FIRST EVALUATION OF PCDD/FS RELEASES TO THE ATMOSPHERE FROM THE MANUFACTURE OF CEMENT IN SPAIN

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Introduction

In the frame of Spanish dioxin inventory (1), it is supplied a first estimate of emissions of dioxin and furans from the cement manufacture sector. It has been made through the data obtained in an intensive monitoring program during 2001, where a detailed information about raw materials, gas filtration systems and temperature distribution was provided by each installation in collaboration with our technical group. The objective was to elaborate a preliminary emission factor according to real samples, operational conditions and data production.

In this paper we present the result of this first step of sampling program elaborated in 20 cement clinker , 18 dry and 2 wet processes, corresponding to 40% of the sector, kilns where only the manufacture process was evaluated and no hazardous wastes were used as secondary fuels in co-combustion. The reporter concentrations refer to 22 PCDD/Fs emissions measured. Emission factors have been obtained with real data and preliminary global estimations show that the contribution of this production activity is not significant in the dioxin release to the atmosphere. Special attention has been presented in the distribution of isomers where interesting correlation has been found.

Materials and Methods

Sector Description

There are four different types of manufacturing processes depending on the way in which the material is processed before being fed into the clinker kiln, that is, the dry process, semi-dry process, semi-wet process or wet process. In Spain there were 36 cement facilities with 58 cement clinker kilns, 6 wet, 4 semi-dry and the rest work in dry processes.

In the dry process, the raw material is fed into the kiln in a dry, powdery from. The kiln system includes a cyclone tower for heat exchange in which the material is preheated in the presence of gases from rotary kiln. The limestone decarbonation process (calcination) could be almost finished before the material is fed into the kiln, if a combustion chamber is installed into which part of the fuel is fed (precalciner kiln). In the wet process, which is normally used for raw materials that have a high moisture content, the material to be fed into the kiln is prepared by wet-grinding, and the resulting paste, with a 30%-40% water content, is fed into the highest end of the inclined rotary kiln. In the semi-dry and semi-wet processes, the material to be fed into the kiln is obtained by respectively adding or removing water (filter presses) to obtain pellets having a 15%-20% moisture content which are placed on moving grates through which the hot gases from rotary kiln are force-fed.

Measurement Methodology

The concentrations of PCDD/Fs were measured under usual operation conditions, sampling and analysis were performed according method UNE-EN 1948(1,2,3). All data have been expressed to

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normal conditions (273°K, 101, kPa, 10% O $_2$ dry gas). The distribution of temperature and description of the gas cleaning systems were pointed in a questionnaire filled up by the technical responsible of each installation to correlate the final results.

Results and Discussion

PCDD/Fs emissions and emission factors

The concentration of PCDD/Fs emissions varied between 5,63E-4 to 4,72E10-2 ng I-TEQ/Nm³, with a mean value of 0,00695 ng I-TEQ/Nm³. Taking into account the clinker and cement production of this 20 installations during 2001, 18,08 ng I-TEQ/Tm clinker and 14,464 ng I-TEQ/Tm cement are the emission factors obtained.

We have considered a production of 32 Millions of Tm of clinker and 40 Millions of Tm of cement during the year of this study (data from the sector), if we apply these factors to all the installations, we obtain a preliminary data of the annual contribution of this sector: 0,578 g I-TEQ/y. (Table 1)

Table 1	. Preliminary	data	from	measurements
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Mean Value Emission ng I-TEQ/Nm ³ (n=20)	Emission Factor ng I-TEQ/Tm clinker	Emission Factor ng I-TEQ/Tm cement	Annual emission (2001) g I-TEQ/y
0,00695	18.08	14.464	0,578

Relationship between temperature conditions and PCDD/Fs emissions

We have not found special relationship between temperature conditions of cleaning systems and I-TEQ PCDD/Fs emissions. Only, if we represent the decreasing of temperature after the gas cleaning system and the total homologues generated, we can see that if the decreasing is higher than 50 °C, the installations appear with lower total homologue groups emissions. (Figure 1). This observation will be taken in account in the next measurement program, but it doesn't appear relevant with I-TEQ content.



Figure 1. Generation of total PCDDs/Fs in 22 measurements in relation with temperature difference before and after cleaning systems.

Typical Patterns and Correlation between I-TEQ 2,3,7,8-TCDFs, I-TEQ 2,3,4,7,8-PeCDF and I-TEQ total

The 2,3,7,8 PCDD/Fs (pg/Nm³) congeners of each installation are plotted in Figure 2, and the mean isomer distribution in I-TEQ is shown in Figure 3. In this pattern we can see the mayor contribution of PCDFs, basically of 2,3,7,8-TCDF and 2,3,4,7,8 PeCDF to the total I-TEQ.





Figure 2. 2,3,7,8 PCDD/Fs congeners (pg/Nm³)

Figure 3. Mean Pattern of cement kilns sampled (pg I-TEQ/Nm³)

The relationships between total and 2,3,7,8-TCDF and 2,3,4,7,8-PeCDF I-TEQ values have been investigated by some authors (2,3,4). We have obtained a positive correlation between those isomers that are represented in Figure 4 and 5. These correlations could be expressed by the following expressions:

- In the case of 2,3,7,8.TCDF, we have found a multiplicative model with a correlation

coefficient = 0.955614 and a R. squared = 91.1288 percent, that represents statistically a significant relationship at a 99% confidence level. The equation of the fitted model is:

(a) Ln [I-TEQ of PCDD/Fs]= 1,2793 + 0,873064*ln[2,3,7,8-TCDF]

– In the case of 2,3,4,7,8-PeCDF, a square root-X model yields the highest correlation coefficient of 0,987364 with R-squared of 97,4888 percent. These results indicate a strong relationship between I-TEQ of PCDD/Fs /Nm³ and I-TEQ of 2,3,7,8-PeCDF, using equation:

(b) [I-TEQ of PCDD/Fs]= -5,18919 + 9,5446*sqrt [2,3,4,7,8-PeCDF]



Figure 5. Correlation plot of (b)

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The correlation plot of 2,3,4,7,8 values from the prediction by equation (b) and the measurement are shown in Figure 6, where only two samples don't prove this lineal model. These measurements correspond to wet processes. The equation of the fitted model is:

 $[I-TEQPCDD/Fs]_{measured} = -4.32216 \text{ E-7} + 1.0 * [I-TEQ PCDD/F]_{predicted}$ Correlation Coefficient = 0,987364 R-squared = 97,4887 percent



Figure 6. Predicted and measured PCDD/F I-TEQ/Nm³ values applying lineal model (b)

Conclusions

- As we can see from these preliminary results, the PCDD/Fs emissions to the atmosphere due to cement manufacture are very low.

- It has been obtained emission factors based in real sampling analysis in 40% of total kilns. In a next future it will be extend to 100% through the monitoring program of spanish inventory.

- It has been established a typical and stable distribution of toxic PCDD/Fs isomers, where are relevant the contribution of furans, basically due to 2,3,7,8-TCDF and 2,3,4,7,8-PeCDF. Positive toxic correlations have been found with both isomers at measured level concentrations in dry processes, considering them as good substitute indices to TEQ values, simplifying and economizing the monitoring of these type of facilities. These conclusions must be confirmed in next sampling programs

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