DIOXINS / FURANS (PCDDs/PCDFs) CONTROL IN CEMENT INDUSTRY IN ROMANIA

CRISTIAN CIOBANU[1], GHEORGHE VOICU[2*], MAGDALENA-LAURA TOMA[2]
SILVIU MARCU[1]

[1]*CEPROCIM SA Bucharest, 6 Preciziei Street, 062203, Romania*
[2]*University POLITEHNICA of Bucharest, 313 Splaiul Independentei, Romania*

Abstract. The most important sources of dioxins are waste incineration, industrial (dioxins are by-products), volcanic eruptions, fire, etc. The Romanian law 278/2013 provides the air emissions limit of 0.1 ng/Nm^3 gases for dioxins and furans emitted by the incineration and co-incineration plants. Some aspects regarding the control of these substances in the gases from a cement factory in Romania are presented in this paper. In incineration plant were used various fuels. However, the substances level mentioned above was within the allowed limits.

Keywords: dioxin, furans, cement industry, incinerator, emissions, I-TEQ, environment

1. INTRODUCTION

1.1. Dioxins and furans (PCDDs/PCDFs)

Dioxins and furans can result from a combination of forming mechanisms depending on kiln type, incineration process design, incineration conditions, emission control systems etc. Moreover, any chlorine intake in presence of organic materials can lead to PCDDs/PCDFs (Polychlorinated dibenzodioxins/Polychlorinated dibenzofurans) forming during heating process. However, detailed investigations and measurements have shown that PCDDs/PCDFs emissions from cement industry can be classified as low, even when combustible wastes are used as fuel. Most clinker kilns can meet the emission level of 0.1 ng I-TEQ/Nm^3 (International Toxic Equivalents) [1, 2, 7–10].

1.2. Dioxins and furans – characteristics and forming during burning processes in clinker kilns

Polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are chlorinated organic compounds whose basic structure is shown in Figure 1.

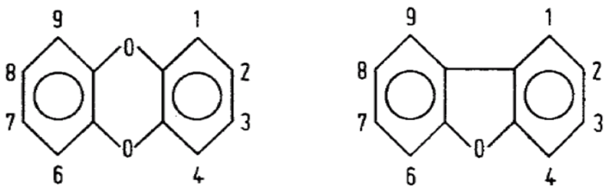

Fig. 1. General structures of PCDDs (left) and PCDFs (right) [1, 4].

In cement kilns, these compounds form depending on kiln design and burning process, characteristics of the crude mixture and dedusting conditions of operating equipment. In modern clinker kilns, in stable operating conditions, if fuel is fed to the main burner, there are conditions for the destruction of organic compounds: a flame temperature of about 2000°C, a long residence time of gases in the furnace (5 – 10 seconds at temperatures between 1200°C

* Corresponding author, email: ghvoicu_2005@yahoo.com

and maxim 2000°C) and a constant oxidizing atmosphere [3–6, 11–14].

Dioxins and furans formed during the first process phases are absorbed in crude mixture and their destruction is favoured because the crude mixture is advancing towards the high temperature zone. Here, they are thermally destroyed or converted into low molecular weight compounds. In the case of secondary combustion, when calcination installation temperature does not exceed 900 – 1100ºC, in order to avoid the formation of dioxins and furans is necessary to limit the halogenated compounds content of alternative fuels [3, 4]. The limit value for dioxins and furans emission for a sampling period of at least 6 hours and up to 8 hours, according to the Romania law 278/2013 regarding industrial emissions in order to ensure a 10% O_2 concentration is 0.1 ng/Nm^3 [8–15].

Graphical representation of toxic dioxin contributions as a percentage of the sample total toxicity, called characteristic profiles, is a way to identify the mechanisms and establishing the differences between the various formation sources of these pollutants and other alike predominant pollutants. According to the literature [6,7], if using traditional fuels, the characteristic profile of toxic dioxin contributions in total toxicity is shown in Figure 2 and it can be observed that tetra- and penta-furans have a very important contribution.

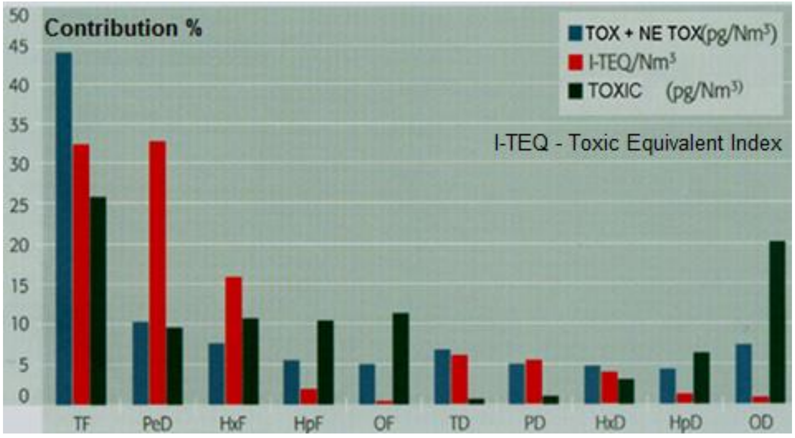

Fig. 2. The characteristic profile of various substances contributions to total toxicity for a cement plant using conventional fuels [6, 7].

The dioxins emission profile when using waste as alternative fuel varies in a very large number of measurements compared to the case in which conventional fuels are used, having different characteristics for each type of fuel. Only in the case of animal flours, the profile is identical to the one obtained in case of using petroleum coke or heavy fuel oil. Figure 3 presents a similar toxic profile, in case of mixing waste oils with solvents from scrapped vehicles. Significant changes of the percentages compared to conventional fuels are noticed.

Figure 4 shows the percentage of the two systems in which used tires have been utilized. Even lines 2 and 4 correspond to an installation and the odd ones 1 and 3 correspond to another facility. As can be seen, the penta- and hexa- furans prevails, while the presence of dioxins vary from one experiment to another [6, 7].

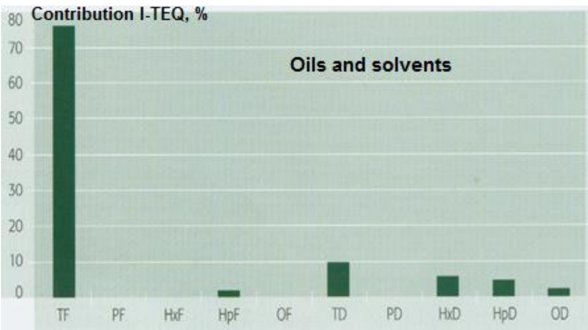

Fig. 3. Characteristic profile of a Spanish cement factory that uses waste oils and solvents [6, 7].

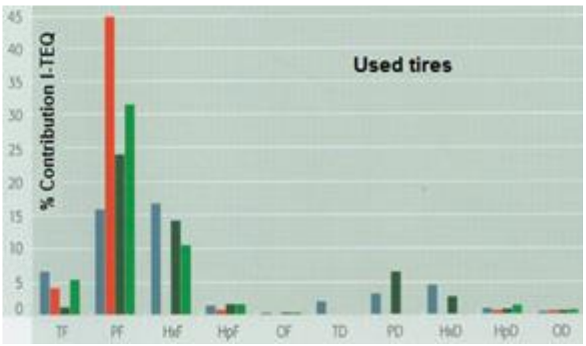

Fig. 4. Profile for two Spanish cement plants that use waste tires as fuel [6, 7].

2. MATERIALS AND METHODS

Sampling and filtering the combustion gases was conducted from stationary emission sources in order to determine the mass concentration of dioxins/furans and their contribution to the overall toxicity of combustion plants. Measurements were carried out between March 2014 – October 2016, at a cement plant from Romania. Burning fuels used were: coal – 5908 kg/h, waste oil – 1800 kg/h, distillation residues – 156 kg/h, animal flour – 681 kg/h for the main burner and plastic – 1024 kg/h for secondary burner.

It has been found that only very low concentrations of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (in short: dioxins and furans) can be detected in the cement kilns exhaust gas.

The fuel supply was stable with fluctuations of no more than ± 5 %. Only fluctuations in plastic supply were slightly higher around ± 15%.

2.1. Standards applied in experiments

- ✓ SR EN 1948-1/2003 specifies the quality control requirements to be met by any PCDDs/PCDFs sampling. In addition, it regulates and stipulates the PCDDs/PCDFs sampling system from the exhaust gases of the stationary sources in order to measure concentrations of about 0.1 ng I-TEQ/m^3.
- ✓ SR EN 1948-1/2003 also specifies the method of sampling, the user being able to choose between three different methods: filtration/condensation method, dilution method and chilled probe method.

CEPROCIM SA testing laboratory opted for PCDDs/PCDFs sampling by filtration/condensation method.

2.2. Sampling line structure

In Figure 5 is shown the CEPROCIM SA Bucharest sampling line diagram.

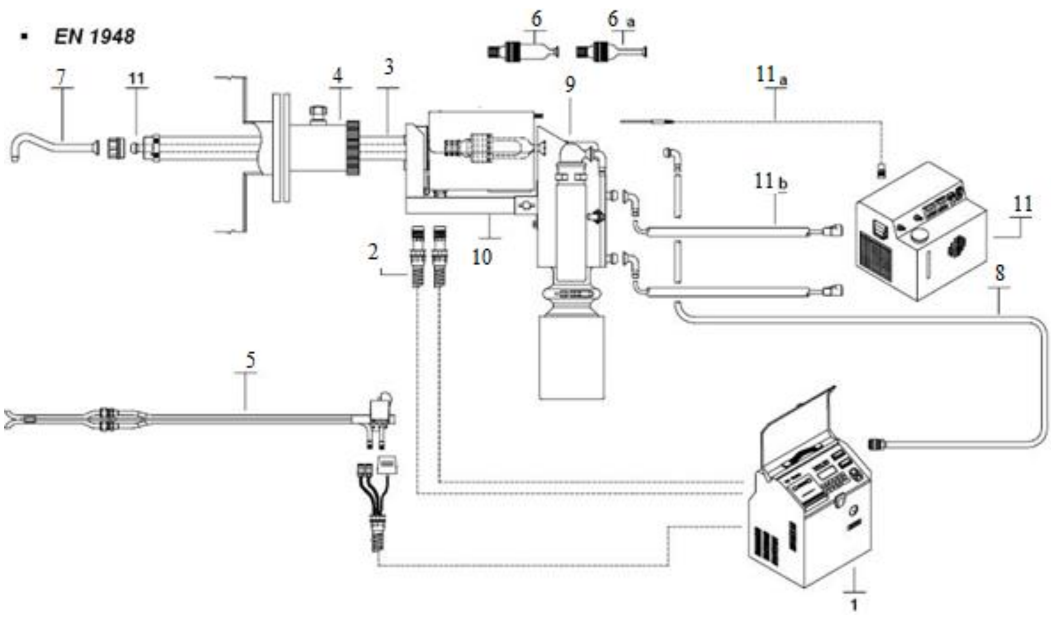

Fig. 5. Gases sampling line:
1 – automatic sampler type ISOSTAK BASIK; 2 – heating device cable (2 pieces); 3 – titanium heated probe; 4 – probe mounting device; 5 – PITOT tube cu thermocouple; 6 – filter holder; 7 – nozzle; 8 – 8 mm silicone connection cable; 9 – condensation and absorption device with resin XAD-2; 10 – heated box; 11a, 11b – ISOFROST input/output.

3. RESULTS AND DISCUSSIONS

The dioxins emission data, in ng I-TEQ/Nm^3, and calculated emission factors are shown in Table 1.

All emissions from the measurements made at the studied clinker kilns are below the dioxins and furans emission limit for cement kilns in which wastes are co-incinerated (0.1 ng I-TEQ/Nm^3, with 10% O_2 and dry gas). In addition, it can be noticed that the emission is higher for waste co-incineration. The same furnace may have a higher or lower dioxins emission, regardless of the type of fuel used, traditional or alternative. Dispersion values for some ovens are relatively higher, so that in some cases, for the same type of fuel, emission can have different values (Figure 6).

Table 1. Emission factors and the dioxins and furans concentrations from burning gases.

Measurement date	Pollutant	Rotary kiln with raw meal mill CR + MF (joint operation)			Pollutant limit according to 278/2013 law
		Concentration (ng/Nm^3) with 10% O_2^*	Measured parameters		
			Average mass flow, µg/h	Measured O_2 concentration in burning gases, %	
March 2014	Dioxins + furans	< 0.024040	< 11.2364	9.00	0.100
August 2014		< 0.014966	< 7.1751	9.99	
March 2015		< 0.027517	< 14.6984	10.48	
July 2015		< 0.034592	< 18.6810	10.13	
May 2016		< 0.029891	< 14.25006	9.46	
October 2016		< 0.039296	< 16.7117	10.78	

Measurement date	Pollutant	Rotary kiln without raw meal mill CR - MF (direct operation)			Pollutant limit according to 278/2013 law
		Concentration (ng/Nm^3) with 10% O_2^*	Measured parameters		
			Average mass flow, µg/h	Measured O_2 concentration in burning gases, %	
March 2014	Dioxins + furans	< 0.023037	< 10.9955	7.64	0.100
August 2014		< 0.009873	< 4.7492	8.86	
March 2015		< 0.025080	< 4.6650	10.65	
July 2015		< 0.035702	< 17.6677	10.09	
May 2016		< 0.025770	< 13.60821	8.60	
October 2016		< 0.034189	< 16.6434	10.48	

NB: Sampling period: 6 hours. Limit values have been related to a 10% O_2 content of the gaseous effluents.

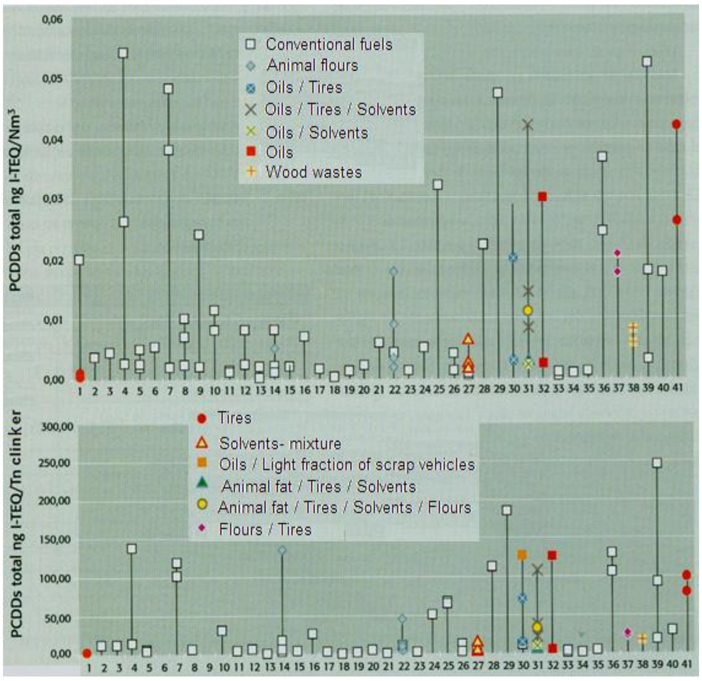

Fig. 6. Dioxide emissions and the combustion gases emission factors in the cement plant [6,7].

The obtained data shows that emissions resulted from the clinkering process are not significant dioxins and furans sources because emissions values are very low (Figure 7). There are no experimental evidences that indicate a higher dioxin emission when using fuels derived from waste.

An isokinetic sample is drawn from the gas source and collected on a fiberglass filter and on an absorbent material column. The sample cannot be separated into a vapour or particle fraction. PCDDs and PCDFs are removed from the sample, separated using the high-resolution gas chromatography (HRCG) method and measured using the high-resolution mass spectrometry (HRMS) method.

The emissions ranges detected with the measuring instrument were:

- cyclone furnaces have emission varying between "undetectable" and 0.06 ng I-TEQ/Nm^3, with an average of around 0.01 ng I-TEQ/Nm^3;
- dry and wet process kilns have emission varying between "undetectable" and 0.30 ng I-TEQ/Nm^3, with an average of around 0.06 ng I-TEQ/Nm^3.

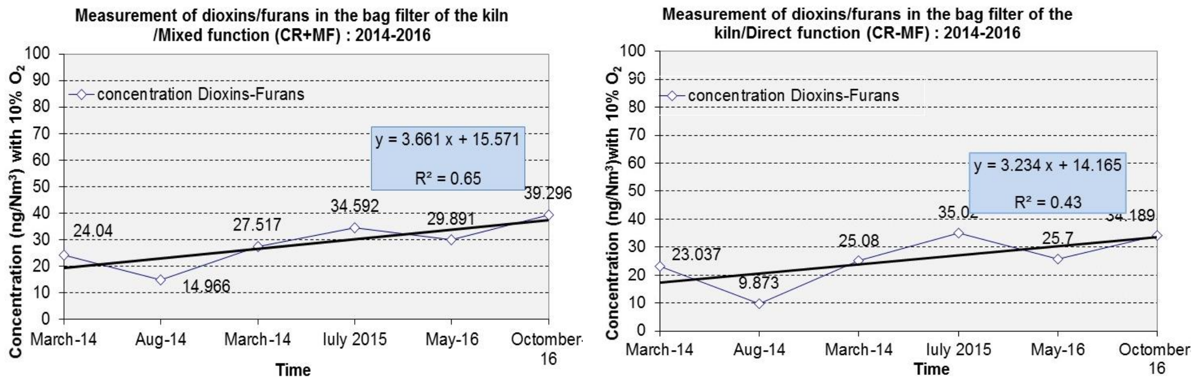

Fig.7. The level of dioxins and furans during the measurements at the monitored cement plant.

In order to determine the total amount of dioxins released into the environment, PCDDs/PCDFs comparative measurements have been carried out to the active coal system output and to the catalytic filtering system. The measurements were based on the treated gases and the dust recovered by the filters. It has been found out that the total dioxin emissions from the exhaust gases and dust filters were 69 g/t of treated waste when activated carbon system is used. The results are based on the measurements carried out between 2014 – 2016.

4. CONCLUSIONS

In all cases, the obtained values of dioxins and furans emissions were slightly lower than the limit of 0.1 ng/Nm^3 I-TEQ. Moreover, there has been found no irreversible contamination of the catalyst.

According to the current state of knowledge, this technology can be applied to many incineration and fusion metals installations and cement factories kilns.

Its main advantage, which facilitates its use in many other cases, is the fact that the filter bags and/or pockets containing the catalyst can replace conventional filter bags. The operating temperature must range between 1800 – 2600ºC, as in most applications. The fire hazard due to active coal is suppressed, which improves safety and reliability. Finally, if compared to the adsorption process, this technique avoids the handling, transportation and disposal of wastes loaded with pollutants.

Data from measurements made at different clinker production facilities at the global and national level, using different processes and types of fossil fuels and alternative fuels (waste fuels), lead to the same conclusion: the emission of dioxins and furans from cement manufacturing processes are insignificant, being able to say that they have a minor impact on the environment (air, water, soil).

There is a slight increase from year to year, considering the allowable limit is 0.1 ng/Nm^3 I-TEQ, in 2016 the actual amount was < 0.039296 ng/Nm^3 I-TEQ, according to the measurement, but within normal limits.

REFERENCES

[1] Polychlorinated dibenzodioxins and dibenzofurans, http://www.euro.who.int/__data/assets/pdf_file/0017/123065/AQG2ndEd_5_11PCDDPCDF.pdf?ua=1.
[2] Agustina, H., Kusnoputranto, H., Sutamiharja, RTM, Emission estimation model of dioxin / furan releases from cement industry used wastes in co-processing, Research Journal of Science and IT Management, vol. 04, no. 04, 2015, p. 56 – 67.
[3] Ames, M., Zemba, S., Green, L., Botelho, M.J., Gossman, D., Linkov, I., Palma-Oliveira, J., Polychlorinated dibenzo(p)dioxin and furan (PCDD/F) congener profiles in cement kiln emissions and impacts, Science of the Total Environment, no. 419, 2012, p. 37 – 43.
[4] Andronescu, E., Puscasu, D.V., Releases dioxins and furans in the cement industry, Romanian Journal of Materials, vol. 42, no. 3, 2012, p. 237 – 241.
[5] Everaert, K., Baeyens, J., Degreve, J., Removal of PCDD/F from incinerator flue gases by entrained-phase adsorption, Journal of the Air & Waste Management Association, no. 52, 2002, p. 1378 – 1388.
[6] Fabrellas, B., Larrazaba, D., Martinez, M.A., Sanz, P., Ruiz, M.L., Abad, E., Rivera, J., Global assessment of PCDD/F emissions from the Spanish cement sector, Effect of conventional/alternative fuels, Non-thermal sources and source inventories, Organohalogen Compounds, vol. 66, 2004, p. 905 – 911.
[7] Fabrellas, B., Sanz, P., Abad, E., Rivera, J., The Spanish dioxin inventory. Part I: Incineration as municipal waste management system, Chemosphere, vol. 43, no. 4 – 7, 2001, p. 683 – 688.
[8] Groschwitz, R., Sommer, E., Joisten, M., Katalysatoren zur abscheidung von dioxinen und furanen in rauchgasen. WLB Wasser, Luft und Boden, no. 5, 1998, p. 52 – 55.
[9] Karstensen, K.H., Formation and Release of POPs in the Cement Industry, Second edition, SINTEF, 2006.
[10] Loo Willem van, Dioxin/furan formation and release in the cement industry, Environmental Toxicology and Pharmacology, vol. 25, no. 2, 2008, p. 128 – 130.
[11] Posthumus, D.L., Woollatt, G.B., Sampling and analyses of polychlorinated dibenzo dioxins (PCDDs) and polychlorinated dibenzo furans (PCDFs) emissions in South Africa: A practitioner’s guide, The Clean Air Journal, vol. 24, no. 2, 2014, p. 29 – 32.
[12] Souza Pereira, M., Polychlorinated dibenzo-p-dioxins (PCDD), dibenzofurans (PCDF) and polychlorinated biphenyls (PCB): Main sources, environmental behaviour and risk to man and biota, Quim. Nova, vol. 27, no. 6, 2004, p. 934 – 943.
[13] Thuong, Van N., et al., The emission of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans from steel. and cement-kiln plants in Vietnam, Aerosol and Air Quality Research, no. 14, 2014, p. 1189 – 1198.
[14] Zainal, S, Onwudili, JA, Williams, PT., Supercritical water oxidation of dioxins and furans in waste incinerator fly ash, sewage sludge and industrial soil, Environmental Technology, vol. 35, no. 13 – 16, 2014, p. 1823 – 1830.
[15] The 278/2013 law regarding industrial emissions (Legea nr. 278/2013 privind emisiile industriale).