EMISIILE DE DIOXINE ŞI FURANI ÎN INDUSTRIA CIMENTULUI▲
RELEASES OF DIOXINS AND FURANS IN THE CEMENT INDUSTRY

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This paper aims at providing more recent information concerning dioxins and furans emissions in cement plants. The evaluated results were obtained from thousands of monitoring tests carried out worldwide and in Romania, after 2006. The measurements cover most of the production technologies and a great variety of waste based alternative fuels.

Due to the conditions inherent to clinker production: high temperatures, approx. 2000 °C for gases and long residence times of flue gases in the kiln (about 10 seconds at temperatures higher than 1100 – 1200 °C and 5 – 6 second at temperatures over 1800°C), the release of dioxins and furans from clinker kilns is very low, no matter the fuels, even when alternative fuels based on hazardous waste are used.

As a result of the existing conditions, a DRE (destruction and removal factor) of 99.9999% can be reached in the clinker kilns for POPs (Persistent Organic Pollutants), like dioxins and furans. The measurements carried out worldwide and in Romania confirm the very low level of dioxin and furan emissions of clinker kilns.

Lucrarea de față are scopul de a aduce informații mai recente privind emisiile de dioxine şi furani în fabricile de ciment. Rezultatele evaluate provin din mii de monitorizări realizate la nivel mondial, precum şi în Romania, după 2006. Masurările acoperă majoritatea tehnologiilor de producție şi o mare varietate de combustibili alternativi pe bază de deşeuri.

Datorită condițiilor specifice pentru producerea clincherului: temperaturi ridicate, de aproximativ 2000 °C pentru gaze şi perioade lungi de staționare a gazelor de ardere în cuptor (circa 10 secunde la temperaturi mai mari de 1100 – 1200 °C şi 5 – 6 secunde chiar la temperaturi peste 1800°C), emisiile de dioxine şi furani ale cuptoarelor de clincher sunt foarte reduse, indiferent de combustibilii utilizați, chiar şi în cazul combustibililor alternativi pe bază de deşeuri periculoase.

Datorită condițiilor existente în cuptoarele de clincher se poate realiza un factor de distrugere şi eliminare (DRE) de 99,9999% pentru compuşii organici persistenți, categorie din care fac parte şi dioxinele şi furanii. Datele măsurărilor realizate în lume, dar şi în România confirmă nivelul foarte redus al emisiilor de dioxine si furani al cuptoarelor de clincher.

Keywords: *dioxins, furans, alternative fuels*

1. Persistent Organic Pollutants

Persistent Organic Pollutants (POPs) have caused a major concern at global level, so the United Nations Environment Program initiated the Stockholm Convention of May 2011.The main target of the Convention is to protect the environment and human health by reducing and eliminating, wherever possible, 12 of the most toxic persistent organic pollutants (pesticides, industrial chemicals and combustion by-products). Out of them, only polychlorinated dibenzodioxins and polychlorinated furans are not intentionally produced by humans, but are secondary substances resulting from combustion processes and uncontrolled combustions in nature.

The main characteristics of POPs are *persistence, bioaccumulation potential (*it accumulates in the adipose tissue of living organisms), *toxicity, volatility, capacity to be transported on large distances and bioavailability* [1].

2. Dioxin and furan emissions inventories. Role of the cement industry

Dioxin and furan emission inventories developed at the European level and in other parts of the world, in particular the USA, are based on studies aimed at assessing the emissions of industrial processes and uncontrolled sources.

In Europe the main sources of dioxin and furan emissions identified in the inventory realized for the year 2000 in 17 countries (Austria, Belgium, Switzerland, Germany, Denmark, Spain, France, Greece, Italy, Ireland, Luxemburg, Norway, Netherlands, Portugal, Sweden, Finland and UK) are [2]:

- solid fuel burning;
- iron ore sinter plant;
- incineration of domestic and municipal waste (legal and illegal)
- incineration of hospital waste
- fires
- preservation of wood

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▲ Lucrare prezentată la / *Paper presented at:* Consilox XI

A special attention is dedicated to the emissions from fugitive, non-industrial sources which are hardly to control and it is estimated that their contribution will increase.

In USA, the main sources of dioxin and furan emission identified in the inventory realized for the year 2000 are [3]:

- backyard barrel burning of waste;
- medical waste incineration;
- municipal wastewater treatment sludge (applied to land or incinerated);
- municipal waste incineration;
- coal-fired thermal plants for electric power generating
- diesel engines

Less than 10 years ago, cement kilns were considered as responsible for most of the dioxins and furans in the air, but recent data provided by more than 2000 measurements at clinker kiln stacks indicate that the cement industry's contribution is less than 1% to the total emissions of dioxins and furans in the air [4].

3. Dioxins and furans – characteristics and formation in the combustion processes in the clinker kilns

Polychlorinated dibenzodioxins (PCDD) and polychlorinated dibenzofurans (PCDF) are chlorinated organic compounds whose basic structure is presented in Figures 1 and 2 [5].

In the cement kilns, these compounds are formed as a result of several factors: kiln configuration and type of process, combustion conditions, characteristics of the raw mix and type and operating conditions of the de-dusting equipment [6].

In modern multistage preheaters kilns, in constant operating conditions and if the fuels are fed in the main burner, all conditions are met for the destruction of organic compounds, at a very high output: flame temperature of about 2000^0C, long residence time of gases in the kiln (over 5 – 10 seconds at temperatures > 1200^0C and maximum 2000^0C) and constant oxidizing atmosphere. Thus, the Destruction & Removal Efficiency – DRE of the clinker kiln for hazardous waste (including chlorinated hydrocarbons) is > 99.9999 % [4].

DRE is defined as follows:

$$DRE = [(W_{in} - W_{stack})/W_{in}] \times 100$$

where:

W_{in} = the mass percentage of a hazardous organic compound in the input waste flow;

W_{stack} = the mass percentage of the same hazardous organic compound found in the stack emissions.

If dioxins and furans would be formed in the preheater, they are decomposed when they reach the hotter areas of the kiln. The dioxins and furans formed in the early phases of the process are absorbed on the raw mix and their destruction is favored as the raw mix advances towards higher temperature areas. Here they are thermally destroyed or transformed into compounds with smaller molecular weight.

In the case of secondary combustion, when the temperature at the kiln inlet or in the calciner does not exceed 900 – 1100 ^{0}C, the factor helping to avoid the formation of dioxins and furans is the limitation of the halogen content in the alternative fuels. The halogen content (especially Cl) is strictly limited in all the fuels used in the clinker kiln, mainly for technological kiln operating considerations.

Dioxins and furans destroyed in the combustion installation at certain temperatures can be formed again if the conditions are met, by the so-called "de-novo synthesis", in the temperature range of 200 – 400 ^{0}C. In order to prevent this process, the flue gases leaving the burning installation should be cooled down rapidly. This happens with the flue gases leaving the kiln, which are cooled down and humidified in the conditioning tower before entering in the bag filter or ESP [6].

4. Dioxin and furan emissions monitored at the clinker kilns of cement plants

Due to the high flame temperature, dioxins and furans are destroyed if the fuels are fed in the main burner, and the hazard of their re-formation can be avoided by rapid cooling in the temperature range of 450 – 200 ^{0}C. With all these precautions, the use of alternative fuels does not result in an increase of dioxin and furan emissions, as highlighted by the data presented below.

A group of 8 international cement companies, with a production of more than 300 million tons

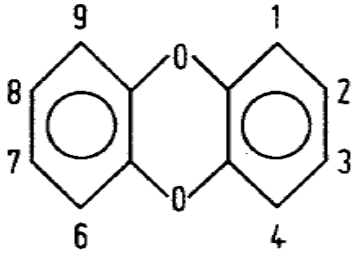


Fig. 1 - Basic structure of polychlorinated dibenzodioxins .
Structura de bază a dibenzodioxinelor policlorurate.

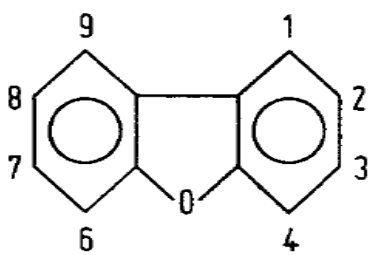


Fig. 2 - Basic structure of polychlorinated dibenzofurans.
Structura de bază a dibenzofuranilor clorurați.

of clinker, have reported in the last period the results of over 500 dioxin and furan measurements carried out in a large number of countries – with most production technologies and using a wide range of waste-based alternative fuels [4]. Some of the values are included in the graphs below.

These detailed investigations and measurements were performed on a large number of kilns of various types – long kilns, Lepol, suspension preheaters kilns, with or without calciner, covering various technologies – wet and dry process, use of alternative fuels and a wide range of hazardous and non-hazardous waste fed into the calciner, in the main burner and at the inlet of the kiln [4].

As shown in Table 1, the distribution of measured concentrations shows that 98% of them are below 0.1 ng TE/Nm^3 [4].

Figure 2 presents the values recorded upon spot measurements of dioxin and furan emissions at 243 kilns, for which the emissions are reported in normal conditions – pressure 1 atm, temperature 273.15 K, 10 % oxygen, dry gases [6].

The value in red is the limit imposed by the Waste Incineration Directive for clinker kilns using waste-based alternative fuels: 0.1 ng/Nm^3, taking into consideration the toxic equivalent TE (TE is calculated by multiplying the gravimetric concentrations of the various species of dioxins and furans with equivalence factors, depending on the degree of toxicity).

As it can be seen, the values of the emissions measured at most kilns are significantly below the emission limit value established by the Directive.

The kilns whose dioxin and furan emissions monitored are presented in figure 3 were grouped into categories, according to the level of emissions and the degree of thermal substitution. The results are presented in figure 3 [6].

As it can be noted, the breakdown of dioxin and furan measurements on the 4 levels of thermal substitution does not depend on the degree of thermal substitution.

The conclusion of the measurements is that the use of alternative fuels and alternative raw materials has no effect on the dioxin and furan

Table 1

Dioxin and furan concentrations measured by large cement companies
Concentraţii ale dioxinelor şi furanilor măsurate de mari companii producătoare de ciment

Producer / *Producător*	Period / *Perioada*	No. of measurements *Număr măsurători*	Range concentrations *Domeniul concentraţiilor* [ng/Nm^3]
Cemex	1999 - 2003	16	0.00049 – 0.024
HeidelbergCement	2001 - 2004	> 170	0.0003 – 0.44 (0.020)
Holcim	2001	71	0.0001 – 0.2395 (0.041)
Holcim	2002	82	0.0001 – 0.292 (0.030)
Holcim	2003	91	0.0003 – 0.169 (0.025)
Lafarge	1996 - 2003	64	0.003 – 0.231 (0.0207)
RMC	2000 - 2004	13	0.0014 – 0.0688
Siam	2003	4	0.0006 – 0.0022
Taiheiyo	-	67	0.011
Uniland	-	2	0.002 – 0.006

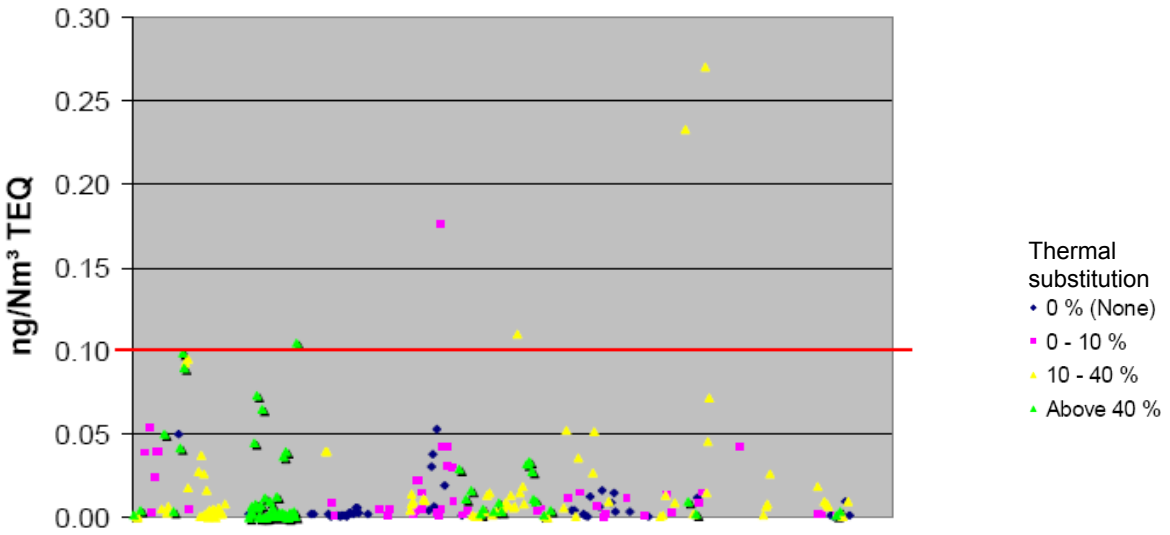
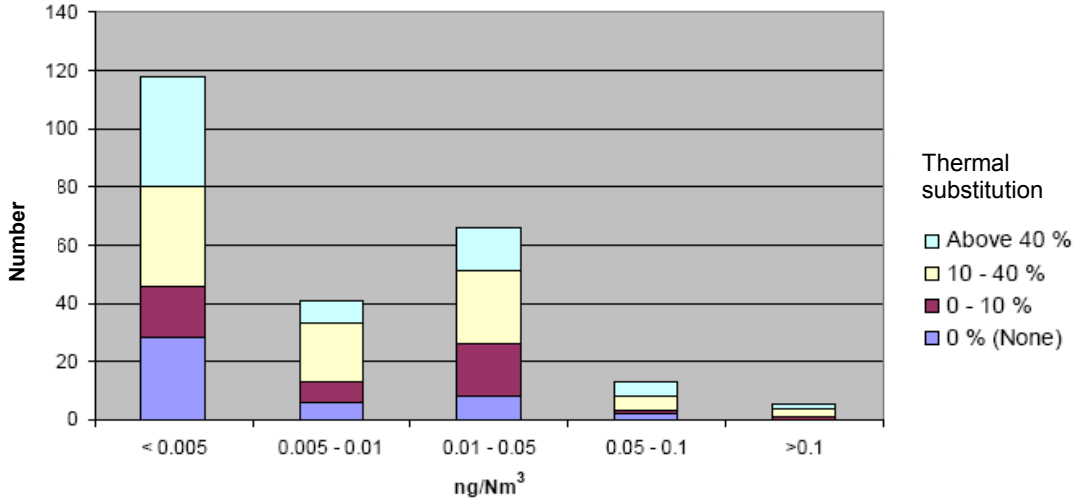


Fig. 2 - Values of spot measurements of dioxins and furans at kiln stack / *Valori ale măsurătorilor discontinue de dioxine şi furani la coş.*



Measurements: 243 Maximum value: 0.27
Average value: 0.016 Standard deviation: 0.31
Minimum value : 0.000012

Fig. 3- Breakdown of spot dioxin and furan measurements by levels of emissions and degrees of thermal substitution / *Încadrarea măsurătorilor discontinue de dioxine şi furani, pe nivele de emisii şi grade de substituție termică.*

Table 2

Dioxin and furan concentrations measured in cement plants in Romania
Concentrații ale dioxinelor şi furanilor măsurate la fabrici de ciment în România

Company *Compania*	Period *Perioada*	No. of measurements *Nr. de masurări*	Range concentrations *Domeniul concentrațiilor* [ng/Nm^3]
SC CARPATCEMENT HOLDING SA	2006 - 2012	17	0.005022 - 0.023731
SC HOLCIM (ROMANIA) SA	2008 - 2011	13	0.006 - 0.0148
LAFARGE ROMANIA	2008-2012	18	0.00145 – 0.0054

emissions. Regardless of the type of fuel used, traditional fossil fuels or alternative fuels, dioxin and furan emissions are in most cases much below the regulated limit.

Tests conducted in Australia since 2001 have shown that cement production is a minor source of dioxins and furans, with concentrations generally below 0.04 ng/Nm^3 [7].

In Canada, measurements reported in the literature are in the range of 0.01 – 0.14 g/year [7], which translates into 0.005 – 0.07 ng/Nm^3 , taking into account an average kiln of 1 million tons /year and a flue gas flow of 2000 m^3/t of clinker.

In the period 2006 – 2011, measurements of dioxin and furan emissions in Romanian cement plants were carried out, according to the provisions of the integrated environmental permits of each installation and of the requirements of EC Waste Incineration Directive 2000/76, transposed into the Romanian legislation by Government Decision 128/2002 as subsequently amended and supplemented.

The samples from the stack were taken and emissions of dioxins and furans were measured according to SR EN 1948:2008 and EPA 8280A:1996 – gas chromatography mass spectrometry method. The spot measurements results of the emissions of clinker kilns from Romania, obtained from measurement carried out by CEPROCIM [8] and based on data provided by CIROM, are presented in Table 2.

The analysis of these data, obtained by measurements in Romanian clinker kilns belonging to Carpatcement Holding, Holcim (Romania) and Lafarge Romania, shows that **all values** are considerably **below** the limit imposed by the Waste Incineration Directive and the Romanian legislation, at a 15-30% substitution rate of traditional fuels with alternative fuels.

5. Conclusions

The literature data resulting from measurements carried out at various installations worldwide, with various cement manufacturing methods, using different types of fossil fuels and waste-based alternative fuels, as well as the measurements on clinker installations from Romania lead to the same conclusion: **the dioxin and furan emissions of cement manufacturing processes using the current technologies are insignificant.**

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MANIFESTĂRI ŞTIINȚIFICE / SCIENTIFIC EVENTS

Date	Title and description	Location
28 – 31 October 2012 31 October – 2 November 2012	**Tenth International Conference on Superplasticizers and Other Chemical Admixtures in Concrete** **Twelfth International Conference on Recent Advances in Concrete Technology and Sustainability Issues** **Contact:** Gordon D. Brearley International Conference Organizing Committee Ottowa, ON Canada K1A 0G1 **Website:** http://www.intconference.org **E-mail:** gordon.brearley@rogers.com **Phone:** (613) 992-6154	**Prague Marriott Hotel** **Prague, CZECH REPUBLIC**
3 – 4 December 2012	**Third Ibero-Aericam Congress on SCC** **Polytechnic University of Valencia, Spain** The congress will bring together technicians, designers, researchers and scientists to promote a better understanding on common interests ranging from the most recent developments in components materials, to construction processes or structural performance. The symposium is an **opportunity** to share **advanced** results and experiences related to self-compacting concrete. **Contact:** Prof. Pedro Serna Polytechnic University of Valencia Camino de Vera 46071 Valencia, MI Spain 48331-3439 **Website:** http://www.autocompacto.net **E-mail:** pserna@cst.upv.es **Phone:** +34 650876595 **Fax:** +34 963877569	**Valencia, Spain**

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