

DIOXIN EMISSION FROM SECONDARY COPPER SMELTER

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Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are present on the Earth since its beginning. They belong to the group of so-called *endocrine disruptors*, i.e. substances which interfere with functions of the endocrine system. Since the 70s of the last century PCDD/Fs have been considered as one of the strongest poisons among the known chemical compounds. However, despite very high toxicity of some dioxins and furans for certain animal organisms, they can hardly be compared to other strong poisons that occur in the environment, because they do not act immediately in concentrations which are encountered in everyday life. According to toxicological data they cannot be considered as acutely toxic for humans¹⁻⁴. The noxious impact of PCDD/Fs includes first of all disruption of endocrine functions of the organism, leading to fertility disorders, pregnancy maintenance problems or even to infertility (the chemical structure of dioxins is similar to that of steroid hormones which include also sex hormones). This refers primarily to disturbances in the secretion of progesterone, a hormone necessary to maintain and develop pregnancy⁵⁻⁷. The information on carcinogenicity of dioxins has not been confirmed^{8,9}. However, the harmful interactions of dioxins and furans on human organism must not be underestimated, so all actions which aim at a reduction of their emission to the environment are fully justified.

In the light of the known publications it can be considered that a source of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans are all high-temperature processes (above 200°C) which involve chlorine molecules, oxygen and organic matter¹⁰. From the point of view of total emission to the atmosphere, thermal sources are most important.

On 23 May 2001 the Stockholm Convention on Persistent Organic Pollutants was signed. It was a response to the necessity of regulations of the problems related to production and handling of some organic substances, the so-called persistent organic pollutants (POPs). The Convention introduced significant limitations on the POPs production, use, export and import, and strict requirements for recording and monitoring. The most important resolutions of the Stockholm Convention cover, among others, the obligation of a continuous minimization or total elimination of the emissions of dioxins and furans (PCDD/Fs), hexachlorobenzene (HCB) and polychlorinated biphenyls (PCBs) to the environment.

Dioxin emissions in individual European countries have been monitored systematically since the 90s of the last century by the Secretariat of Long-Range Transboundary Air Pollution Convention within the European Monitoring and Evaluation Programme (EMEP) affiliated at the Norwegian Meteorological Institute in Oslo. In view of results of the European Inventory of Dioxin Emission¹¹, less than 50% of the emission comes from industrial sources, in which combustion (including waste incineration) and metallurgical processes prevail.

The rate of dioxin emissions from metallurgical processes has been widely described in literature¹². First researches in this field started at the turn of the 80s and 90s of the last century. Majority of the researches refer to the emission of dioxins from the sintering process (in agglomerating plants). Recently, formation of dioxins in this process and their emission was a subject of intensive studies. The concentrations of dioxins in dusty gases from the sintering process range usually from several to dozens ng TEQ/m³, although there are cases in which 150 ng TEQ/m³, or even 250 ng TEQ/m³ is obtained. Steel mills are also the source of dioxin emission, although concentrations in flue gases are usually lower than in agglomerating plants and they do not exceed several ng TEQ/m³. Emission from electric arc furnaces has also been a subject of investigation in the last years. Concentrations in the flue gases are usually in the range from 0.1 to 15 TEQ/m³. In non-ferrous metals industry the most serious problem is zinc making, and the Waelz process in particular. The determined dioxin

concentrations in flue gases from the Waelz process can reach even 1200 ng TEQ/m³. Aluminum production is also a source of dioxin emission. According to available data, dioxin concentrations in flue gases can range from 0.01 to 45 ng TEQ/m³. Other metallurgical processes such as these in copper, nickel, lead and cobalt metallurgy, as well as processing of scrap metal, e.g. cables, and magnesium are also dioxin emission sources^{12,13}.

Metallurgy is now one of the biggest sources of dioxin emissions in industry. Studies on the rate of emissions from both iron and non-ferrous metals metallurgy, and also on pyrometallurgical processes have been continued and results of investigations on emission rates, dioxin formation mechanisms and methods of emission reduction are published systematically. In Poland, first studies of dioxin emissions from metallurgical processes were carried out lately by Grochowalski¹⁴. In general, dioxin concentrations which he determined are relatively low and stay within the lower limit quoted in literature. These results were used to develop a strategy for the reduction of dioxin emissions from this industrial branch in Poland contained in the National Program for Implementation of the Stockholm Convention^{15,16}.

Materials and methods

It is known that PCDD/Fs are produced during thermal processes which include secondary copper smelting. It follows from literature data that the quantity of dioxins formed in such processes increases with the content of copper in the cast material¹⁷ and that the main mechanism of dioxin formation is a de novo synthesis¹⁸.

PCDD/Fs emissions from secondary scrap copper smelting were investigated in a plant in which this process was carried out in a converter. Cast alloys are mainly bronze, zinc alloys and brass. The smelting process proceeds in the following way. At the first stage, scrap copper and other substances are loaded into a converter heated to the temperature ca. 1250°C. The converter is equipped with a tuyere fed with natural gas to smelt the metal. Air supplied through the tuyere is blown also through the crude metal. As a result of this process, phosphorus is oxidized and in the form of oxides is accumulated on the crude metal surface as slag. This part of the process takes around 2 hours. After this time the converter is tilted and the slag is poured off. To determine elemental composition, samples of the produced alloy are taken and analyzed in a laboratory. Results of the analyses determine the amount and composition of the second load for the next stage of the process. The load composition and quantity is so determined as to obtain a desired alloy composition. The second stage of the process begins when second part of the load is added. The converter returns to its original position and the second stage of smelting starts. In this stage of the process another tuyere is used to remove formed contaminants. This stage takes about 2.5 hours. Smelting ends with pouring off the produced alloy first to a ladle and then to final moulds. Casting takes around 1 hour. After this time the converter is loaded with a next load and the smelting process starts from the beginning. Eventually, during the process about 5 Mg of smelted metal is obtained. The entire production cycle takes around 7-8 hours, in which the smelting itself lasts for about 5 hours. Gases leaving the converter are cooled down in the flue (cooled walls) and filtered through a cloth filter. After dust removal, the gases are emitted to the atmosphere.

Dioxin emissions were measured in the point on the flue before the cloth filter where gas temperature was ca. 50-70°C. Samples were taken according to the EN-1948-1 standard. Next, the samples were prepared for analysis according to EN-1948-2 and PCDD/Fs concentrations were determined according to EN-1948-3.

Results and discussion

Results of PCDD/Fs determinations in flue gases from secondary copper smelting are given in Table 1. Measurements of samples no. 5 and 6 and also 7 and 8 were made during one smelting cycle. Other results were obtained in subsequent production cycles in two series. In the first series measurements 1-4 were made, while the remaining measurements were taken in the second series.

While analyzing the obtained results, a significant diversity of PCDD/Fs concentrations can be easily observed. They range from 0.0389 ng TEQ/m³ to even 8.0716 ng TEQ/m³. A comparison of these results with the ones published in literature leads to a conclusion that they do not diverge much from the results obtained by other researchers. For instance, Yu¹⁹ obtained PCDD/Fs concentration in gases from a secondary copper smelter in South Korea ranging from 0.007 to 32.401 ng TEQ/m³ (at average ca. 4.23 ng TEQ/m³). For a similar smelter in Taiwan, Hung²⁰ obtained 1.0-27.3 ng TEQ/m³. Eduljee²¹ obtained slightly lower values – 0.1-2.2 ng TEQ/m³, Ba²² – 0.3 to 2.84 ng TEQ/m³ and Wang²³ – 0.31 ng TEQ/m³. Based on the analysis of samples no. 5 and 6 as well as 7 and 8 it can be observed that the PCDD/Fs emission is higher in the first stage of the process (in the first 2 hours) than in the second one (after the second loading of material) during subsequent 2 hours of the

process. The flow rates of flue gases also differ – they are higher in the first stage than in the second one. The case is opposite with flue gas temperature which is higher in the second stage of the process. The profiles of PCDD/Fs congeners obtained in each sample were analyzed (cf. Fig. 1). It was found that the profiles were similar in all samples and that these with 7 and 8 atoms of chlorine prevailed, which confirmed that they were products of the de novo synthesis.

Table 1. PCDD/Fs concentration in flue gas from a secondary copper smelter

No.	Flue gas flow [m ³ /h]	Temperature [K]	PCDD/Fs concentration [ng TEQ/m ³ *]
1	24 000	340	0.2952
2	26 000	340	1.5437
3	22 000	329	0.5502
4	29 000	329	4.9978
5	25 000	325	0.4695
6	20 000	335	0.0389
7	26 000	329	8.0716
8	19 000	344	1.7659
9	28 000	332	0.2428

* in terms of normal conditions (273 K, 1013 hPa)

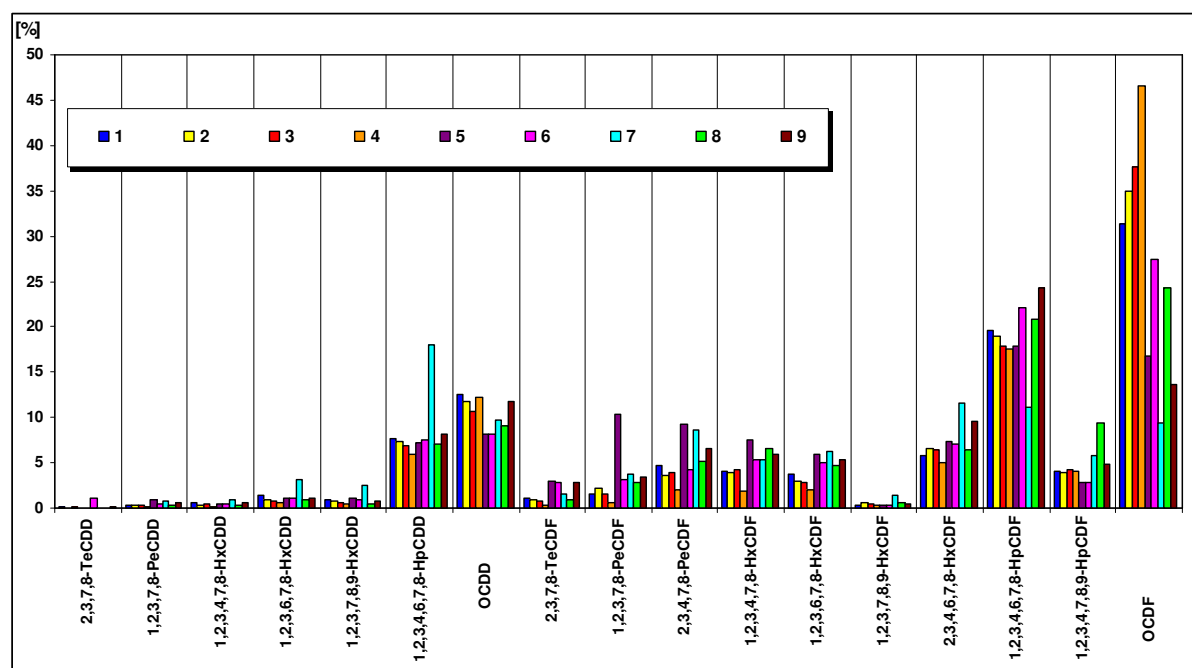


Fig. 1. Profiles of PCDD/Fs congeners in the samples obtained

An important conclusion from the investigations is that the process is characterized by high variability both in reference to the load used and technological parameters which, combined with its periodicity, causes that results of the determination of PCDD/Fs concentrations in emissions from subsequent production lots are not repeatable.

Acknowledgements

This work was prepared within grant No. N N523 417935 sponsored by the Polish Ministry of Science and Higher Education.

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