GLOBAL ASSESMENT OF PCDD/F EMISSIONS FROM THE SPANISH CEMENT SECTOR. EFFECT OF CONVENTIONAL/ALTERNATIVE FUELS

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Introduction

This paper presents the results of the survey on polychlorinated dibenzodioxin and dibenzofuran (PCDD/F) emissions to the air in cement manufacture sector carried out in Spain over the period 2000-2003. It includes 89 samples from 41 furnaces, which represents 69.5% of coverage. It constitutes the subsequent stage of the monitoring program presented previously[1], enlarging number of facilities assessed as well as considering plants operating with both conventional and waste-derived fuels.
The purpose of this survey was to quantify the total emission of dioxins from cement manufacture sector, to study the effect of using waste-derived materials as alternative fuels on total PCDD/F emission and to calculate experimental emission factors. Finally, specific emission profiles were obtained for installations using both conventional fossil and residue-derived fuels and compared in order to establish the influence of fuel composition on PCDD/F releases.

Methods and Materials

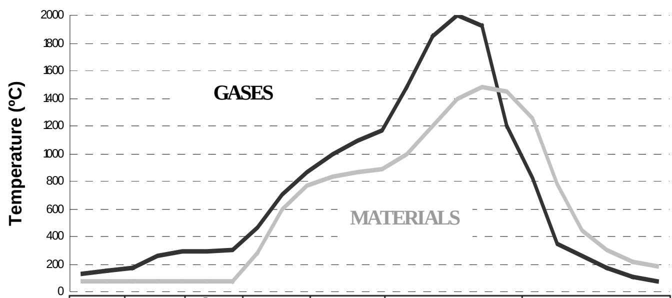
General Aspects of Process and Dioxin Formation: **The cement production process is well known and has been detailed previously in numerous documents[2]. In Spain the dry process is most abundant (98%). In contrast to other combustion facilities, the particular configuration employed allows the kiln to be fed with fuel substitutes or waste-derived materials if some aspects are considered[3]. Apart from conventional fuels (petroleum coke and coal), the**

use of residue-derived materials such as waste oil, tyres, organic liquid mixtures, plastics, sewage sludge, or sawdust, is gaining in importance within cement manufacturers. However, an increasing public concern is linked to this controversial activity, being frequently associated to likely higher emission of contaminants such as heavy metals or PCDD/Fs.

Dioxin formation is subjected to the presence of organic matter, chlorinating agents and a temperature range between 200ºC and 450ºC. A graph of the temperature profile for gases and materials and their typical residence times in each stage of a clinker kiln with cyclonic pre-heater and pre-calciner is shown in Figure 1.

In the last processing stages the gas stream flows through the pre-heating and gas cooling column, wherein temperatures fall into the "critical PCDD/F

Figure 1: Temperature profile in a clinker kiln



	Filter	Meal Grinding	Gas Cooling Column	Preheater	Precalciner	Rotary kiln	Cooler
Res. Time of gases	~ 15 sec	~ 2 sec	~ 10 sec	~ 10 sec	~ 3 sec	~ 10 sec	~ 1 sec
Res. Time of materials	60 sec-30 min	30 sec-30 min		~ 50 sec	~ 5 sec	~ 30 min	~ 30 min

window". This would explain potential formation, regardless of being a high-temperature combustion process.

Fossil fuel employed may incorporate aromatic hydrocarbons in its composition, such as benzene and phenol compounds, which may lead to formation of chlorinated ring structures in the presence of a chlorinating agent. Substitutions are thought to occur through a Deacon's mechanism of reaction, providing Cl_2 needed from HCl available at an optimal temperature of 400ºC[4]. Such chlorinated structures may then promote thermolytic formation of PCDD/Fs onto the active surface of the carbonaceous particulate matter. Alternatively, *de novo synthesis* with a catalytic agent being present such as $CuCl_2$ has also been proposed to explain PCDD/F formation onto the active surface of the carbonaceous particulate matter[5].

Cement Manufacturing in Spain: **Spanish cement manufacture sector has substantially improved in its development in recent years. In 2002 production figures reached 40.2 Mg of finished product. Currently, the sector comprises 36 facilities owned by 21 different companies. Since several kilns are possible in each plant, the total number of furnaces accounts for 59, 48 of which are being operated on dry (81%), six on semi-wet (10%) and five on wet process (9%). Petroleum coke (88%), coal (8%) and gas (< 5%) are the fuels more commonly used. Certain residue-derived materials are being also added to the aforementioned fossil fuels prior loading into the kiln. The set of results evaluated in this study were 89 samplings, 58 using conventional fuels, and 31 working with alternative ones.**

On a regulatory scale, Directive 2000/76/CE, on the incineration of waste, lays down a maximum PCDD/F emission value of 0.1 ng I-TEQ/Nm^3 for those facilities using hazardous waste materials as alternative fuels. In addition, more restrictive measures are set in regulatory framework of most counties in Spain. The amount of heat released from the use hazardous materials will not overpass 40%, being the limit value of 0.1 ng I-TEQ/Nm^3 applicable in all cases.

Methodology: **In order to correlate the total dioxin emission and operational parameters, plant operators completed an extensive questionnaire. Information related to Air Pollution Control Device (APCD) systems (bag filter, electrostatic precipitator) temperature distribution, chlorine content, particulate emission, SO_2 emission was recorded. Conventional fuels used were coke, coal and fuel-oil. Special attention was paid on the use of alternative fuels. In this case, fuel type and composition, input location (main burner, precalciner/preheater kilns) and temperature distribution were considered of main interest. Types of waste materials used as fuels were:**

- **waste oils**
- **residual organic solvent mixtures (varnish wastes, paints, cleaning wastes, photograph liquids)**
- **used tyres (entire/pieces)**
- **light fraction of end-of-life vehicles**
- **animal fatty materials**
- **carcass meal from animal origin**
- **sawdust/woodchip**

Sampling and analysis were made in accordance with UNE-EN 1948-1,2,3 and final results were expressed in normalized conditions (10% O_2 content, 101.3 kPa, 273 K)

Results and Discussion

Quantitative Approach: **Levels of PCDD/F emission in ng I-TEQ/Nm^3 are showed in Figure 2a. Maximum, minimum and mean values are given in Table 1. The values of PCDD/F emission in all samples analysed were far below 0.1 ng I-TEQ/Nm^3. Regarding kilns being operated with conventional fossil fuels large dispersion of data was noticed in some cases, even when similar operating conditions are supposed. Related observations have been previously reported[1].**

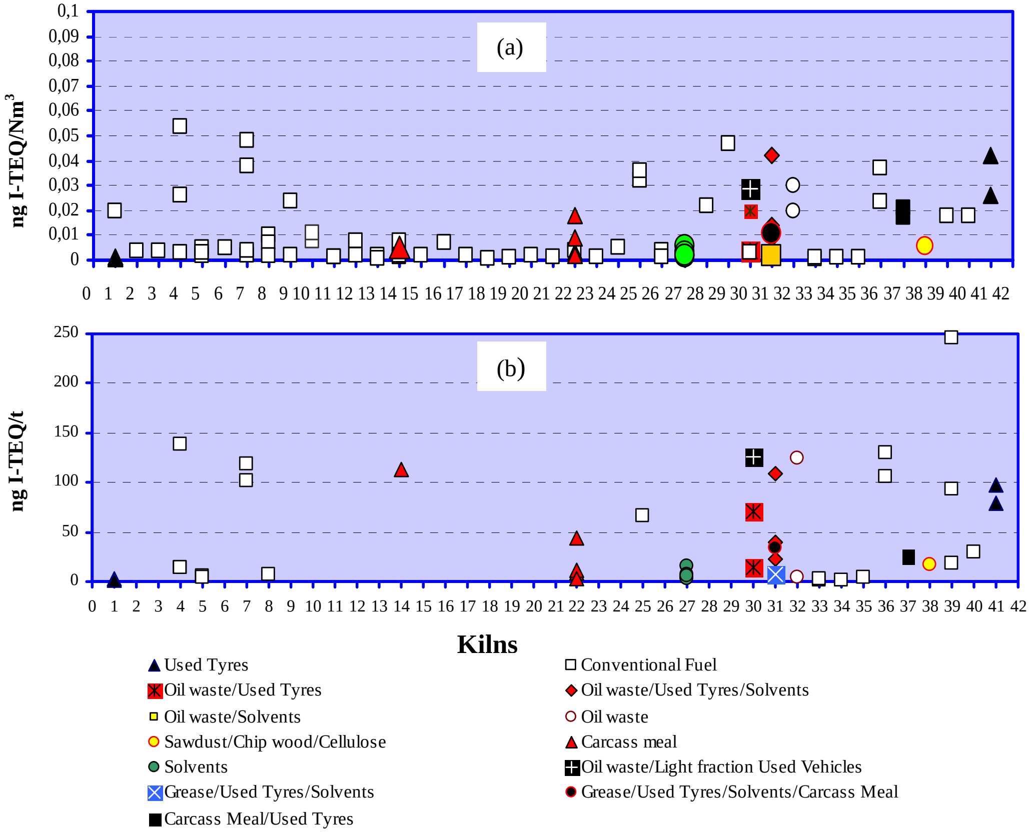
For those kilns using residue-derived fuel, range of emission (Table 1) was quite comparable with that obtained for conventional feedings. According to these results, no evidence of higher PCDD/F emissions when using alternative fuels can be concluded, what may suggest a fully optimisation of the substitution process. Considering annual production figures of 30 and 40 million tonnes of clinker and cement, respectively (data of year 2002), the annual emission obtained was 1.07 g I-TEQ/yr. Although this value is higher than that reported in our previous work (0.578 g I-TEQ/yr), it should be considered as more representative since number of facilities has been substantially enlarged. It is important to state that present value is about 3-fold lower than the corresponding estimated for Spain in the European Dioxin Inventory (3.6 g I-TEQ/yr).

When comparing with other European countries with similar production figures, Germany, 4.88 g I-TEQ/yr, United Kingdom, 1.71 g I-TEQ/yr, Spanish value is between 1.7 and 4.9 fold lower.

On a similar approach, emission factors per tonne of clinker and cement were also calculated, average value being of 36.53 and 28.82 ng I-TEQ/t respectively. Emission factors for kilns evaluated are plotted in Figure 2b, with minimum, maximum and mean values listed in Table 1. No higher values for plants co-incinerating waste materials were realised.

Homologue Distribution Profiles: A comparison of homologue distribution profiles between conventional and alternative fuels was also considered. Regarding conventional fuels, no significant differences with respect to previous data[1,6] were identified, with major contribution of 2,3,7,8-TCDF and 2,3,4,7,8-PeCDF. Figure 3a shows some examples of average homologue profiles for different alternative feedings. In this case, excepting for carcass meal, quite different patterns are noticed, with large variations according to type of materials.

Figure 2: (a) PCDD/F emission (ng I-TEQ/Nm^3) and (b) Emission Factor (ng I-TEQ/t clinker)



- Alternative Fuel	**0,83 – 133,01**
- Mean Value	**36,53**

Finally, the effect of APCD system on homologue profile is illustrated in Figure 3b. For a particular kiln being partially fed with used tyres, different profile was obtained when using electrostatic precipitator or hybrid filter (electrostatic precipitator + filter bag) as APCD system, what may suggest different PCDD/F formation pathways. In this sense, significantly lower PCDD/F emissions were recorded for the hybrid option.

Experimental data allow confirming cement manufacture sector as a non-relevant source of PCDD/F in Spain. According to our observations, there is no evidence of higher PCDD/F emissions when residue derived materials are incorporated into the clinker kiln as alternative fuel.

Table 1: PCDD/F emission range, annual emission and emission factor calculated.

Range of emission (ng I-TEQ/Nm^3)	
- Conventional Fuel **- Alternative Fuel** **- Mean Value**	**0.0002 - 0.054** **0.0004 - 0.049** **0.01**
Annual Emission (g I-TEQ/yr)	**1.06**
Emission Factor (ng I-TEQ/t clinker)	
- Conventional Fuel **- Alternative Fuel** **- Mean Value**	**0.67 – 246** **0.83 – 133** **36.5**

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Figure 3: Average homologue profiles: (a) conventional vs alternative fuel and (b) effects of APCD systems.