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An Assessment of Pollution with Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofuranes (PCDFs) at Steelmaking

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Abstract

Polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofuranes (PCDFs) are types of persistent organic pollutants (POPs) with a wide range of toxic responses and carcinogenic properties. These pollutants have a negative impact on the steelworkers, environment and population. The aim of this paper is to assess the polychlorinated dibenzodioxins and polychlorinated dibenzofuranes emissions from steelmaking in the electric arc furnace in order to improve the gaseous emissions management. The analyses of polychlorinated dibenzodioxins and polychlorinated dibenzofuranes was performed using a high resolution gas chromatograph/high resolution mass spectrometer (HRGC/HRMS). After evaluating the pollution levels of polychlorinated dibenzodioxins and dibenzofuranes during steelmaking it results that: the total PCDDs and PCDFs concentrations in the stack flue gases was 0.9886 ng/Nm^3; in the composition of flue gases predominates the following compounds: tetrachloro dibenzofuran (TCDF) 40.55%, pentachloro dibenzofuran (PeCDF) 19.4%, tetrachloro dibenzo-p-dioxin (TCDD) 12.5%, pentachloro dibenzo-p-dioxin (PeCDD) 10.7% and hexachloro dibenzofuran (HxCDF) 10.5%; the calculated total value of Toxic Equivalent Quantity (Total TEQ) is 0.326482 ng I-TEQ/Nm^3; the level of PCDD and PCDF concentrations depends on the plastic (such as polyvinylchloride) content of material input. The reduction of pollution with polychlorinated dibenzodioxins and dibenzofuranes to the steelmaking in the electric arc furnace is possible by charge component selection and by the use of raw materials with reduced plastics content.

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1. Introduction

Polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofuranes (PCDFs) (Figure 1) are types of persistent organic pollutants (POPs) with a wide range of toxic responses and carcinogenic properties. These pollutants can be considered as environmental quality indicators of anthropogenic activities. One of the most important anthropogenic sources of polychlorinated dibenzodioxins and polychlorinated dibenzofurans from the ferrous metals industry includes steelmaking in the electric arc furnaces [1,2,3,4,5,6]. The generation of these compounds requires carbon, oxygen and chlorine, as well as metallic catalysts and adequate temperature. The optimal temperature range for pyrosynthesis of these compounds is between 400 - 700^{o}C [7].

In order to achieve a higher level of uniformity and comparability of results defining PCDDs and PCDFs content in samples of different materials of different origin, there was adopted the International Toxicity Equivalent Factor (I-TEF). Nowadays, the analysis of PCDDs/Fs in various samples commonly includes 17 compounds (7 PCDDs and 10 PCDFs) and their level in the sample is described as toxic equivalent (I-TEQ) in correlation with 2,3,7,8-tetrachlorinated dibenzo-p-dioxin (2,3,7,8-TCDD). In the Table 1 are presented the International Toxicity Equivalent Factor (I-TEF) reported in various references from specialized literature [7,8,9].

The dioxin toxic equivalent quantity (TEQ) is a way to express a concentration of a mixture of dioxins based on its estimated toxicity compared to tetrachloro dibenzo-p-dioxin (TCDD). The levels of dioxin congeners measured in environmental samples are multiplied by their I-TEF to produce a TCDD toxic equivalent or TEQ concentration. The resulting TEQs for all dioxin congeners measured in a sample are then added together to determine the total dioxin TEQ concentration for that sample [7].

According to [10] a pilot study was conducted on a ten tons electric arc furnace in Sweden and reported the highest emissions as 1.5, 0.3, and 0.1 ng Nordic TEQ/Nm^3 during continuous charging operations, batch charging with a feedstock consisting of scrap metal with plastics, and scrap metal with cutting oils, respectively. In the reference [11] there was conducted an experimental study on investigating polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofuranes (PCDFs) emissions from a variety of electric arc furnaces in Germany. They found out that emissions from these facilities ranged from 0.1-1.3 ng International-Toxicity Equivalents (I-TEQ)/Nm^3. In the United States [12] a preliminary estimation of potential TEQ annual emissions for electric arc furnaces was made by using the average emission factor (1.15 ng I-TEQ/kg-scrap) derived from the data reported by reference [11], obtained from six electric arc furnaces. There was no reported testing of polychlorinated dibenzodioxins and dibenzofuranes emissions in United States electric arc furnaces. This led to an annual emission estimation of 44.3 g I-TEQ for electric arc furnaces [13].

According to the results presented in the reference [7] the total dioxins and furans concentrations in the stack off gases of two electric arc furnaces were 0.2098 and 0.022603 ng I-TEQ/Nm^3.

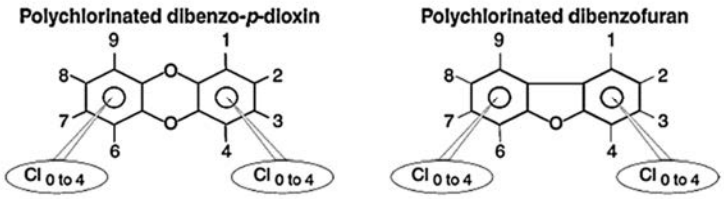

Fig. 1. Structural formula of polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofuranes (PCDFs)

In Romania there are no studies on assessing the emissions of dioxins and furans emissions from steelmaking in the electric arc furnaces. From the industrial / technical point of view it is important to assess the polychlorinated

dibenzodioxins (PCDDs) and polychlorinated dibenzofuranes (PCDFs) emissions from steelmaking in order to identify the level of pollution and to reduce the concentration of these pollutants.

The aim of this paper is to assess the polychlorinated dibenzodioxins and dibenzofurans emissions from steelmaking in the electric arc furnaces, in order to improve the industrial emissions management, by identifying the sources that generates these persistent organic pollutants (POPs).

The objectives of the paper are:

- the assessment of the dioxin and furan concentrations in the stack flue gases from electric arc furnace;
- the identification of the dioxins and furans emitting sources to the steelmaking in the electric arc furnaces;
- establishing methods to reduce dioxins and furans to the steelmaking.

Table 1. International Toxicity Equivalent Factors (TEF) for dioxin and furan congeners [7**,8*,9**].

Dioxin and furan congeners	I-TEF*	I-TEF**
2,3,7,8-Tetrachloro dibenzo-p-dioxin (2,3,7,8- TCDD)	1	1
1,2,3,7,8-Pentachloro dibenzo-p-dioxin (1,2,3,7,8-PeCDD)	1	0.5
1,2,3,4,7,8-Hexachloro dibenzo-p-dioxin (1,2,3,4,7,8-HxCDD)	0.1	0.1
1,2,3,6,7,8- Hexachloro dibenzo-p-dioxin (1,2,3,6,7,8-HxCDD)	0.1	0.1
1,2,3,7,8,9- Hexachloro dibenzo-p-dioxin (1,2,3,7,8,9-HxCDD)	0.1	0.1
1,2,3,4,6,7,8- Heptachloro dibenzo-p-dioxin (1,2,3,4,6,7,8-HpCDD)	0.01	0.01
1,2,3,4,6,7,8,9 - Octachloro dibenzo-p-dioxin (1,2,3,4,6,7,8,9 -OCDD)	0.0003	0.001
2,3,7,8-Tetrachloro dibenzofuran (2,3,7,8-TCDF)	0.1	0.1
1,2,3,7,8-Pentachloro dibenzofuran (1,2,3,7,8-PeCDF)	0.03	0.05
2,3,4,7,8- Pentachloro dibenzofuran (2,3,4,7,8-PeCDF)	0.3	0.5
1,2,3,4,7,8-Hexachloro dibenzofuran (1,2,3,4,7,8-HxCDF)	0.1	0.1
1,2,3,6,7,8-Hexachloro dibenzofuran (1,2,3,6,7,8-HxCDF)	0.1	0.1
1,2,3,7,8,9-Hexachloro dibenzofuran (1,2,3,7,8,9-HxCDF)	0.1	0.1
2,3,4,6,7,8-Hexachloro dibenzofuran (2,3,4,6,7,8-HxCDF)	0.1	0.1
1,2,3,4,6,7,8-Heptachloro dibenzofuran (1,2,3,4,6,7,8-HpCDF)	0.01	0.01
1,2,3,4,7,8,9-Heptachloro dibenzofuran (1,2,3,4,7,8,9-HpCDF)	0.01	0.01
1,2,3,4,6,7,8,9-Octachloro dibenzofuran (1,2,3,4,6,7,8,9-OCDF)	0.0003	0.001

2. Material and Method

The stack flue gas samples were collected from an electric arc furnace with alkaline lining. The type of steel produced was carbon steel and in the charge composition as a raw material was used scrap resulted from the

automobile industry. The sampling procedures followed the European Standard EN 1948-1:2006 [9]. The range of parameters during the sampling procedure was: waste gas temperature 77°C, pressure 756 mm Hg, oxygen (O_2) content 19.7% and gas velocity 26 m/s. The sampling tests lasted over 6 h, using the procedure mentioned above.

The analysis of polychlorinated dibenzodioxins and polychlorinated dibenzofuranes was performed using a high resolution gas chromatograph/high resolution mass spectrometer (HRGC/HRMS) Polaris Q. The method HRGC/HRMS is considered to be very effective for the analysis of dioxins and furans, because this method has a number of advantages: high sensitivity and detection limits down to the picograms for solid samples, respectively fentograms for air samples; high selectivity, specificity, distinguishes between different isomers; high accuracy and precision [14].

Stack emission testing was carried out using EN 1948-2:2006 and EN 1948-3:2006 methods for determining PCDDs/PCDFs from stationary sources [15,16].

The calculation of the Toxic Equivalent Quantity (TEQ) was based on the International Toxicity Equivalent Factors (I-TEF) (Table 1). The Total Toxic Equivalent Quantity (Total TEQ) was calculated using the following formula:

$$Total\,\mathrm{TEQ} = C_1 \cdot ITEF_1 + C_2 \cdot ITEF_2 + \ldots + C_{10} \cdot ITEF_{10} \ [\mathrm{ngI\text{-}TEQ/Nm^3}] \quad (1)$$

where Total TEQ is total Toxic Equivalent Quantity [ngI-TEQ/Nm^3];

C_1 - the concentration of the tetrachloro dibenzo-p-dioxin (TCDD) [ng/Nm^3];

$ITEF_1$ - International Toxicity Equivalency Factor for the tetrachloro dibenzo-p-dioxin (TCDD);

C_2 - the concentration of the pentachloro dibenzo-p-dioxin (PeCDD) [ng/Nm^3];

$ITEF_2$ - International Toxicity Equivalency Factor for the pentachloro dibenzo-p-dioxin (PeCDD);

C_{10} - the concentration of the octachloro dibenzofuran (OCDF) [ng/Nm^3];

$ITEF_{10}$ - International Toxicity Equivalency Factor for the octachloro dibenzofuran (OCDF);

3. Results and Discussions

In Figure 2 there are shown the percentage concentrations of polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofuranes (PCDFs) in the stack flue gases from steelmaking in the electric arc furnace.

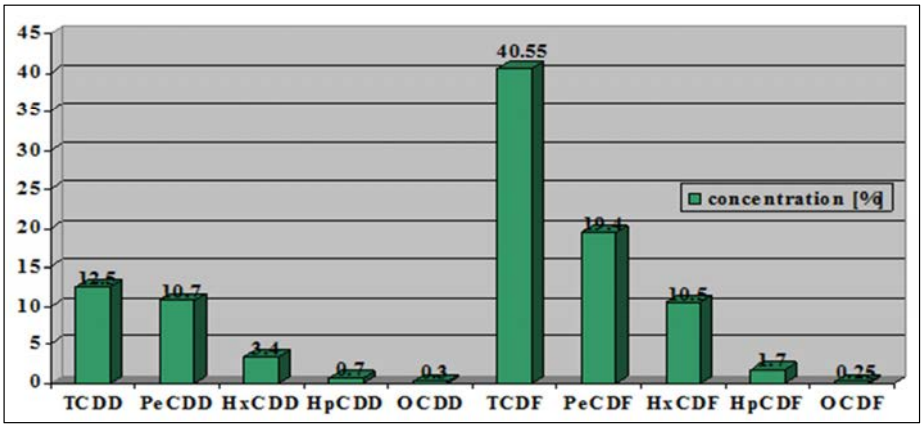

Fig. 2. Percentage concentrations of polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofuranes (PCDFs) in the stack flue gases from electric arc furnace

In Figure 3 there are shown the concentrations and the total concentrations of polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofuranes (PCDFs) in the stack flue gases from steelmaking in the electric arc furnace.

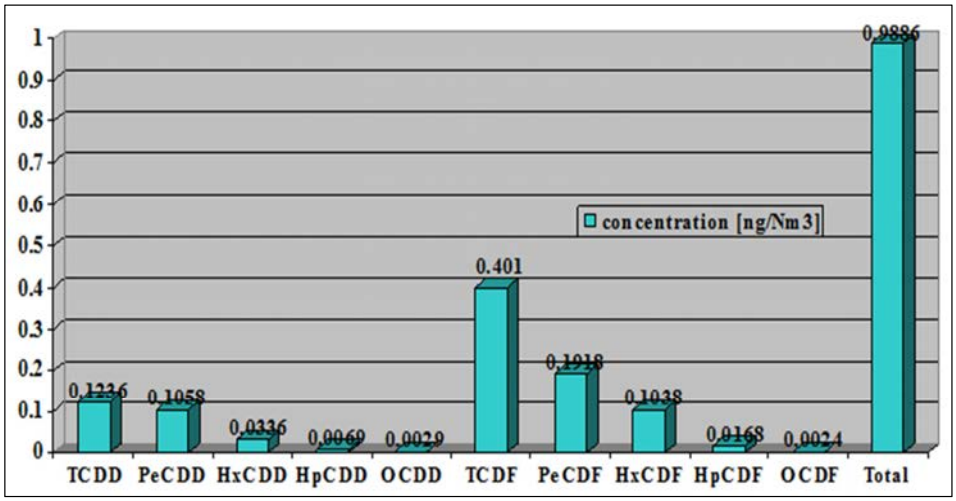

Fig. 3. Polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofuranes (PCDFs) concentrations in the stack flue gases from electric arc furnace

In Figure 4 there are shown the computed values for the Toxic Equivalent Quantity (TEQ) and Total Toxic Equivalent Quantity (Total TEQ). The International Toxicity Equivalency Factor (I-TEF) was used to compute the toxicity weight of dioxin and furan concentrations.

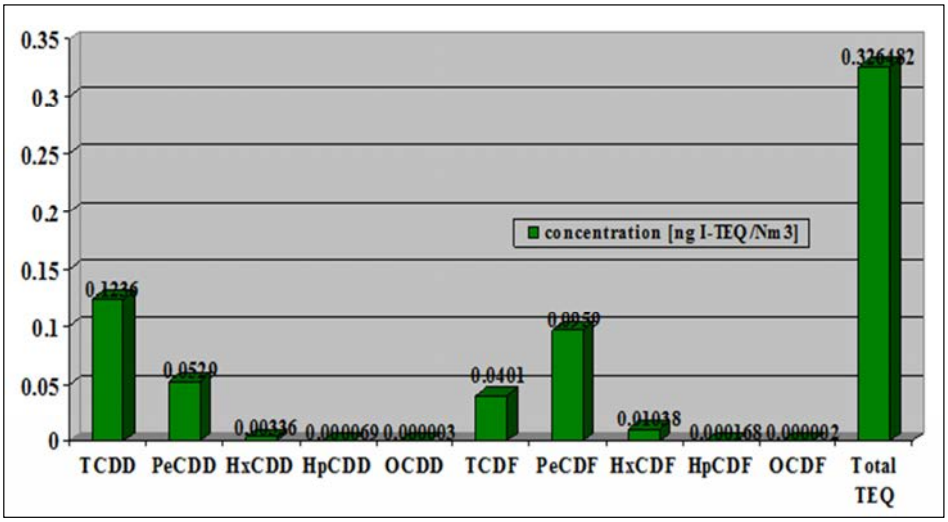

Fig. 4. Toxic Equivalent Quantity (TEQ) for each dioxins and furans and Total Toxic Equivalent Quantity (Total TEQ)

From the analysis of the data presented in Figure 1, 2 and 3 it results that:

- in the composition of flue gases predominates the following compounds: tetrachloro dibenzofuran (TCDF) 40.55%, pentachloro dibenzofuran (PeCDF) 19.4%, tetrachloro dibenzo-p-dioxin (TCDD) 12.5%, pentachloro dibenzo-p-dioxin (PeCDD) 10.7% and hexachloro dibenzofuran (HxCDF) 10.5%;
- the total polychlorinated dibenzodioxins and polychlorinated dibenzofuranes concentration in the stack flue gases was 0.9886 ng/Nm^3;
- the computed total value of Toxic Equivalents (TEQs) for dioxins and furans is 0.326482 ng I-TEQ/Nm^3;
- the level of polychlorinated dibenzodioxins and polychlorinated dibenzofuranes concentrations depends on the plastic (such as polyvinyl chloride) content of the charge.

The potential sources that generate the dioxins and furans emissions in the steelmaking are: polyvinyl chloride, coatings and paintings from the scrap resulted from the automobile industry.

The results of the experiment showed that the total dioxins and furans Toxic Equivalent Quantity (TEQ) from steelmaking in the electric arc furnace were higher than the dioxins and furans emissions presented in the Directive 2010/75/EU for a stationary source (0.1 ng TEQ/Nm^3) [17].

4. Conclusions

Because of the content of polyvinyl chloride, coatings and paintings as well as other nonferrous materials in the charge during melting dioxins and furans are emitted.

According to the results obtained the Total Toxic Equivalent Quantity (Total TEQ) for dioxins and furans from steelmaking in the electric arc furnace was 3.2 times higher than the limit specified in the Directive 2010/75/EU.

The reduction of pollution with dioxins and furans to the steelmaking in the electric arc furnace is possible by charge component selection and by the use of raw materials with reduced plastics content.

Therefore, using some air pollution control methods, such as activated carbon injection and bag filter, are necessary to reduce polychlorinated dibenzodioxins and polychlorinated dibenzofuranes concentrations from the steelmaking in the electric arc furnace.

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