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DIOXINS AND FURANS IN IRON AND STEEL INDUSTRY

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ABSTRACT:
The paper presents polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) formation in steelworks plant. Based on the results of tests, basic sources of dioxins have been determined in the iron ore sintering process in one of the Polish integrated steel plants. The work is presents Persistent Organic Pollutants (POPs) in the iron and steel industry. Most POPs emission is generated in sinter plants. Adaptation to the European Union emission standards is the main challenge for steel producers. In the nearest future investigations of POPs emission in Polish steelworks will be necessity.

KEYWORDS:
polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), iron ore sintering process.

1. INTRODUCTION

The main industrial sources of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans emissions are: municipal waste incineration, iron ore sintering, industrial as well as hospital waste incineration. The iron and steel industry, among others, generates various kinds of wastes: gaseous, dusts, wastes and sewage. Steel companies constitute a considerable source of PCDDs and PCDFs. The sintering process is the largest source of dioxins and furans in the iron and steel industry. Strong toxic, carcinogenic and mutagenic properties of dioxins brought about implementation of a very strict permissible emission level these compounds in the European Union countries.

2. REQUIREMENTS OF THE STOCKHOLM CONVENTION

Poland is the signatory to the Stockholm Convention. Ratification processes for this are in progress. From May 1st, 2004, Poland is also a European Union Member State. On November 16th, 2004 the Stockholm Convention was approved by the European Union. Hence, the provisions of the national environmental protection law are generally consistent with the EU requirements. The process of adjustment of the Polish law to the provisions of the Union is taking place since several years.

The Stockholm Convention refers in principle to 12 persistent organic pollutants (POPs): aldrin, chlordane, dieldrin, endrin, heptachlor, hexachlorobenzene, mirex, toxaphene, PCBs, DDT, PCDDs and PCDFs. The general objective of the Convention, which took effect on May 17th, 2004, is the prevention of negative impacts of POPs on the environment and the human health as result of co-ordinated efforts made on the global scale aimed at neutralisation of POPs residues from their common use in the past [13].

According the Stockholm Convention polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), hexachlorobenzene (HCB) and polychlorinated

biphenyls (PCBs) are unintentionally formed and released from thermal processes involving organic matter and chlorine as a result of incomplete combustion or chemical reactions.

The following industrial source categories have the potential for comparatively high formation and release of these chemicals to the environment [9]: waste incinerators, cement kilns firing hazardous waste, production of pulp using elemental chlorine or chemicals generating elemental chlorine for bleaching and thermal processes in the metallurgical industry (secondary copper production; sinter plants in the iron and steel industry; secondary aluminium production and secondary zinc production).

3. PROPERTIES OF PCDDs AND PCDFs

Dioxins and furans are an abbreviation for polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). PCDDs and PCDFs are persistent and lipophilic compounds which bioaccumulate and concentrate in natural organisms and in humans. Dioxins are not manufactured as commercial products or ingredients, but occur as unintended by-products of incomplete combustion and certain chemical processes.

Many of the primary sources of dioxins in the environment remain unknown. Due to their persistence and toxicity, it is important to obtain a good understanding of their sources.

PCDDs and PCDFs are tricyclic, aromatic compounds formed by two benzene rings connected by two oxygen atoms in polychlorinated dibenzo-p-dioxins and by one oxygen atom and one carbon-carbon bond in polychlorinated dibenzofurans and the hydrogen atoms of which may be replaced by up to eight chlorine atoms. PCDDs consist of 75 congeners and PCDFs of 135 congeners. Congeners mean organic compounds groups, which have the same core but different quantity and place of substituents. Some congeners such as 2,3,7,8-tetrachlorodibenzodioxin (2,3,7,8- TCDD) are known to be among the most toxic compounds with potential carcinogenic and mutagenic effects [7,10].

4. PCDDs AND PCDFs SOURCES IN IRON AND STEEL INDUSTRY

Persistent Organic Pollutants (POPs) are hazardous chemical substances that persist in the environment, bioaccumulate through the food web, and pose a risk of causing adverse effects to human health and the environment. POPs emission in Polish iron and steel industry are shown in Table 1.

Table 1. POPs emission in Polish iron and steel industry [6,8].

POPs	PCDDs/PCDFs ng I-TEQ/m^3	PCBs ng/m^3	HCB ng/m^3
Sinter plant	1,2714	2,935	12
Blast - furnace	0,0029	1,328	0,304
Converter steel plant	0,0177	5,311	1,941

The most of all POPs in metallurgical processes appear polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDDs/PCDFs) [5].

Four different processes performed in iron and steel industry are known as PCDDs/PCDFs sources: sintering of iron ore, iron production (blast furnace), steel production (basic oxygen furnace) and melting of iron and steel scraps [8].

The main sources of PCDDs/PCDFs are processes occurring on a sinter strand [3,4]. Iron ore sinter plants are the major source of these pollutants in the environment. Non-ferrous metal processes, are poorly characterized at present, but may represent a significant source, especially secondary smelting. Secondary smelting involves reclamation of metals from scrap, which may also contain organic waste materials [10].

5. DIOXINS AND FURANS IN IRON ORE SINTERING PROCESS

Based on the results of tests [3], basic sources of PCDDs/PCDFs have been determined in the iron ore sintering process in one of the Polish integrated steel plants.

Author of the study [3] has stated that organic compounds contained in the sinter mix (particularly in dust, sludge and scale) and the coke breeze, are main sources of dioxins and

furans, and the temperature of waste gases in which the largest volume of PCDDs/PCDFs is formed ranges from 200 to 500°C. Table 2 presents results of a comparative analysis of PCDDs/PCDFs content in waste gases in the Polish and other EU sinter plants.

Table 2. Content of PCDDs/PCDFs in the iron ore sintering process in different countries

Country	PCDDs/PCDFs ng I-TEQ/m³	Reference
Poland	1,05 – 1,27	[8]
Germany	0,02 – 0,56	[12]
Austria	0,20 – 0,50	[2]
Great Britain	0,60 – 1,60	[2]
Belgium	0,50 – 2,00	[1]

PCDDs/PCDFs emissions from Polish sinter plants are higher than in the case of other European Union sinter plants. Presence of chlorine and hydrocarbons (oil) favours formation of PCDDs/PCDFs in the process of iron ore sintering.

Carried out by author [3] the balance of chlorine and oil drawn up for one of the Polish integrated steel plant has shown that: main sources of chlorine are as follows: homogenized sinter mix, coke breeze and water used for cooling the return. Main sources of oil are as follows: homogenized sinter mix, return sinter, lubricant and coke breeze. The largest volume of chlorine amongst the by- products (sludge, dust, converter slag, scale) utilized in the sinter plant of the analyzed integrated steel plant is introduced by dusts.

In Japan, the emission level of dioxins in iron ore sintering process was regulated by law in 1999 [11]. Limits of PCDDs/PCDFs content in waste gases have been fixed for the sinter plants: 0,1 ng-TEQ/m³ for the new sinter plants and 1 ng-TEQ/m³ for the existing sinter plants.

In Poland, so far there have been no legal regulations pertaining to PCDDs/PCDFs emission from the sinter plants.

6. THE CONCLUSIONS

The iron ore sintering process is the largest source of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in the iron and steel industry. Based on the results of tests, sources of PCDDs/PCDFs have been determined in the iron ore sintering process. The balances of chlorine and oil were made by author. It shows that main sources of PCDDs/PCDFs are organic compounds contained in sinter mix and coke breeze. In the future research author plans to determine PCDDs/PCDFs catalysts in the iron ore sintering process.

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