Section V.D.3.

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

Secondary aluminium production

Coordinated by Mr. Patrick Finlay (Canada)

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

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1.0 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 pre-treatment and smelting/refining. Pre-treatment methods include mechanical, pyro- and hydrometallurgical cleaning. Smelting is conducted using reverberatory or rotary furnaces.

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

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

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

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

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

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

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

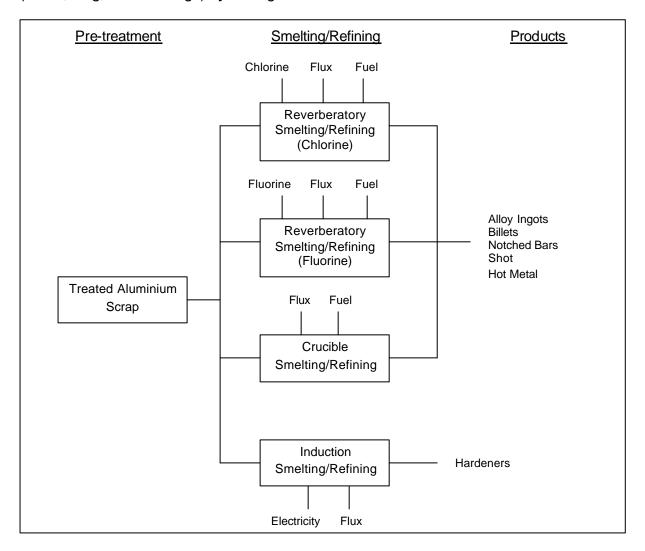


Figure 1 Secondary Aluminium Smelting³

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

³ İbid.

2.0 Sources of Unintentionally Produced POPs

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

2.1 General Information on Emissions from Secondary Aluminium Smelters ⁴

Potential emissions to air include dust, metal compounds, chlorides, nitrogen oxides (NO_x) , sulphur dioxide (SO_2) and organic compounds such as PCDD/PCDF and carbon monoxide (CO). Ammonia can also be generated from the improper storage, treatment and transport of skimmings. Chlorine compounds can be removed using wet/dry scrubbers and their formation minimised by good control and the use of mixtures of chlorine and inert gases. Low NO_x burners and low sulphur fuels can be used to decrease emissions of NO_x and SO₂.

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

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 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

⁴ European Commission, Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries, December 2001, p.294-300.

of cooling systems to minimise the residence time in the window is practised to prevent de-novo synthesis."5

"Poor combustion of fuel or the organic content of the feed material can result in the emission of organic materials. The provision of effective burner and furnace to controls is used to optimise combustion. Peak combustion rates from included organic materials needs to be taken into account if they are fed to the furnace. It is reported that precleaning 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."⁶

2.3 Releases to Other Media⁷

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

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

3.0 Recommended Processes

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

⁵ European Commission, Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries, December 2001, p. 133.

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

¹ European Commission, Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries, December 2001, p.294-300.

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

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

Scrap material should be cleaned of oils, paints and plastics during pre-treatment. The removal of organic and chlorine compounds will reduce the potential for PCDD/PCDF formation. Methods used include the swarf centrifuge, swarf drying or other thermal de-coating techniques. Thermal de-coating and de-oiling processes for oil removal should be followed by afterburning to destroy any organic material in the off-gas.⁸

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.⁹

2. Effective Process Control

Process control systems should be utilized to maintain process stability and operate at parameter levels that will contribute to the minimization of PCDD/PCDF generation, such as maintaining furnace temperature above 850 °C to destroy PCDD/PCDF. Ideally, PCDD/DF emissions would be monitored continuously to ensure reduced releases. Continuous emissions sampling of PCDD/PCDF has been

⁸ European Commission, Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries, December 2001, p.310. ⁹ European Commission, Integrated Pollution Prevention and Control Reference Document on Best

Available Techniques in the Non Ferrous Metals Industries, December 2001, p.294-300.

demonstrated for some sectors (e.g. waste incineration), but research is still developing in this field. In the absence of continuous PCDD/PCDF monitoring, other variables such as temperature, residence time, gas components and fume collection damper controls should be continuously monitored and maintained to establish optimum operating conditions for the reduction of PCDD/PCDF.

4.2 Secondary Measures

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

1. Fume and Gas Collection¹⁰:

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

2. High Efficiency Dust Removal

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

Scrubbing off-gases with sodium bicarbonate will remove chlorides produced by the salt flux, resulting in sodium chloride, which can then be removed by fabric filters to be recharged to the furnace. In addition, use of a catalytic coating on fabric filter bags could destroy PCDD/PCDF by oxidation while collecting particulate matter on which these contaminants have adsorbed.¹¹

3. Afterburners and quenching:

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

¹¹ European Commission, Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries, December 2001, p.294-300.

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 guenching of hot gases to temperatures below 250°C. Oxygen injection in the upper portion of the furnace will promote complete combustion. 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 as this material is an ideal medium on which PCDD/PCDF can adsorb due to its large surface area. Off-gas treatment techniques include using fixed or moving bed reactors or injection of carbon into the gas stream followed by high efficiency dust removal systems such as fabric filters. Lime/carbon mixtures can also be used.

5.0 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 between 370 to 450°C, whereas incineration occurs typically at 980°C. Catalytic oxidation has been shown to destroy PCDD/PCDF with shorter residence times, lower energy consumption and 99% efficiency, and should be considered. Off-gases should be de-dusted prior to catalytic oxidation for optimum efficiency. This method is effective for the vapour phase of contaminants. The resulting hydrochloric acid is treated in a scrubber while the water and CO₂ are released to the air after cooling.¹⁵

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. ¹⁵ Parvesse, T., Chemical Processing, Controlling Emissions from Halogenated Solvents, April 2001.

URL: www.chemicalprocessing.com/Web_First/cp.nsf/ArticleID/NJEC-4VPKAW/

6.0 Summary of Measures

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

Table 6.1 Measures for Recommended Processes

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

Measure	Description	Considerations	Other Comments	
Primary Measures	Primary Measures			
Pre-sorting of feed material	The presence of oils, plastics and chlorine compounds in the feed material should be avoided to reduce the generation of PCDD/PCDF during incomplete combustion or by de-novo synthesis.	Processes to be considered include: - Prevention or minimisation of the use of chloride salts where possible. - Cleaning scrap material of oils, paints and plastics during pre-treatment. - 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 de-coating and de- oiling processes for oil removal should be followed by afterburning to destroy any organic material in the off-gas	
Effective process control	Process control systems should be utilized to maintain process stability and operate at parameter levels that will contribute to the minimization of PCDD/PCDF generation.	PCDD/PCDF emissions may be minimized by controlling other variables such as temperature, residence time, gas components and fume collection damper controls after having established optimum operating conditions for the reduction of PCDD/PCDF.	Continuous emissions sampling of PCDD/PCDF has been demonstrated for some sectors (e.g. waste incineration), but research is still developing in this field.	
Secondary Measu	Ires			
Fume and Gas Collection	Effective fume and off-gas collection should be implemented	Processes to be considered include:	Where primary extraction and enclosure of fumes is not	

Measure	Description	Considerations	Other Comments
High Efficiency Dust Removal	in the capture of air emissions from all stages of the process. 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.	 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. Processes to be considered include: 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 	practicable, the furnace should be enclosed so that ventilation air can be extracted, treated and discharged. 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: - 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 on which PCDD/PCDF can adsorb due to its large surface area.	Processes to be considered include: - Treatment with activated carbon using fixed or moving bed reactors - injection of carbon into the gas stream followed by high efficiency de-dusting	Lime/carbon mixtures can also be used.

Measure	Description	Considerations	Other Comments
		methods such as	
		fabric filters.	
Emerging Resear	rch		•
Catalytic	Catalytic oxidation is an emerging	Considerations	Has been shown to destroy
Oxidation	technology which 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.	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	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 aluminium smelters are identified as follows:

	Table 7.1	Performance Standards for Secondar	y Aluminium Smelters
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Туре	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.