

Section V.D.1.

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

Secondary copper production

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

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1.0 Process Description

Secondary copper smelting is comprised of pyro-metallurgical processes dependant 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 de-coating methods or by correct design of the furnace and abatement system.¹ Copper can be infinitely recycled without loss of its intrinsic properties.

“Secondary copper recovery is divided into 4 separate operations: scrap pre-treatment, smelting, alloying, and casting. Pre-treatment 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 pre-treatment may be achieved through manual, mechanical, pyrometallurgical, or hydrometallurgical methods. Manual and mechanical methods include sorting, stripping, shredding, and magnetic separation. Pyrometallurgical pre-treatment 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 pre-treatment 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.

¹ European Commission, *Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p. 201-202.

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.²

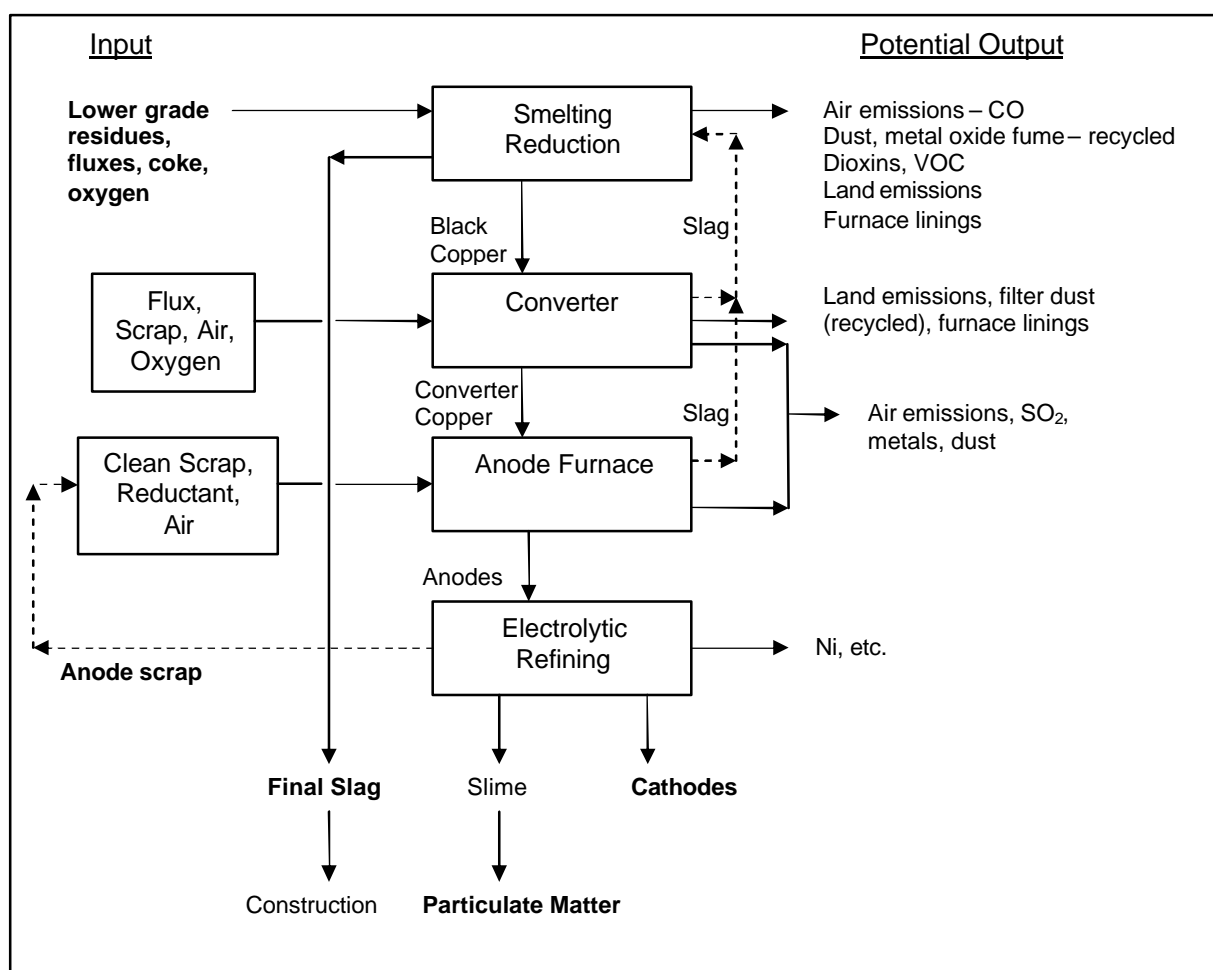


Figure 1 Secondary Copper Smelting³

² US Environmental Protection Agency, *Background Report AP-42 Section 12.9, Secondary Copper Smelting, Refining and Alloying*, January 1995. URL: www.epa.gov/ttn/chief/ap42/ch12/final/c12s09.pdf

³ European Commission, *Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p. 217.

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. As copper is the most efficient metal to catalyse PCDD/PCDF formation, copper smelting is a concern.

2.1 General Information on Emissions from Secondary Copper Smelters⁴

Airborne emissions consist of nitrogen oxides (NO_x), carbon monoxide (CO), dust and metal compounds, organic carbon compounds and PCDD/Fs. 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 is removed from collected and cooled combustion gases by electrostatic precipitators (ESPs) 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 minimised in low NO_x burners, while CO is burnt in hydrocarbon afterburners. Burner control systems are monitored to minimize CO generation during smelting.

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.

“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

⁴ European Commission, *Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p. 218-229.

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

2.3 Releases to Other Media

Process, surface and cooling water can be contaminated by suspended solids, metal compounds and oils. Most process and cooling water is recycled. Wastewater treatment methods are used before discharge. By-products and residues are 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.

3.0 Recommended Processes

Process design and configuration is influenced by the variation in feed material and quality control. Processes considered as BAT for smelting/reduction include the Blast Furnace, Mini-Smelter (totally enclosed), Sealed Submerged Electric Arc furnace, and ISA Smelt. The Top Blown Rotary Furnace (totally enclosed) and Peirce-Smith converter are BAT for converting. The submerged electric arc furnace is sealed and cleaner than other designs if the gas extraction system is adequately designed and sized.

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

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:

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

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. Feed material should be classified according to composition and possible contaminants. Storage, handling and pre-treatment techniques will be determined by feed size distribution and contamination.

Methods to be considered are: ⁶

- Oil removal from feed (e.g. thermal de-coating 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 (e.g. possible cryogenic techniques to make plastics friable and easily separable)
- Sufficient blending of material to provide a homogenous feed in order to promote steady-state conditions

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. These methods do not eliminate the generation of contaminants, but serve as means to contain and prevent emissions.

1. Fume and Gas Collection⁷:

Air emissions should be controlled at all stages of the process, from material handling, smelting and material transfer points, to control the emission of

⁶ European Commission, *Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p. 232.

⁷ European Commission, *Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p. 187-188.

PCDD/PCDF. Sealed furnaces are essential to contain fugitive emissions while permitting heat recovery and collecting off-gases for process recycling. Proper design of hooding and ductwork is essential to trap fumes. Furnace or reactor enclosures may be necessary. If primary extraction and enclosure of fumes is not possible, the furnace should be enclosed so that ventilation air can be extracted, treated and discharged. Roofline collection of fume should be avoided due to high energy requirements. The use of intelligent damper controls can improve fume capture and reduce fan sizes and hence costs. Sealed charging cars or skips used with a reverberatory furnace can significantly reduce fugitive emissions to air by containing emissions during charging.

2. High Efficiency Dust Removal:

The smelting process generates high volumes of particulate matter with large surface area on which PCDD/PCDF can adsorb. These dusts and metal compounds should be removed to reduce PCDD/PCDF emissions. Fabric filters are the most effective technique, while wet/dry scrubbers and ceramic filters are also to 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 developments include online cleaning methods and use of catalytic coatings to destroy PCDD/PCDF⁸.

3. Afterburners and quenching:

Afterburners (post-combustion) should be used at a minimum temperature of 950°C to ensure full combustion of organic compounds.⁹ 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.¹⁰

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.¹¹

4. Adsorption on Activated Carbon:

⁸ European Commission, *Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p.139-140.

⁹ Hübner C., et. al., *State-Of-The-Art Measures For Dioxin Reduction In Austria*, 2000. URL: www.ubavie.gv.at/publikationen/Mono/M116s.htm

¹⁰ European Commission, *Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p. 189.

¹¹ European Commission, *Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001, p. 133.

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 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.

5.0 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.¹²

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

6.0 Summary of Measures

Table 6.1 Measures for Recommended Processes

Measure	Description	Considerations	Other comments
<i>New Secondary Copper Smelters</i>			
Recommended Processes	Various recommended smelting processes should be considered for new facilities.	Processes to be considered include: - The blast Furnace, mini-smelter, Top Blown Rotary Furnace, Sealed Submerged Electric Arc furnace, ISA Smelt, and the Peirce-Smith	These are considered to be BAT in configuration with suitable gas collection and abatement The submerged electric arc furnace is sealed and cleaner than other designs if the gas extraction system is adequately designed and sized.

¹² Parvesse, T., Chemical Processing, *Controlling Emissions from Halogenated Solvents*, April 2001. URL: www.chemicalprocessing.com/Web_First/cp.nsf/ArticleID/NJEC-4VPAKAW/

Measure	Description	Considerations	Other comments
		converter. - The reverberatory hearth furnace, the hearth shaft furnace and Contimelt process to treat clean copper scrap devoid of organic contamination.	

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

Measure	Description	Considerations	Other Comments
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: - 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 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 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: - Sealed furnaces to contain fugitive emissions while permitting heat recovery and collecting off-gases. Furnace or reactor	Roofline collection of fume is to be avoided due to high energy requirements.

Measure	Description	Considerations	Other Comments
		enclosures may be necessary - Proper design of hooding and ductwork to trap fumes.	
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: - 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 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 possesses large surface area on which PCDD/PCDF can be adsorbed from smelter off-gases.	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 dedusted prior to catalytic oxidation for optimum efficiency.

7.0 Achievable Levels

Achievable levels for emissions of PCDD/PCDF from secondary copper smelters are identified as follows:

Table 7.1 Achievable Levels for Secondary Copper Smelters

Type	Suggested Timeline	Emission Limit ¹³
New	Entry into force	<0.1 ng /Rm ³ TEQ
Existing	Within 10 years of entry into force	<0.1 ng /Rm ³ TEQ

¹³ Rm³ indicates a reference volume at 298 K (25°C), 101.3 kPa (1 atmosphere), dry gas basis and operating O₂ levels.