Section V.D.4.

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

Secondary zinc production

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

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1.0 Process Description[1]

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

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

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

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

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

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

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

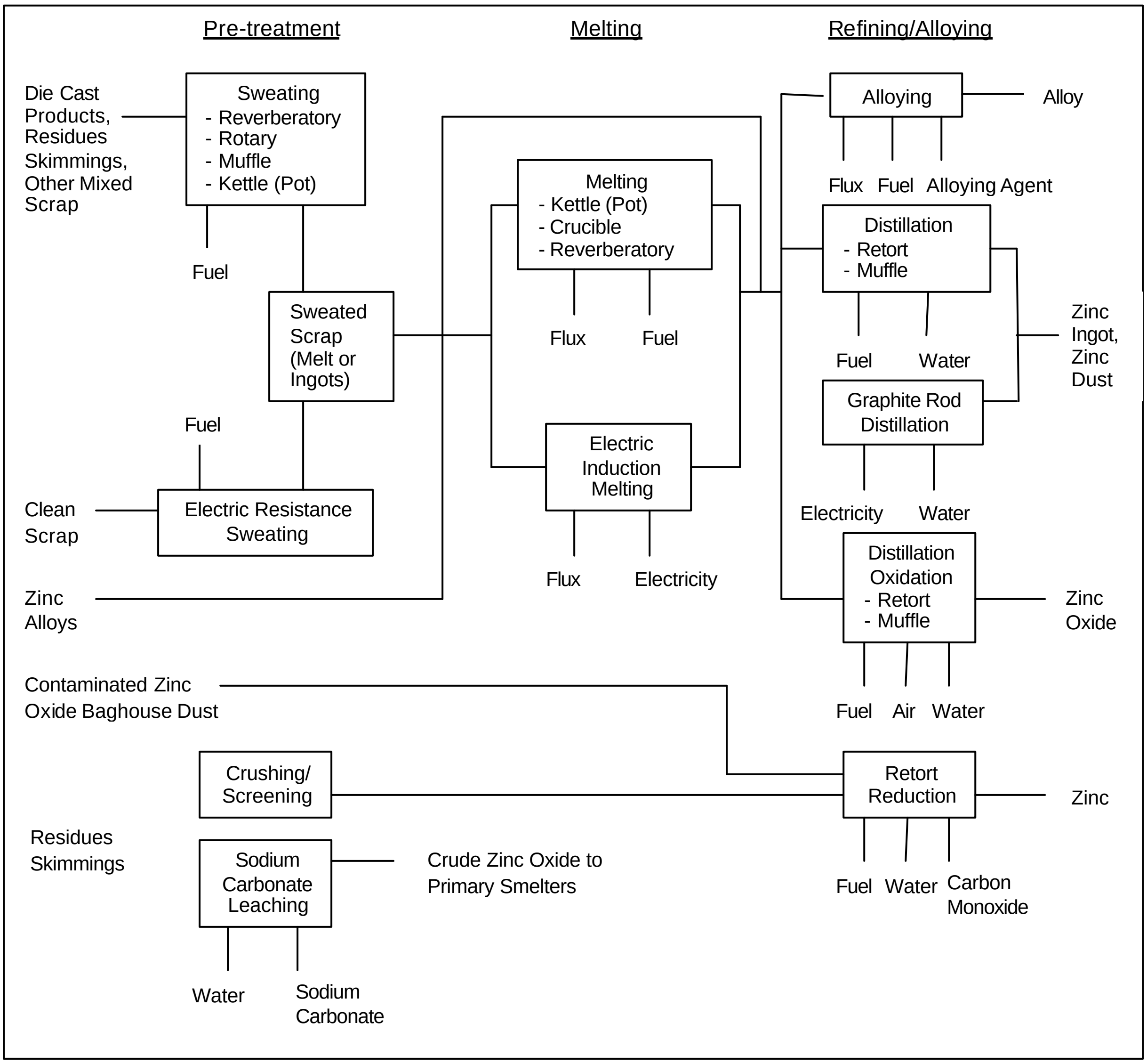

Figure 1 Secondary Zinc Smelting[2]

2.0 Sources of Unintentionally Produced POPs

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

[2] Ibid.

2.1 General Information on Emissions from Secondary Zinc Smelters[3]

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

2.2 Emissions of PCDD/PCDF to Air

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

"The processing of impure scrap such as the non-metallic fraction from shredders is likely to involve production of pollutants including PCDD/PCDF. Relatively low temperatures are used to recover lead and zinc (340 and 440°C). Melting of zinc may occur with the addition of fluxes including zinc and magnesium chlorides." [4]

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

"Although PCDD/PCDF are destroyed at high temperature (above 850 °C) in the presence of oxygen, the process of de-novo synthesis is still possible as the gases are cooled through the "reformation window". This window can be present in abatement systems and in cooler parts of the furnace e.g. the feed area. Care taken in the design of cooling systems to minimise the residence time in the window is practised to prevent de-novo synthesis."[5]

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[3] European Commission, *Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p. 359-368.
[4] UNEP, *Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases*, May 2003, p.78. URL: www.pops.int/documents/guidance/Toolkit_2003.pdf
[5] European Commission, *Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p. 133.

2.3 Releases to Other Media

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

3.0 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 BAT include:

- *"Physical separation, melting and other high temperature treatment techniques followed by the removal of chlorides.*
- *The use of Waelz kilns, cyclone or converter type furnaces to raise the temperature to volatilise the metals and then form the oxides that are then recovered from the gases in a filtration stage."* [6]

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

4.0 Primary and Secondary Measures

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

4.1 Primary Measures

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

1. Pre-sorting of Feed Material:

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

   Milling and grinding, in conjunction with pneumatic or density separation techniques, can be used to remove plastics. Thermal de-coating and de-oiling processes for oil

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

removal should be followed by afterburning to destroy any organic material in the off-gas.[7]

2. Effective Process Control:

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

4.2 Secondary Measures

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

1. Fume and Gas Collection:

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

   "The fume collection systems used can exploit furnace-sealing systems and be designed to maintain a suitable furnace [vacuum] that avoids leaks and fugitive emissions. Systems that maintain furnace sealing or hood deployment can be used. Examples are through hood additions of material, additions via tuyeres or lances and the use of robust rotary valves on feed systems. An [effective] fume collection system capable of targeting the fume extraction to the source and duration of any fume will consume less energy. BAT for gas and fume treatment systems are those that use cooling and heat recovery if practical before a fabric filter…."[8]

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

[7] European Commission, *Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p. 232.
[8] European Commission, *Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p. 397.

fabric filters, wet/dry scrubbers and ceramic filters. Collected particulate matter is usually recycled in the furnace.

Fabric filters using high performance materials are the most effective option. Innovations regarding this method include bag burst detection systems, online cleaning methods, and catalytic coatings to destroy PCDD/PCDF. [9]

3. Afterburners and quenching:

   Afterburners (post-combustion) should be used at a minimum temperature of 950°C to ensure full combustion of organic compounds.[10] 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. [11]

   It has been observed that PCDD/PCDF are formed in the temperature range of 250 to 500°C. These are destroyed above 850°C in the presence of oxygen. Yet, *de novo* synthesis is still possible as the gases are cooled through the reformation window present in abatement systems and cooler areas of the furnace. Operation of cooling systems to minimise reformation time should be implemented.[12]

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.

5.0 Emerging Research

Catalytic Oxidation:

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

[9] European Commission, *Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p.139-140.
[10] Hübner C., et. al., *State-Of-The-Art Measures For Dioxin Reduction In Austria*, 2000. URL: www.ubavie.gv.at/publikationen/Mono/M116s.htm
[11] European Commission, *Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p. 189.
[12] European Commission, *Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p. 133.

Catalytic oxidation processes organic compounds into water, carbon dioxide (CO_2) and hydrochloric acid using a precious metal catalyst to increase the rate of reaction at 370 to 450°C. In comparison, incineration occurs typically at 980°C. Catalytic oxidation has been shown to destroy PCDD/PCDF with shorter residence times, lower energy consumption and 99% efficiency, and should be considered. Off-gases should be de-dusted prior to catalytic oxidation for optimum efficiency. This method is effective for the vapour phase of contaminants. The resulting hydrochloric acid is treated in a scrubber while the water and CO_2 are released to the air after cooling.[13]

6.0 Summary of Measures

Table 6.1 Measures for Recommended Processes

Measure	Description	Considerations	Other comments
New Secondary Zinc Smelters			
Recommended Processes	Various recommended smelting processes should be considered for new facilities.	Processes to be considered include: - Physical separation, melting and other high temperature treatment techniques followed by the removal of chlorides. - The use of Waelz kilns, cyclone or converter type furnaces to raise the temperature to volatilise the metals and then form the oxides that are then recovered from the gases in a filtration stage.	These processes should be applied in combination with good process control, gas collection and abatement systems.

Table 6.2 Summary of Primary and Secondary Measures for Secondary Zinc Smelters

Measure	Description	Considerations	Other Comments
Primary Measures			
Pre-sorting of feed material	Oils and plastic in zinc scrap should be separated from the furnace feed to reduce the formation of PCDD/PCDF from incomplete combustion or by de-novo synthesis.	Processes to be considered include: - Milling and grinding, in conjunction with pneumatic or density separation techniques, can be used to remove	Thermal de-coating and de-oiling processes for oil removal should be followed by afterburning to destroy any organic material in the off-gas.

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

Measure	Description	Considerations	Other Comments
		plastics. - Oil removal conducted through thermal de-coating and de-oiling processes	
Effective process control	Process control systems should be utilized to maintain process stability and operate at parameter levels that will contribute to the minimization of PCDD/PCDF generation.	PCDD/PCDF emissions may be minimized by controlling other variables such as temperature, residence time, gas components and fume collection damper controls, after having established optimum operating conditions for the reduction of PCDD/PCDF.	Continuous emissions sampling of PCDD/PCDF has been demonstrated for some sectors (e.g. waste incineration), but research is still developing in this field.
Secondary Measures			
Fume and Gas Collection	Effective fume and off-gas collection should be implemented in all stages of the smelting process to capture PCDD/PCDF emissions.	Processes to be considered include: - 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.	BAT for gas and fume treatment systems are those that use cooling and heat recovery if practical before a fabric filter except when carried out as part of the production of sulphuric acid
High Efficiency Dust Removal	Dusts and metal compounds should be removed as this material possesses high surface area on which PCDD/PCDF easily adsorb. Removal of these dusts would contribute to the reduction of PCDD/PCDF emissions.	Processes to be considered include: - 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: - PCDD/PCDF formation at 250-500°C, and destruction >850°C with O_2. - Requirement for sufficient O_2 in the upper region of the	- De novo synthesis is still possible as the gases are cooled through the reformation window.

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

7.0 Achievable Levels

Achievable levels for emissions of PCDD/PCF from secondary zinc smelters are identified as follows:

Table 7.1 Performance Standards for Secondary Zinc Smelters

Type	Suggested Timeline	Emission Limit[14]
New	Entry into force	<0.1 ng /Rm^3 TEQ
Existing	Within 10 years of entry into force	<0.1 ng /Rm^3 TEQ

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