

Section VI.B.1.

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

Secondary lead production

Coordinated by Mr. Patrick Finlay (Canada)

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

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1.0 Process Description

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

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

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

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

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

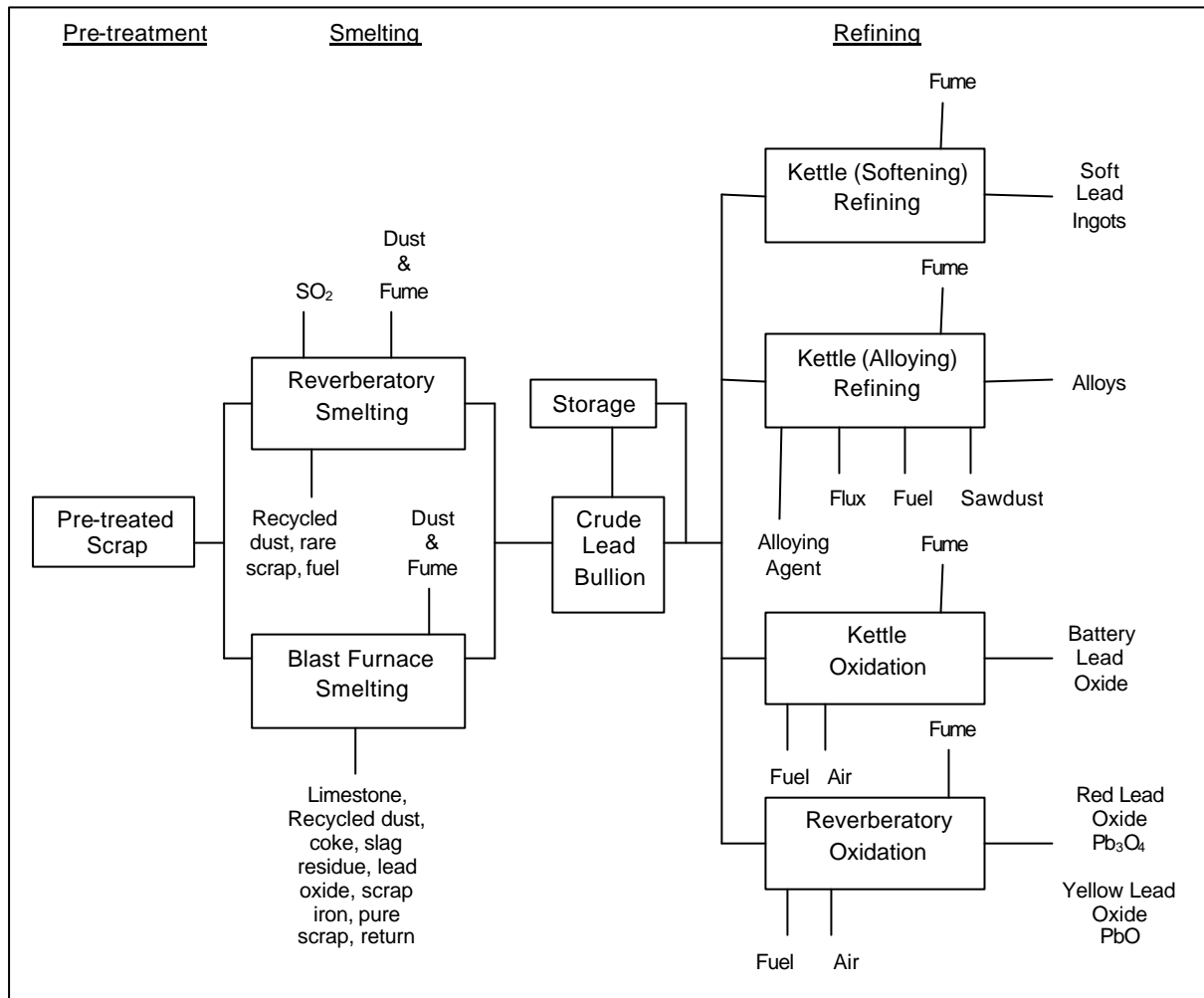


Figure 1 Secondary Lead Smelting²

2.0 Sources of Unintentionally Produced POPs

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

2.1 General Information on Emissions from Secondary Lead Smelters³

Air emissions from secondary lead smelting can escape as stack or fugitive emissions depending on the facility age or technology. Main contaminants are sulphur dioxide

² Ibid.

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.

(SO₂), other sulphur compounds and acid mists, nitrogen oxides (NO_x), metals, especially lead, and their compounds, dusts and PCDD/PCDF. SO₂ is collected and processed into sulphuric acid in acid plants. 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.

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.

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

The presence of oils and other organic materials on scrap or other sources of carbon (partially burnt fuels and reductants, such as coke), can produce fine carbon particles which react with inorganic chlorides or organically bound chlorine in the temperature range of 250 to 500 °C to produce PCDD/PCDF. This process is known as de-novo synthesis and is catalysed by the presence of metals such as copper or iron.

Although PCDD/PCDF are destroyed at high temperature (above 850 °C) in the presence of oxygen, the process of de-novo synthesis is still possible as the gases are cooled through the “reformation window”. This window can be present in abatement systems and in cooler parts of the furnace e.g. the feed area. Care taken in the design of cooling systems to minimise the residence time in the window is practised to prevent de-novo synthesis.”⁴

2.3 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 as BAT include

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

the blast furnace (with good process control), the ISA Smelt/Ausmelt furnace, the Top Blown Rotary furnace, the electric furnace and the rotary furnace.⁵

The submerged arc electric furnace is a sealed unit for mixed copper and lead materials. It is cleaner than other processes if the gas extraction system is well designed and sized.⁶

“The injection of fine material via the tuyeres of a blast furnace has been successfully used and reduces the handling of dusty material and the energy involved in returning the fines to a sinter plant.”⁷ This technique minimises dust emissions during charging and thus reduces the release of PCDD/PCDF through adsorption on particulate matter.

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

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

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

⁵ European Commission, *Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p. 379.

⁶ European Commission, *Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p. 395.

⁷ European Commission, *Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p. 404.

removal should be followed by afterburning to destroy any organic material in the off-gas.⁸

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.

“Particular attention is needed for the temperature measurement and control for furnaces and kettles used for melting the metals in this group so that fume formation is prevented or minimised.”⁹

4.2 Secondary Measures

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

1. Fume and Gas Collection:

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

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

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

⁹ European Commission, *Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p. 390.

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

2. High Efficiency Dust Removal

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

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

3. Afterburners and quenching:

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

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

4. Adsorption on Activated Carbon:

Activated carbon treatment should be considered for PCDD/PCDF removal from smelter off-gases. Activated carbon possesses large surface area on which PCDD/PCDF can be adsorbed. Off-gases can be treated with activated carbon using fixed or moving bed reactors, or 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.

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

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

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

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

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.

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 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 CO₂ are released to the air after cooling.¹⁵

6.0 Summary of Measures

Table 6.1 Measures for New Secondary Lead Smelters

Measure	Description	Considerations	Other comments
<i>New Secondary Lead Smelters</i>			
Recommended Processes	Various recommended smelting processes should be considered for new facilities.	Processes to be considered include: - Blast furnace (with good process control), ISA Smelt/Ausmelt furnace, Top Blown Rotary furnace, electric furnace and rotary furnace - Submerged electric arc furnace (it is a sealed unit for mixed copper and lead materials, cleaner than other processes if gas extraction system is well designed and sized) -injection of fine material via the tuyeres of a blast furnace reduces handling of dusty material	These processes should be applied in combination with good process control, gas collection and abatement systems.

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

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

Measure	Description	Considerations	Other Comments
Primary Measures			
Pre-sorting of feed material	Scrap should be sorted and pre-treated to remove organic compounds and plastics to reduce PCDD/PCDF generation from incomplete combustion or by de-novo synthesis.	Processes to be considered include: - Avoidance of whole battery feed or incomplete separation. - Milling and grinding, followed by pneumatic or density separation techniques, to remove plastics - Oil removal conducted through thermal de-coating and de-oiling processes	Thermal de-coating and de-oiling processes for oil removal should be followed by afterburning to destroy any organic material in the off-gas
Effective process control	Process control systems should be utilized to maintain process stability and operate at parameter levels that will contribute to the minimization of PCDD/PCDF generation.	PCDD/PCDF emissions may be minimized by controlling other variables such as temperature, residence time, gas components and fume collection damper controls after having established optimum operating conditions for the reduction of PCDD/PCDF.	Continuous emissions sampling of PCDD/PCDF has been demonstrated for some sectors (e.g. waste incineration), but research is still developing in this field. Particular attention is needed for the temperature measurement and control for furnaces and kettles used for melting the metals in this group so that fume formation is prevented or minimised
Secondary Measures			
Fume and Gas Collection	Fume and off-gas collection should be implemented in all stages of the smelting process to capture PCDD/PCDF emissions.	Processes to be considered include: - 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.
High Efficiency Dust Removal	Dusts and metal compounds should be removed as this material possesses high surface area on	Processes to be considered include: - Use of fabric filters,	Fabric filters using high performance materials are the most effective option.

Measure	Description	Considerations	Other Comments
	which PCDD/PCDF easily adsorb. Removal of these dusts would contribute to the reduction of PCDD/PCDF emissions.	wet/dry scrubbers and ceramic filters.	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 furnace for complete combustion. - Need for proper design of cooling systems to minimise reformation time.	- De novo synthesis is still possible as the gases are cooled through the reformation window.
Adsorption on Activated Carbon	Activated carbon treatment should be considered as this material is an ideal medium for adsorption of PCDD/PCDF due to its large surface area.	Processes to be considered include: - 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/PCDF from secondary lead smelters are identified as follows:

Table 7.1 Performance Standards for Secondary Lead Smelters

Type	Suggested Timeline	Emission Limit ¹⁶
New	Entry into force	<0.1 ng/Rm ³ TEQ
Existing	Within 10 years of entry into force	<0.1 ng/Rm ³ TEQ

¹⁶ Rm³ indicates a reference volume at 298 K (25°C), 101.3 kPa (1 atmosphere), dry gas basis and operating O₂ levels.