favourable to formation of persistent organic pollutants.

2.1 General information on emissions from secondary aluminium smelters

Potential emissions to air include dust, metal compounds, chlorides, nitrogen oxides (NO_x), sulphur dioxide (SO₂) and organic compounds such as polychlorinated dibenzo-*p*-dioxins (PCDD), polychlorinated dibenzofurans (PCDF) and carbon monoxide (CO). Ammonia can also be generated from the improper storage, treatment and transport of skimmings. Chlorine compounds can be removed using wet or dry scrubbers and their formation minimized by good control and the use of mixtures of chlorine and inert gases. Low-NO_x burners and low-sulphur fuels can be used to decrease emissions of NO_x and SO₂ (European Commission 2001, p. 294–300).

“Afterburning is used to destroy organic materials that escape the combustion zone, while injection of treatment materials such as lime, sodium bicarbonate and carbon is also practised. Most installations then use (high-efficiency) bag filters or ceramic filters to remove dust and emissions can lie in the range 0.6 to 20 mg/Nm³. A spark arrester or cooling chamber often precedes them to provide filter protection. Energy recovery can be practised, most commonly recuperative burners are used” (European Commission 2001).

Figure 2. Input and output from secondary aluminium production



Note: Smoke and dust can be associated with volatile organic compounds and dioxins (European Commission 2001).

2.2 Emissions of PCDD/PCDF to air

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

“The presence of oils and other organic materials on scrap or other sources of carbon (partially burnt fuels and reductants, such as coke), can produce fine carbon particles which react with inorganic chlorides or organically bound chlorine in the temperature range of 250 °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” (European Commission 2001, p. 133).

“Poor combustion of fuel or the organic content of the feed material can result in the emission of organic materials. The provision of effective burner and furnace to controls is used to optimise combustion. Peak combustion rates from included organic materials need to be taken into account if they are fed to the furnace. It is reported that pre-cleaning of scrap removes much of the organic material and improves the melting rate. The use of chlorine mixtures for degassing and magnesium removal and the use of chlorides (salt flux) will provide a source of chlorine for the potential formation of PCDD/PCDF” (European Commission 2001, p. 297).

Based on information obtained from Japanese secondary aluminum operations, emissions have been found to vary according to the furnace type employed. The highest-emitting furnace type in this study was the open well reverberatory furnace. These units were found to average 0.38 ng I-TEQ/Nm³. These results are believed to relate to the fact that this is the only furnace design that permits the introduction of large pieces of scrap material, and this material is often the most contaminated with organic compounds that may contribute to PCDD/PCDF formation (Government of Japan 2005).

2.3 Releases to other media

(European Commission 2001, p. 294–300)

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

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

3. Recommended processes

Process design and configuration is influenced by the variations in feed material and quality control. Processes considered as best available practices are the reverberatory furnace, rotary and tilting rotary furnaces, the induction furnace and the Meltower shaft furnace. All techniques should be applied in conjunction with suitable gas collection and abatement systems.

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

4. Primary and secondary measures

Primary and secondary measures for 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

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

Scrap material should be cleaned of oils, paints and plastics during pretreatment. The removal of organic and chlorine compounds will reduce the potential for PCDD/PCDF formation. Methods used include the swarf centrifuge, swarf drying or other thermal decoating techniques. 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. 310).

Scrap sorting using laser and eddy current technology is being tested. These methods could provide more efficient selection of materials for recycling and the ability to produce desired alloys in recycling plants (European Commission 2001, p. 294–300).

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 (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.

4.1.3 Demagging

An essential measure to control chemicals listed in Annex C appears to be correct demagging (removal of magnesium from the melt). The use of hexachloroethane tablets has been shown to give rise to high releases of PCDD/PCDF and particularly hexachlorobenzene (HCB), and the practice has been banned in Europe. This is an important aspect of the process. The choice of a demagging approach requires careful assessment of the options since there are practical and health and safety considerations as well as environmental ones.

4.2 Secondary measures

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

4.2.1 Fume and gas collection

Fume and off-gas collection should be implemented in the control of air emissions from all stages of the process. The use of sealed feeding systems and furnaces should be practised. Fugitive emissions should be controlled by maintaining negative air pressure within the furnace to prevent leaks. If a sealed unit is not possible, hooding should be used. Furnace or reactor enclosures may be necessary. Where primary extraction and enclosure of fumes is not practicable, the furnace should be enclosed so that ventilation air can be extracted, treated and discharged (European Commission 2001, p. 187–188). Additional benefits of fume and off-gas collection from rooflines include reducing exposure of the workforce to fumes and heavy metals.

4.2.2 High-efficiency dust removal

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

Scrubbing off-gases with sodium bicarbonate will remove chlorides produced by the salt flux, resulting in sodium chloride, which can then be removed by fabric filters to be recharged to the furnace. In addition, use of a catalytic coating on fabric filter bags could destroy PCDD/PCDF by oxidation while collecting particulate matter on which these contaminants have adsorbed (European Commission 2001, p. 294–300). Note that rapid cooling should be assured (see below) to ensure that formation does not take place in the dust abatement system.

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. They 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). A benefit of cooling the flue gases before scrubbing would be reduced gas volume, hence reducing the size of abatement equipment, the duct size and the energy needs for gas movement.

4.2.4 Adsorption on activated carbon

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

4.2.5 Catalyst-coated filter

Japanese researchers have used a catalyst-coated filter on an experimental basis, and results are encouraging. This filter system consists of two filters, one to collect the soot and another coated with a catalyst to decompose dioxins and furans. The experimental work has demonstrated that the catalyst was effective at decomposing dioxins and furans at temperatures in the range of 180° to 200° C.

4.3 Best environmental practices

The following guidelines are derived from the Japan Aluminium Alloy Refiners Association (March 2004) and may be considered as best environmental practices:

Practical operation guidelines are presented below. The following main items are common to these guidelines:

- Do not purchase anything that is likely to generate smoke. Melt materials gradually;
- Perform smelting and combustion with no soot or smoke generation;
- Perfectly burn generated soot and smoke promptly;
- Quickly cool down exhaust gas at high or middle temperatures to 170 °C or below;
- CO control in exhaust gas ($\text{CO} \leq 50$ ppm, air-fuel ratio management).

Operation guidelines:

1. Matters related to materials and scraps:
 - Reinforce sorting on and after accepting materials;
 - Sort and eliminate resin and oil;
 - Sort and eliminate foreign substances and resin after shredder processing;
 - Return materials where resin or oil is stuck. Do not accept them at discount prices.
2. At time of combustion and smelting at smelting chamber:
 - Avoid turning the burner on and off as much as possible in order to reduce imperfect combustion and soot generation;
 - Supply materials while the burner is on, and set generated smoke and soot in flame for secondary combustion.
3. At time of combustion and smelting in open well:
 - Adjust the air-fuel ratio by measuring the CO and O₂ concentration in flue exhaust gas;
 - In order to heat and burn smoke and soot generated from materials supplied to the open well, put the smoke and soot in burner flame;
 - Adjust the supply of smelting materials according to the extent of smoke and flame (soot) generation:
 - Equalize the supply of burnable material (repetitively and little by little);
 - Keep the combustion space with no imperfect combustion;
 - Do not leak smoke from the exhaust gas hood;
 - Maintain the performance of the dust collector (with regular inspection and bag replacement).
4. At time of demagnesium processing:
 - Maintain the interval between the extinguishment of the burner and the start of chlorine processing, and between the completion of chlorine processing and burner ignition, for 5 to 10 minutes, while performing air suction (residual gas discharge);
 - Make improvement in efficiency by an increase in the initial temperature of molten metal processing;
 - Sort combined materials according to the quantity of Mg contained;
 - Standardize the quantity of chlorine and that of flux used.

5. At time of drying turnings:
 - Demand improvement in cut dust with excessive cutting oil (cutting oil with a high chlorine content);
 - Reheat at high temperature, maintain the exhaust gas of the drying furnace, and quickly cool down the exhaust gas (i.e., keep good temperature control);
 - Measure the CO concentration in exhaust gas regularly.
6. At time of paint removal and baking of can scraps (used beverage cans):
 - Removal of foreign substances, such as resin and resin bags;
 - Stable operation of the reheating furnace at constant circulation and exhaust gas temperature.
7. General:
 - Maintenance and inspection of the capacity of the dust collector, bag replacement, shaking cycle, and suction pressure;
 - Regular implementation of in-house environmental education for smelting workers;
 - Targeting at the concentration of dioxins and furans in exhaust gas ($< 1 \text{ ng I-TEQ/Nm}^3$) for existing facilities.

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. 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.

Catalytic oxidation processes organic compounds into water, carbon dioxide (CO₂) and hydrochloric acid using a precious metal catalyst to increase the rate of reaction between 370 °C and 450 °C, whereas incineration occurs typically at 980 °C. Catalytic oxidation has been shown to destroy PCDD/PCDF with shorter residence times, lower energy consumption and 99% efficiency, and should be considered. Off-gases should be 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 CO₂ 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 recommended processes for new secondary aluminium smelters

Measure	Description	Considerations	Other comments
Recommended processes	Various recommended smelting processes should be considered for new facilities	Processes to consider include reverberatory furnace, rotary and tilting rotary furnaces, induction furnace, and Meltower shaft furnace	All techniques should be applied in conjunction with suitable gas collection and abatement systems

Table 2. Summary of primary and secondary measures for secondary aluminium smelters

Measure	Description	Considerations	Other comments
<i>Primary measures</i>			
Presorting of feed material	The presence of oils, plastics and chlorine compounds in the feed material should be avoided to reduce the generation of PCDD/PCDF during incomplete combustion or by de novo synthesis	Processes to consider include: <ul style="list-style-type: none"> • Prevention or minimization of the use of chloride salts where possible • Cleaning scrap material of oils, paints and plastics during pretreatment • Using thermal decoating techniques such as the swarf centrifuge or swarf dryer 	Sorting of feed material should be conducted prior to smelting to suit furnace type and abatement and to permit the transfer of unsuitable raw materials to other facilities better suited for their treatment. 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
Choice of demagging chemicals	Carefully consider choice of chemicals and control process to ensure that off-gases are treated	Hexachloroethane for demagging can lead to high releases of PCDD/PCDF and HCB (no information on PCB) but has significant process advantages	
<i>Secondary measures</i>			
Fume and gas collection	Effective fume and off-gas collection should be implemented in the capture of air emissions from all stages of the process	Processes to consider include: <ul style="list-style-type: none"> • Use of sealed feeding systems and furnaces • Control of fugitive emissions by maintaining negative air pressure within the furnace to prevent leaks • Use of hooding if a sealed unit is not possible • Use of furnace or reactor enclosures 	Where primary extraction and enclosure of fumes is not practicable, the furnace should be enclosed so that ventilation air can be extracted, treated and discharged

Measure	Description	Considerations	Other comments
High-efficiency dust removal	Particulate matter generated during the smelting process should be removed as this material possesses large surface area on which PCDD/PCDF can adsorb. Proper isolation and disposal of these dusts will aid in PCDD/PCDF control	Processes to consider include: <ul style="list-style-type: none"> • Fabric filters, wet/dry scrubbers and ceramic filters • Catalytic coatings on fabric filter bags to destroy PCDD/PCDF by oxidation while collecting particulate matter on which these contaminants have adsorbed 	Collected particulate should be treated in high-temperature furnaces to destroy PCDD/PCDF and recover metals
Afterburners and quenching	Afterburners should be used at temperatures > 950 °C to ensure full combustion of organic compounds, followed by rapid quenching of hot gases to temperatures below 250 °C	Considerations include: <ul style="list-style-type: none"> • PCDD/PCDF formation at 250 °C to 500 °C, and destruction > 850 °C with O₂ • Requirement for sufficient O₂ in the upper region of the furnace for complete combustion • Need for proper design of cooling systems to minimize reformation time 	De novo synthesis is still possible as the gases are cooled through the reformation window
Adsorption on activated carbon	Activated carbon treatment should be considered as this material is an ideal medium on which PCDD/PCDF can adsorb due to its large surface area	Processes to consider include: <ul style="list-style-type: none"> • Treatment with activated carbon using fixed or moving bed reactors • Injection of carbon into the gas stream followed by high-efficiency dedusting methods such as fabric filters 	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, carbon dioxide (CO ₂) and hydrochloric acid using a precious metal catalyst	Considerations include: <ul style="list-style-type: none"> • Process efficiency for the vapour phase of contaminants • Hydrochloric acid treatment using scrubbers while water and CO₂ are released to the air after cooling 	Has been shown to reduce PCDD/PCDF with shorter residence times, lower energy consumption and 99% efficiency. Off-gases should be dedusted prior to catalytic oxidation for optimum efficiency

7. Performance levels associated with best available techniques and best environmental practices

PCDD/PCDF performance levels in air emissions associated with best available techniques and best environmental practices for secondary aluminium smelters are $< 0.5 \text{ ng I-TEQ/Nm}^3$ (at operating oxygen concentrations).

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(iv) Secondary zinc production

Summary

Secondary zinc smelting involves the production of zinc from materials such as dusts from copper alloy production and electric arc steel making, and residues from steel scrap shredding and galvanizing processes.

Production processes include feed sorting, pretreatment cleaning, crushing, sweating furnaces to 364 °C, melting furnaces, refining, distillation and alloying. Contaminants in the feed (including oils and plastics), poor combustion and temperatures between 250 °C and 500 °C may give rise to chemicals listed in Annex C of the Stockholm Convention.

Best available techniques include feed cleaning, maintaining temperatures above 850 °C, fume and gas collection, afterburners with quenching, activated carbon adsorption and fabric filter dedusting.

PCDD/PCDF performance levels in air emissions associated with best available techniques and best environmental practices for secondary zinc smelters are < 0.5 ng I-TEQ/Nm³ (at operating oxygen concentrations).

1. Process description

Secondary zinc smelting involves the processing of zinc scrap from various sources. Feed material includes dusts from copper alloy production and electric arc steel making (both of which have the potential to be contaminated with chemicals listed in Annex C of the Stockholm Convention), residues from steel scrap shredding, and scrap from galvanizing processes. The process method is dependent on zinc purity, form and degree of contamination. Scrap is processed as zinc dust, oxides or slabs. The three general stages of production are pretreatment, melting and refining (EPA 1981).

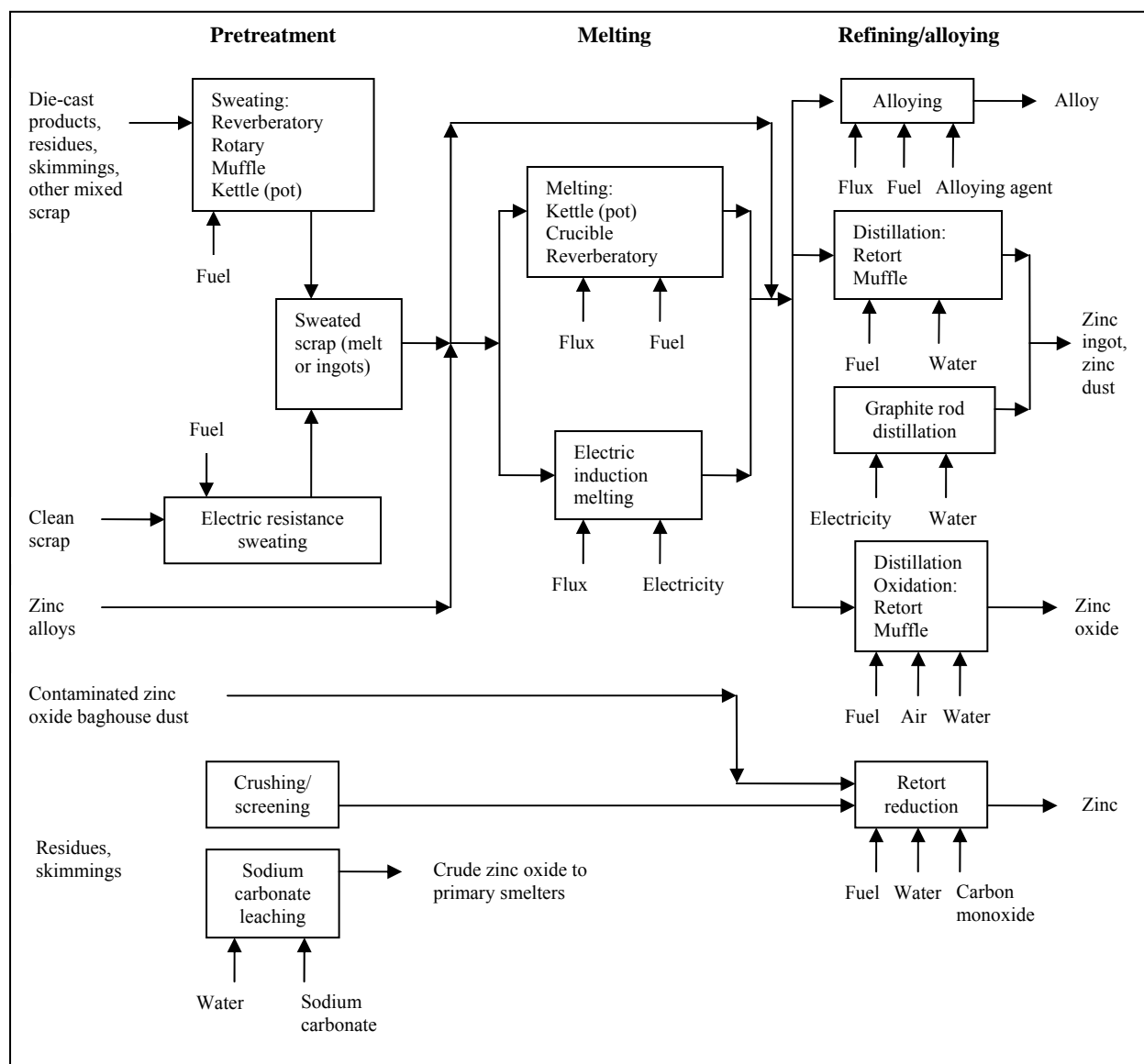
During pretreatment scrap is sorted according to zinc content and processing requirements, cleaned, crushed and classified by size. A sweating furnace is used to heat the scrap to 364 °C. At this temperature only zinc is melted, while other metals remain solid. The molten zinc is collected at the bottom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

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

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

Refining removes further impurities in clean zinc alloy scrap and in zinc vaporized during the melt phase in retort furnaces. Distillation involves vaporization of zinc at temperatures from 982 °C to 1,249 °C in muffle or retort furnaces and condensation as zinc dust or liquid zinc. Several forms can be recovered depending on temperature, recovery time, absence or presence of oxygen and equipment used during zinc vapour condensation. Pot melting is a simple indirect heat melting operation whereby the final alloy cast into zinc alloy slabs is controlled by the scrap input into the pot. Distillation is not involved.

Final products from refining processes include zinc ingots, zinc dust, zinc oxide and zinc alloys. Figure 1 shows the production process in diagrammatic form.

Figure 1. Secondary zinc smelting

Source: EPA 1981.

Artisanal and small enterprise metal recovery activities may play a significant international role, in particular in developing countries and countries with economies in transition. These activities may contribute significantly to pollution and have negative health impacts. For example, artisanal zinc smelting is an important atmospheric mercury emission source. The techniques used to smelt both zinc and mercury are very simple. The ores are heated in a furnace for a few hours, and zinc metal and liquid mercury are produced. In many cases there are no pollution control devices employed at all during the melting process. Other metals that are known to be produced by artisanal and small enterprise metal recovery activities include antimony, iron, lead, manganese, tin, tungsten, gold, silver, copper and aluminum.

These are not considered best available techniques or best environmental practices. However, as a minimum, appropriate ventilation and material handling should be carried out.

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

The formation of chemicals listed in Annex C of the Stockholm Convention (PCDD/PCDF being the most studied) can result from the presence of carbon and chlorine in regions of the process where temperatures are in the range 250 °C to 450 °C. Note that the use of dusts from electric arc furnace and copper processes can also carry high levels of contamination into the process.

2.1 General information on emissions from secondary zinc smelters

Air emissions from secondary zinc smelting can escape as stack or fugitive emissions, depending on the facility age or technology. Main contaminants are sulphur dioxide (SO₂), other sulphur compounds and acid mists, nitrogen oxides (NO_x), metals (especially zinc) and their compounds, dusts and PCDD/PCDF. SO₂ is collected and processed into sulphuric acid in acid plants when processing secondary material with high sulphur content. Fugitive SO₂ emissions can be controlled by good extraction and sealing of furnaces. NO_x can be reduced using low-NO_x or oxy-fuel burners. Particulate matter is collected using high-efficiency dust removal methods such as fabric filters and returned to the process (European Commission 2001, p. 359–368).

2.2 Emissions of PCDD/PCDF to air

PCDD/PCDF may be formed during metals smelting through carry-over from contaminated feed (e.g. electric arc furnace dust), formation as a result of incomplete combustion, or by de novo synthesis from unburnt organics and chlorine compounds present in the downstream region as the gases cool.

“The processing of impure scrap such as the non-metallic fraction from shredders is likely to involve production of pollutants including PCDD/PCDF. Relatively low temperatures are used to recover lead and zinc (340 °C and 440 °C). Melting of zinc may occur with the addition of fluxes including zinc and magnesium chlorides” (UNEP 2003, p. 78).

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

“Although PCDD/PCDF are destroyed at high temperature (above 850 °C) in the presence of oxygen, the process of de novo synthesis is still possible as the gases are cooled through the ‘reformation window’. This window can be present in abatement systems and in cooler parts of the furnace e.g. the feed area. Care taken in the design of cooling systems to minimise the residence time in the window is practised to prevent de novo synthesis” (European Commission 2001, p. 133).

A report prepared by the Government of Japan studied dioxin reduction technologies and their effects in secondary zinc production facilities of Japan. Various exhaust gas technologies were introduced in line with guidelines on best available techniques and best environmental practices at five existing facilities. Dioxin emissions were found to vary depending on the type of furnace employed. Dioxin discharge concentrations were found to range from 0.91 to 40 ng I-TEQ/Nm³ before the introduction of the exhaust gas technologies, and from 0.32 to 11.7 ng I-TEQ/Nm³ after their introduction. When a state-of-the-art two-step bag filter and two-step activated carbon injection system was introduced into the reduction furnace at one facility, dioxin concentration was reduced from 3.30 ng I-TEQ/Nm³ to 0.49 ng I-TEQ/Nm³ (Government of Japan 2005).

2.3 Releases to other media

Wastewater originates from process effluent, cooling water and run-off and is treated using wastewater treatment techniques. Process residues are recycled, treated using downstream methods to

recover other metals, or safely disposed of. The use of wet scrubbing can lead to contaminated effluent as well as residues requiring treatment; dry particulate capture results in solid residues that may be contaminated. These residues require proper management to avoid releases.

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 to be best available techniques include: physical separation, melting and other high temperature treatment techniques followed by the removal of chlorides. (European Commission 2001, p.396)

No information is available on alternative processes to smelting for secondary zinc 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

Contaminated feed such as dusts from electric arc furnace and copper processing may well contain elevated levels of PCDD/PCDF and other chemicals listed in Annex C. Consideration should be given to ensuring that any carry-over into the process will be effectively destroyed or captured and disposed of.

Impurities in the charge such as oils, paints and plastics in zinc scrap should be separated from the furnace feed to reduce the formation of PCDD/PCDF from the incomplete combustion of organic compounds or by de novo synthesis. However, the bulk of the organic material charged will come from the fuel added in many cases. Methods for feed storage, handling and pretreatment are influenced by material size distribution, contaminants and metal content.

Milling and grinding, in conjunction with pneumatic or density separation techniques, can be used to remove plastics. Thermal 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.

4.2 Secondary measures

Secondary measures are pollution control techniques to contain and prevent emissions. These methods do not prevent the formation of contaminants. Quenching may be used to reduce or virtually eliminate formation in the cooling zone and is a primary measure, although it may be implemented in conjunction with secondary measures.

4.2.1 Fume and gas collection

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

“The fume collection systems used can exploit furnace-sealing systems and be designed to maintain a suitable furnace [vacuum] that avoids leaks and fugitive emissions. Systems that maintain furnace sealing or hood deployment can be used. Examples are through hood additions of material, additions via tuyeres or lances and the use of robust rotary valves on feed systems. An [effective] fume collection system capable of targeting the fume extraction to the source and duration of any fume will consume less energy. Best available techniques for gas and fume treatment systems are those that use cooling and heat recovery if practical before a fabric filter.” (European Commission 2001, p. 397).

4.2.2 High-efficiency dust removal

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

Fabric filters using high-performance materials are the most effective option. Innovations regarding this method include bag burst detection systems, online cleaning methods, and catalytic coatings to destroy PCDD/PCDF (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. 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 (CO₂) 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 CO₂ 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 recommended processes for new secondary zinc smelters

Measure	Description	Considerations	Other comments
Recommended Processes	Various recommended smelting processes should be considered for new facilities	Processes to consider include: <ul style="list-style-type: none"> Physical separation, melting and other high-temperature treatment techniques followed by the removal of chlorides The use of Waelz kilns, cyclone- or converter-type furnaces to raise the temperature to volatilize the metals and then form the oxides that are then recovered from the gases in a filtration stage 	These processes should be applied in combination with good process control, gas collection and abatement systems. Waelz kilns can be a major source of PCDD/PCDF (and other chemicals listed in Annex C) – control of their use and operation is key to reducing overall releases

Table 2. Summary of primary and secondary measures for secondary zinc smelters

Measure	Description	Considerations	Other comments
<i>Primary measures</i>			
Presorting of feed material	Electric arc furnace and copper processing dusts used as zinc-bearing feedstock may contain high levels of PCDD/PCDF (and other chemicals listed in Annex C). Oils and plastic in zinc scrap should be separated from the furnace feed to reduce the formation of PCDD/PCDF from incomplete combustion or by de novo synthesis	Processes to consider include: <ul style="list-style-type: none"> Milling and grinding, in conjunction with pneumatic or density separation techniques, can be used to remove plastics Oil removal conducted 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

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	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
<i>Secondary measures</i>			
Fume and gas collection	Effective fume and off-gas collection should be implemented in all stages of the smelting process to capture PCDD/PCDF emissions	Processes to consider include: <ul style="list-style-type: none"> • Furnace-sealing systems to maintain a suitable furnace vacuum that avoids leaks and fugitive emissions • Use of hooding • Hood additions of material, additions via tuyeres or lances and the use of robust rotary valves on feed systems 	Best available techniques for gas and fume treatment systems are those that use cooling and heat recovery if practicable before a fabric filter except when carried out as part of the production of sulphuric acid
High-efficiency dust removal	Dusts and metal compounds should be removed as this material possesses high surface area on which PCDD/PCDF easily adsorb. Removal of these dusts would contribute to the reduction of PCDD/PCDF emissions	Processes to consider include: <ul style="list-style-type: none"> • Use of fabric filters, wet/dry scrubbers and ceramic filters 	Fabric filters using high-performance materials are the most effective option. Collected particulate matter should be recycled in the furnace
Afterburners and quenching	Afterburners should be used at temperatures > 950 °C to ensure full combustion of organic compounds, followed by rapid quenching of hot gases to temperatures below 250 °C	Considerations include: <ul style="list-style-type: none"> • PCDD/PCDF formation at 250 °C to 500 °C, and destruction > 850 °C with O₂ • Requirement for sufficient O₂ in the upper region of the furnace for complete combustion • Need for proper design of cooling systems to minimize reformation time 	De novo synthesis is still possible as the gases are cooled through the reformation window
Adsorption on activated carbon	Activated carbon treatment should be considered as this material is an ideal medium for adsorption of PCDD/PCDF due to	Processes to consider include: <ul style="list-style-type: none"> • Treatment with activated carbon using fixed or moving bed reactors • Injection of carbon particulate into the gas 	Lime/carbon mixtures can also be used

Measure	Description	Considerations	Other comments
	its large surface area	stream followed by removal as a filter dust	
<i>Emerging research</i>			
Catalytic oxidation	Catalytic oxidation is an emerging technology which should be considered due to its high efficiency and lower energy consumption. Catalytic oxidation transforms organic compounds into water, CO ₂ and hydrochloric acid using a precious metal catalyst	Considerations include: <ul style="list-style-type: none"> • Process efficiency for the vapour phase of contaminants • Hydrochloric acid treatment using scrubbers while water and CO₂ are released to the air after cooling 	Catalytic oxidation has been shown to destroy PCDD/PCDF with shorter residence times, lower energy consumption and 99% efficiency. Off-gases should be treated for particulate removal prior to catalytic oxidation for optimum efficiency

7. Performance levels associated with best available techniques and best environmental practices

PCDD/PCDF performance levels in air emissions associated with best available techniques and best environmental practices for secondary zinc smelters are < 0.5 ng I-TEQ/Nm³ (at operating oxygen concentrations).

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