



POLLUTANT EMISSIONS, CONTROL AND PREVENTION IN THE SECONDARY COPPER INDUSTRY

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ABSTRACT

This paper presents an analysis of pollutant emissions specific to copper waste valorization. There are made appreciations of the role and importance which have the characteristics of mixed charge with waste having a variable content of copper (copper and copper alloy waste, residues, sludges, slimes, dusts etc.) having impurities or contaminants (especially organic pollutants) as well as fluxes and fondants (NaCl, KCl etc) used as first important source of pollutant emissions for secondary copper metallurgy.

KEYWORDS: secondary copper metallurgy, pollutant emissions

1. Introduction

The diversity of aspects and factors involved in secondary copper obtaining processes make the pollutant emissions have big variations from qualitative and quantitative point of view.

In the secondary copper metallurgy are used the flow sheets with multiple configurations of processes; it is possible to use a big variety of smelting aggregate types with possibility to operate in different mode, with different capabilities to monitor and control the pollutant emissions.

At the same time, the input materials are proceeded from different sources, so they have different characteristics and are prepared by different methods, before introduction in the processing steps.

2. Emissions at the secondary copper obtaining

At the secondary copper metallurgy, emissions which contain microelements reported to the total amount evacuated in the atmosphere, to the global level, at the beginning of 1980 for Europe, were appreciated as non significant: less then 1% from the total emissions of copper, arsenic, selenium, and zinc [1-3]. At the local level, the secondary copper smelting or copper refining process can be considered important source of contamination with microelements. According to CORINAIR90 Report (made for 28 countries), the rate of participation of emissions generated by secondary copper production to the total emissions, microelements, respectively emissions generated at the fuel burning, specific to the secondary copper production sectors from this countries, are presented in tables 1, 2 and 3 [4].

Table 1. Emissions generated from secondary copper production to the total emissions according to the CORINAIR90 Report

Source	Cod SNAP	Contribution to the total emissions, %							
		SO ₂	NO _x	NMVOC	CH ₄	CO	CO ₂	N ₂ O	NH ₃
Secondary copper production	030309	●	-	●	-	●	-	-	-

- emissions are reported by the countries in the limit of 0,1%, but without the exact value;
- emissions are not reported.



Table 2. Element emissions in the secondary copper metallurgy, g/t copper made

Element	Estimate Pacyma (1986)	Estimate in Canada (Jacques 1987)	Program PARCOM (1992)	Estimate in England (Leech 1993)	Estimate in Austria (Schneider 1994)	Interval or resulted values
As					2	2
Sb	3					3
Cd	4		5	5	2	2-4
Cu	150	200-400				
Pb	50-200	230	130	130	50	50-130
Ni		1				1
Zn	500-1600		500	500	250	250-500

Table 3. Emissions of gaseous compounds in the secondary copper metallurgy, on the different type of fuel [CORINAIR90]¹⁾

Fuel type	Cod	Emission factors						
		SO ₂ ²⁾	NO _x ³⁾	NMCOV ⁴⁾	CH ₄	CO	N ₂ O	CO ₂ , kg/GJ
		g/GJ						
Liquid	203	495-1.470 ¹⁾	150 ¹⁾	30 ¹⁾	30 ¹⁾	15 ¹⁾	2 ²⁾	76-78 ¹⁾
Liquid	204	94-1.410 ¹⁾	100 ¹⁾	1,5 ¹⁾	1.5 ¹⁾	12 ¹⁾	2 ¹⁾	73-74 ¹⁾
Natural gas	301	0.8 ¹⁾	100 ¹⁾	4 ¹⁾	4 ¹⁾	13 ¹⁾	1 ¹⁾	57 ¹⁾ , 60 ⁵⁾ , 59 ⁶⁾
Liquid gas	303	0.04 ¹⁾	100 ¹⁾	2.1 ¹⁾	0,9 ¹⁾	13 ¹⁾	1 ¹⁾	65 ¹⁾

¹⁾ The adnotation under the table can make references at the emission factors which include the burning fuels and other processes from secondary copper metallurgy

²⁾ SO_x: (EPA, 1990)

750g/t charge – dry waste (rotary furnace)

6400g/t charge – burning cable, incinerator

250g/t charge – crucible furnace, input brass and bronze wastes

15g/t charge – electric arc furnace, input brass and bronze wastes

15g/t charge - induction furnace, input brass and bronze wastes

2182g/t charge – refining process

17209 S g/m³ fuels – secondary copper production (fuel with sulfur content)

19006 S g/m³ fuels - secondary copper production (fuel with sulfur content)

³⁾ NO_x: (EPA, 1990)

6400g/t charge - burning cable, incinerator

40g/t charge – reverberation furnace, input brass and bronze wastes

300g/t charge - rotary furnace, input brass and bronze wastes

2397g/m³ fuel - secondary copper production

6591g/m³ fuel - secondary copper production

⁴⁾ COV (volatile organic compound): (EPA, 1990)

2g/t charge – dry waste (rotary furnace)

300g/t charge – burning cable, incinerator

300g/t charge - rotary furnace, input brass and bronze wastes

60g/t charge – furnace with selective smelting

223500g/t coke charge – cupola furnace, input copper wires waste or copper and brass wastes

90g/t charge – cupola furnace, input copper and brass waste or copper waste

2600g/t charge - reverberatory furnace, input copper or brass and bronze

1200g/t charge - rotary furnace, input brass and bronze wastes

3350g/t charge – crucible furnace, input brass and bronze waste

1950g/t charge – electrical arc furnace, input copper

0g/t charge – electrical arc furnace, input brass and bronze

0g/t charge – induction furnace, input copper or brass and bronze

24g/m³ fuel - secondary copper smelting

34g/m³ fuel - secondary copper smelting

44851g/Mm³ fuel - secondary copper smelting

⁵⁾ CO₂: input local contaminated waste, brass production (Bremmer 1995)

⁶⁾ CO₂: input highly contaminated waste, brass production (Bremmer 1995).

The analysis of presented data can appreciate that, in general, the secondary copper metallurgy



represents a minor source of pollutant emissions in comparison with primary copper metallurgy.

However recently, the thermal processes from secondary copper metallurgy, together with the specific processes of the primary copper metallurgy (and other thermal processes from metallurgical industry and sintering preparation of ores in steelmaking industry, aluminum and zinc production from non-ferrous metallurgy), has been defined as an important source of dioxins generation. UNEP (United Nations Environment Programme) convention respecting the persistence organic pollutants, adopted at Stockholm in May 2001, placed the thermal processes from copper industry in the second category of dioxin source (after the waste incineration placed in the first category 1, the most important generator of dioxins), table 4 [5].

3. Generating sources of pollutant emissions in the secondary copper industry

3.1. Raw materials

Raw materials used for copper smelting, the mixed charged compounds of wastes with variable contents of copper (copper waste, alloys with copper content, together with dross, slag, slime and dust, etc.) with an impurity and contaminate content (especially the organic pollutants), and salts used as flux (NaCl, KCl etc.) represent the main source for the pollutant emissions in the secondary copper metallurgy.

Therefore, the chemical composition of the input materials is considered the determinant factor in the quantity and chemical composition of generated emissions at the secondary copper production.

Table 4. UNEP matrix for the dioxin sources placed in the second category and emissions factors for the modern technologies from the ferrous and non-ferrous metallurgy, $\mu\text{g I-TEQ/t product}$

Category. UNEP	Cod SNAP	Sector	Dioxins in:				
			Air	Water	Soil	Product	Waste
2a	30301/40209	Sinter plant	0.3				0.003
2b	-	Coke production	0.3	0.06	X	X	X
2c	40200/30303	Iron and steelmaking industry, Foundry	0.01-0.03				0.2-15
2d	30306/30309	Copper production	0.01				0-630
2e	40301/303010	Aluminium production	0.5-150 (wastes)				100-400
2f	30304/30307	Lead production	0.5				X
2g	30305/30308	Zinc production	0.3				X
2h	-	Brass production	0.1				
2i	40304/30323	Magnesium production	50	24			9000
2j	-	Other non-ferrous metals production	2	X			X
2l	-	Mechanical preparation by shredder	0.2				X
2m	-	Wires recuperation	3.3	(X)	X		X

The burning impurities present to the input metallic materials and the participation of the fluxes with chlorine content in different process steps can lead to dioxine formation. Undesired elements (sulfur, arsenic, lead, zinc, cadmium, mercury etc.) and their combination, presented in small quantities in waste used to obtain secondary copper (unlike the copper ores utilized to obtain primary copper), are emission generators. The zinc, characterized by a high vapor pressure and a big oxidation tendency (it forms a important quantities of zinc oxide particles with micrometric dimensions) is the most important

element which needs to be taken into consideration [6]. Without pre-treatment operations, the input materials with a cable waste content carry in furnaces and in other installations or process equipment, impurities like organic substances (from plastic materials, paints, solvents, oils), and lead compounds (from stabilizer present in old cable isolation). These impurities lead to the formation of pollutant substances with the other types of gaseous compounds or solid waste materials, corporate like waste and emissions resulted from secondary copper obtaining fluxes steps.

3.2. Processes and aggregates generating pollutant emissions

Starting with input materials preparation and finishing with the secondary copper or its alloy casting, results dust and volatile compounds distributed in effluents or solid waste from secondary

copper processes, with allocation in air, soil, water (fig.1).

Thermal processes, from the waste pre-treatment and from elaboration steps (smelting, refining and alloying) are responsible for generating the pollutant emissions.

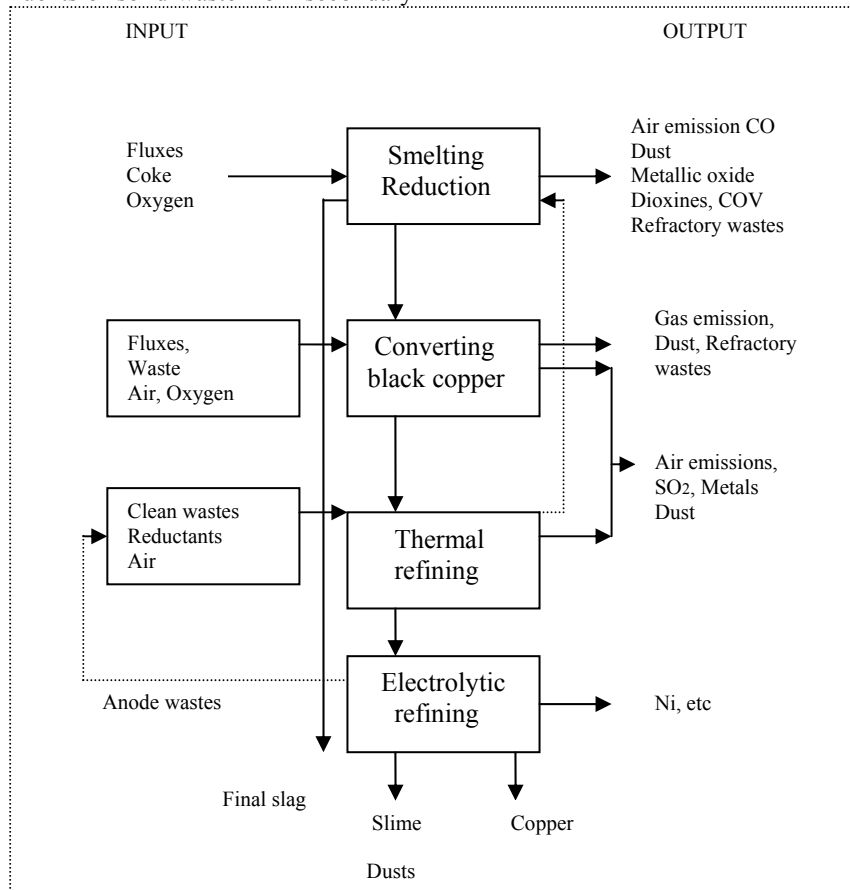


Fig.1. Emissions from different secondary copper metallurgy [7]

a. Raw materials preparation. In the preparation operations, thermal processes are utilized to remove the cables isolations, oil excess and other technological fluids from cuttings, turning, etc.

These processes are generating the volatile organic compounds and products from the incomplete burning and because of these off gas needs to have a cleaning treatment.

The gas post-combustion in the special rooms, at temperatures more than 1000°C, can determine purification efficiency bigger than 90%. The combustion is not sufficient if the isolations contain PVC, the chloride acid in gaseous stage is produced and because it cannot be controlled in the post-combustion stage, it is necessary its capture before the off gas evacuation. In this case, the cable waste preparation is recommended to remove the isolations by mechanical methods, even if the burning can be the most used method for its easiness.

For minimisation of pollutant emissions it is imposing a mechanical preparation of raw material (metallic materials) for compacting and bringing to the necessary dimensions to charge them in the furnaces by single step. In the case of insufficient compacted materials, charging the materials through on the surface of metallic bath, can produce important quantities of gases which can exceed the capacity of installations capture. In this situations we need to locate a supplementary gas capturing system to take the exceed gases from accidental production.

b. Processes and furnaces. From qualitative and quantitative point of view, the pollutant emissions are determined by the furnace type and the technologies applied. For pollutant emissions minimisation, it is recommended as the best technological solutions those in which the processes are made in aggregates which work in isolated or hermetic spaces with



possibility to install systems for collecting and capturing gases.

c. Copper and copper alloys casting. Gases and pulverous emissions are made during the casting operations time. Those results from the interaction of alloy with the forming materials, refractory paints etc. Important quantities of gases are made in the graphite dust burning used for casting metals interface protection.

4 Pollutant emissions, measured and admissible levels

For secondary copper metallurgy, the most significant and important are air emissions. Emissions level can be found from measurements and results of different monitoring published in branch literature. For water emissions, this type of data isn't published, since these emissions are less important. This is due on the one hand to their reduced solubility of dioxins in water (these is an accumulation of dioxins in water sediments) and on the other hand, the lightness that the admissible pollutant substances concentrations may have in water by treatment before the evacuation in environment. The air emissions consist in nitrogen oxides (NO_x), carbon monoxide (CO), dust, organic compounds, dioxins (PCDD/PCDF). Normally, the evacuated gases don't have sulphur dioxide (SO₂), small quantities can be presented at utilisations of the same materials with sulphur content [7]. The most important are the solid particles. The powders are situated in the hazardous pollutants category (especially the PCDD/PCDF type) because these are harmful compounds deposited on the dust surface (by condensation and absorption) [8, 9]. For the secondary copper metallurgy, the typical emission factor for Europe is 50µg-TEQ/ton of copper refined (with variation between minimal and maximal limits, by 5 and 500µg-TEQ/ton). The reported emission factor by Germany for the shaft furnace or converter and reverberatory furnaces is variable 5.6 and 110µg-TEQ/ton and between 0.005 and 1.56µg-TEQ/ton. The reported emission factors for two furnace from Sweden (for charging was used clean wastes) was 0.024 and 0.04µg-TEQ/ton.

At the secondary copper production in Austria was reported an emission factor of 4µg-TEQ/ton. In

Portugal, at utilisation of a gas cleaning system (cyclone and filter bag, including a cooling step to prevent the novo-synthesis process of the dioxins) for electrical furnace utilised for zinc and copper, respectively for brass elaboration, the emission factors were variable between 0.09 and 0.4µg-TEQ/ton.

For Holland, with three companies for the brass (48kt/year) and copper with bronze (1kt/year) (gifted later with filtering systems), the undertake emission factors are 5µgI-TEQ/ton for brass elaboration from charges lightly polluted, respectively 35µgI-TEQ/ton for secondary copper and bronze elaboration from charges with more impurities [10]. For SUA, according to EPA Dioxin Inventory (US EPA, 2000) which takes into consideration the recent data related to the elaboration in shaft furnaces provided with burner for post-combustion of evacuated gases and dry cleaning systems, when was used the mixed charges from copper contaminated with plastic materials, the emission factor was 779µg-TEQ/t waste (810µg-WHO-TEQ/ton). The measurements made for other furnaces of the same type, used to obtain the blister copper and gifted with post-combustion systems, cooling towers and filter bags get the value of 16.618µg-TEQ/t waste or 16.917µg-WHO-TEQ/t (diminution, of the work condition). For the third company where were made measurements and which worked in oxidation conditions with charges from relatively clean wastes and rotary furnace with a primary cooling system and Venturi scrubber, was obtained an emission factor of 3.6µg-TEQ/t waste or 3.66µg-WHO-TEQ/t [11]. For cooper metallurgy the air and water emission levels, accepted by World Bank Group (related to the legislation of the most important countries copper producers and Pollution Prevention and Abatement Handbook, adapted to the local conditions of this producers), are presented in next tables 5 and 6 [12]. The most dangerous substances which need to taken into consideration to the secondary copper elaboration from wastes are dioxins (PCDD/PCDF), the identified pollutants in the big family known under the name of "dioxin" and classified as belonging to the dangerous substances category.

Table 5. Maximal admissible level of air emissions from copper production, mg/Nm³

Parameter	Maximal value
SO ₂	1000
Arsenic	0.5
Cadmium	0.05
Copper	1
Lead	0.2
Mercury	0.05
Powdery emissions from elaboration	20
Powdery emissions from other sources	50



Table 6. Maximal admissible level of effluents at the copper elaboration, mg/Nm³

Parameter	Maximal value *)
pH	6-9
Total of solid particles in suspension	50
Arsenic	0.1
Cadmium	0.1
Copper	0.5
Iron	3.5
Lead	0.1
Mercury (total)	0.01
Zinc	1.0
Total metals	10
Advance temperatures	≤3 ^o C **)

*) the value is referred to the direct discharge to the surface water;

***) the effluent can determine the advance temperature but not with more than 3^oC in the initial blend zone. If this zone is not definite, than there can be considered 100 m from the discharge point.

The most important part of them is in air emissions, his presents in emissions from the gases current have at origins the chlorine of plastic materials from wire isolation or the remain of other organic contaminants presents at the surface of waste used at the secondary copper elaboration. The PCB existence in the wire insulations, included in the dangerous substance category (according to Council Directive 91/689/EEC regarding the dangerous wastes), creates supplementary problems for the treatment of cable waste by thermal methods.

The dioxins are chemical compounds very stable in generally at temperatures higher than 750^oC. PCDD/PCDF is formed in thermal processes when the organic compounds and chlorine are presented in wastes which compose the charging materials (because of the incomplete burning or as a result of novo-synthesis specific processes). The presence of precursors as well as PCB from some insulation accelerates the dioxins forming. The PCDD/PCDF are easily adsorbed and condensed on the bigger surface of the solid fine particle, being especially in suspension in gases and in a less quantity in other outlet processes (waste water, soil etc.).

The presences of organic materials and oils in waste or the presence of other carbon sources (incomplete fuel burning or reducer like coke) can do that the carbon fine particles go into reaction with chlorine compounds, and determine at temperatures less than 500^oC the forming of PCDD/PCDF. For dioxins generations are necessary the combustion conditions, but are also important the cooling conditions of gases formed in the capture installations. With the oxygen presence, the optimal interval of temperatures for dioxins formations is 250–500^oC.

The specific synthesis processes are accelerated by the presence of same metals like copper or iron which have a catalyst role. Because of this the thermal processes from the copper obtaining play an

important role in the dioxin formation, copper being the most efficient catalyst of the forming process for PCDD/PCDF.

5. Measurements for prevention and control of processes generating of pollutant emissions

- *charges preparation* need to have a pre-sorting of the wastes used in the charges, in correlation between dimensions and contamination degree in that way to easily eliminate the insulations, followed by the gases post-combustion to destroying any organic compound. Is necessary to use mechanical preparation techniques for charging materials treatment with possibility of collecting and capturing the generated dust. The resulted particles can be treated for metallical fractions recuperation by gravimetric and pneumatic separation methods. The modern methods are necessary in order to remove the cable insulations (for example by cryogenic treatment, when these are crumbly and can be easily separated). It is also necessary to adequately mix the materials in order to realize homogenous charges, capable to ensure the processes deployment in constant parameters, easily controllable.

- *effective control of process* which need to develop in constant and stable parameters, at certain values, can lead to minimisation of the PCDD/PCDF generated quantities. It is ideal to have the continuous monitoring of PCDD/PCDF emissions level. If this is not possible, the other variables like temperatures and gases compositions, maintaining–stationary time, smoke parameters at the basket register, need to have a continuous monitoring and to be maintained at the optimal values in order to have a minimal PCDD/PCDF formation.

Other measures, which do not eliminated the pollutant substance generation, but can offer prevention tools are:



- *smoke and gas collection* by furnace isolation or work space (the manipulation and transport installations) and correct selection of the cleaning systems to eliminate the non-controlled emissions.

- *separation with maximal efficiency of dust them the gases collected.* The elaboration processes generate important quantities of pulverous particles with small adsorption surface for PCDD/PCDF. By reducing the quantities of dust and metallic compounds the PCDD/PCDF emissions are indirectly reduced.

The particles can be collected in the filtering and dust collection systems which need to be chosen in function of physical and chemical characteristics. The maximal retention efficiency of the pulverous materials from gases is given by the filter with texture. For copper or copper alloys making process, the filters with texture (so called filter with bags or dust bags) are considered the most efficient cleaning gas treatment in the secondary copper metallurgy. The electrostatic precipitator is not recommended because it has diminished efficiency and oxides, lead or zinc dense particles retention. The installations with scrubbers are inefficient because they are recommended for particles with dimensions bigger than 1 μ m and solid particles presented in gases from copper elaboration having submicrometer dimensions. For emissions generated in dry processes (which take place at temperatures more than 150 $^{\circ}$ C) these can be used filter bags situated after electro-filter.

Separately, the collected dust can be treated at bigger temperatures for absorbed PCDD/PCDF destruction. The modern capture equipments have included "on-line" systems for purification and use the catalytic principles for PCDD/PCDF destruction.

- *post-combustion and rapid cooling.* Because the PCDD/PCDF dioxins are formed in the 250–500 $^{\circ}$ C temperatures interval and are destroyed up to 850 $^{\circ}$ C in oxygen presence, to reduce the dioxin content, gases are conducted into a supplementary burning (post-combustion) chamber, where PCDD/PCDF are destroyed at temperatures up than 950 $^{\circ}$ C. To prevent the dioxin formation process after the combustion chamber, gases are rapidly cooled into "reforming windows". This processing loop can be placed on the evacuated gasses flow in the capture systems and in some cold places of furnace, such as the superior one in which takes place the feeding with charges and is necessary to oxygen injection. In the same time, to limit this phenomena it is necessary to reduce to the minimum the stationary time of the gases in these windows. The active carbon can be utilized to remove the PCDD/PCDF from evacuated gases. For this treatment can be used reactors with fixed or mobile bed or can inject carbon particles in gases, after this

operation taking place the dust separation in filters and its treatment.

Recent researches in this domain to reduce and eliminate emissions of PCDD/PCDF are concentrated on the catalytic oxidation. In looking to oxidation process course of components from evacuated gases until H₂O, CO₂ and HCl, in the temperature interval of 370–450 $^{\circ}$ C (comparative with typical temperatures necessary to destroy the PCDD/PCDF which need to be more than 950 $^{\circ}$ C) by utilisations of some metals as catalyst. Catalytic oxidation need to take place in a short time, with small energetic consumption and maximal efficiency (over 99%). A big efficiency can be obtained if the evacuated gases are before dust separated. This method can be applied for contaminants which are in vaporous stage.

The level of PCDD/PCDF emissions at the secondary copper elaboration, obtained by application of the enumerated methods is <0.1ng/Rm³ TEQ (in standard conditions at 298K and 101.3kPa for dry gas) or for air 0.01 μ g I-TEQ/t product and for waste in 0 - 630 μ gI-TEQ/t copper interval, for copper production [7, 11]. The given factor by UNEP for non-modern sectors of secondary copper elaboration is 800 μ gI-TEQ/t copper product, to the non-controlled burning of cable waste is 5.000 μ gI-TEQ/t waste [11].

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