# EVALUATION OF CATALYTIC EFFECT OF CEMENT RAW MATERIAL AT VERY LOW POLLUTANT CONCENTRATION

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**Abstract**
Nowadays the use of waste as secondary fuel in clinker kilns is an extensive practice but the interaction between cement raw material (CRM) and the combustion gases of the fuels has not been studied extensively. Because of that, in this work the effect of the interaction of some pollutants and CRM is studied in a laboratory furnace. The temperature used in the interaction is 300ºC, similar to the temperature at the cyclones in a cement industry.
The pollutants are studied at very low concentrations, similar to those observed in industrial furnaces.

## Introduction

In industrial incineration systems concentrations of about 250 compounds in the order of 50 ng/Nm$^3$ were observed [1]. These compounds include biphenyls, diphenyl ethers, dioxins and furans. Zimmermann et al. indicate values of the order of 1-500 μg/m$^3$ in a pilot plant incinerator for the aromatic hydrocarbons [2].
On the other hand, several authors indicate the importance to get in the laboratory similar concentrations to those found in industrial systems, and they found that the formation of dioxins from precursors is much more important in laboratory conditions than the de-novo pathway [3].

Stanmore also indicates that there are great differences between the reaction rates measured in laboratory systems and those measured in industrial furnaces [4]. Finocchio et al. indicate that the runs performed by several authors studying the destruction of pollutants are not representative because of the high concentrations usually used in the laboratory [5].

In runs carried out in previous papers the pollutant concentration is probably several orders of magnitude higher than those found in an industrial equipment [6,7]. For sewage sludge decomposition the level of pollutants produced are approximately 1000 mg/kg sludge decomposed, that bearing the experimental conditions in mind (100 mg sludge, 300 mL/min), produces gas concentrations around 10000 - 100000 μg/m$^3$.[8]

## Materials and Methods

With the objective to study the behaviour of pollutants in conditions close to those observed in industrial equipments, a system based on a diffusion cell has been implemented (diffusion delivery system or DDS[13]). In the system it is necessary to dispose of a small amount of the pollutant to be studied, for example phenol or naphthalene, in a cell that is inside a furnace with known and controlled temperature. The cell is connected by using a tube of known length and diameter to the main gas flow (see Figure 1). Inert gas or air is used, in such a way that the gas is impregnated by the pollutant(s) to be studied. Assuming that the gas surrounding the pollutant is in equilibrium with the pollutant, the partial pressure of the compound equals its vapour pressure at the temperature of the furnace. The pollutant diffuses to the main gas flow at a rate that can be controlled by the length and diameter of the tubing. A higher length or lower diameter will reduce the concentration of the pollutant in the main gas.

It is possible to estimate, by using correlations of the vapour pressure as the Antoine law, and the diffusion laws, the amount of pollutant that arrives to the main gas flow, but it will be better for the present study to experimentally determinate the obtained concentration.

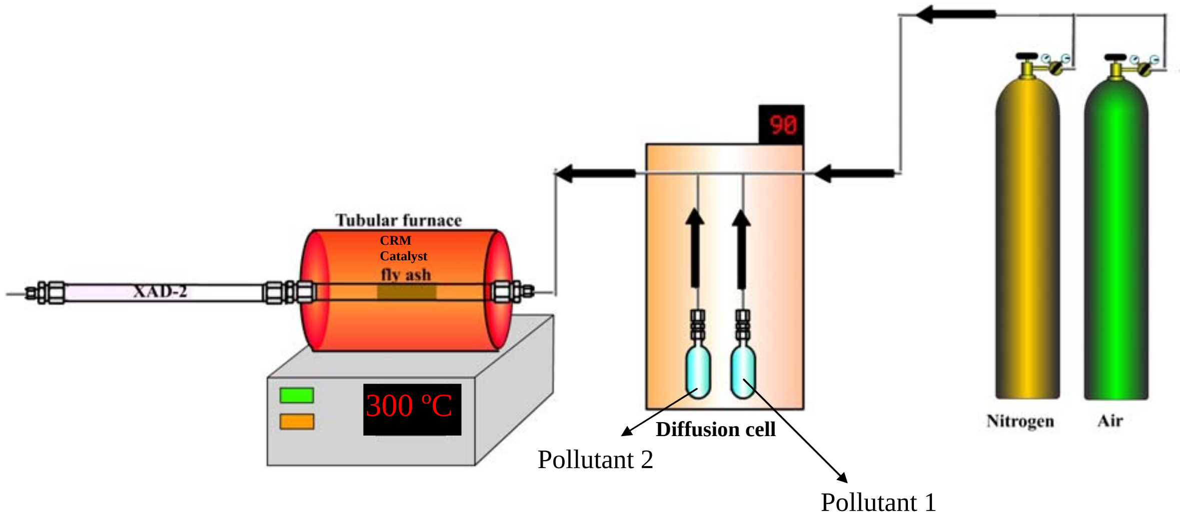


Figure 1. Experimental diffusion cell.

In the diffusion cell it is possible to dispose of solids with a certain vapour pressure or liquids. Furthermore, it is possible to run experiments where the liquid is not a pure pollutant, but the liquid fraction collected in a previous combustion or pyrolysis run.

Due to the very low concentrations achieved with the system described, the runs are carried out for a very long period of time (12-24 h), in order to get a considerable amount of analyte. The gas impregnated with the pollutant is passed through a furnace in which different beds (catalysts, fly ashes, cement raw materials…) could be deposited in order to study the interaction. XAD-2 resin is disposed at the exit of the system to get the pollutants that later are extracted with the appropriate solvent to be analysed.

Only naphthalene has been studied in this work but another polyaromatics have being consired, like phenanthrene as a precursor of PCDD/F production or PCDD/F directly.

## Results and Discussion

The first runs have been performed by using naphthalene in the diffusion cell. First of all, a calibration of the equipment has been performed in order to know the exact amount of naphthalene evolved from the cell. The diffusion cell was maintained at 90 ºC and runs were performed at different total times. Figure 2 presents the results. As can be observed, the linearity is almost fulfilling.

Bearing in mind that a total of 100 mL/min of air are fed to the system, the results obtained imply that in the furnace an atmosphere of about 10 mg/Nm$^3$ is achieved, that is 1000 or 10000 times lower than that obtained previously in other equipment [6,7].

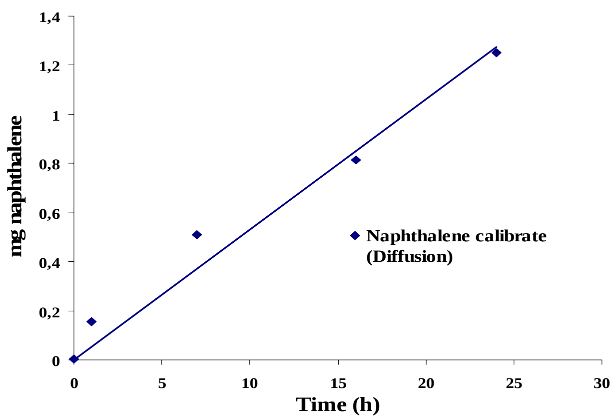


Figure 2. Calibrate of naphthalene diffusion in the cell.

Naphthalene is one of the most volatile PAHs, and so the concentration for other PAHs will be much minor. Also the use of a lower temperature or longer/narrower tube would diminish the concentration of the pollutant even more. For example, working with phenanthrene (solid at 90 ºC, temperature of the cell) we can get concentrations of about 10 μg/Nm$^3$.

Some preliminary runs have been performed in the equipment introducing in the tubular furnace, on the one hand, cement raw material, and, on the other hand, a commercial catalyst used in the automotive escapes. This last material has been characterised by elemental analysis (6.5 % N, 72.5 % C, 6.2 % H, 7.6 % S) and ICP-MS analysis for metal content, where it is found that the catalyst is Pt based probably contaminated with La. Both runs were performed at 300 ºC in the catalyst zone and using 0.3 grams of solid. Runs at different total time were performed. Figure 3 presents the results.

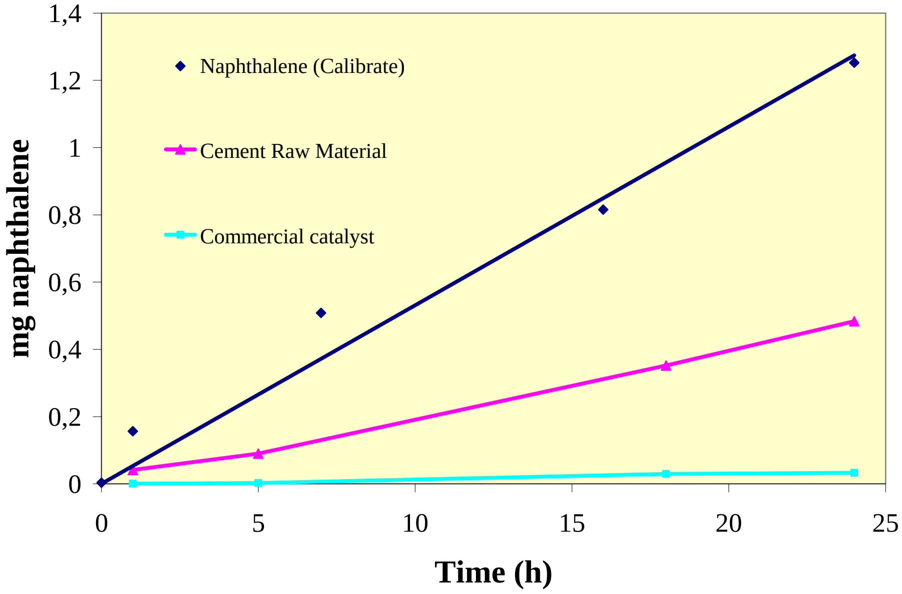


Figure 3. Naphthalene analysed after its diffusion for different total time with and without a bed inside the furnace

In the results it is clear the high efficiency of the commercial catalyst for the elimination of naphthalene, and also a catalytic activity is found for the cement raw material. It is possible that in the runs performed a longer time would produce a saturation of the capacity of the cement raw material, but it has not been observed.

The catalytic effect of elimination has been quantified calculating the percentage of naphthalene eliminated after the experiment runs 24 hours, comparing with the calibrate results. The solids (CRM and catalyst) were extracted and analysed to prove the adsorption effect on them, and the results (see Table 1) show it is not significant. These results reveal the elimination is due to the total destruction of the aromatic.

| | **Elimination %** | **Adsorption %** |
|---|---|---|
| **Cement Raw Material** | 61 % | 0.04 % |
| **Commercial Catalyst** | 94% | 0.006 % |

Table 1: % Elimination and % adsorption of solids.

The cement raw material has already be found as a material able to destroy some pollutants [9]. Probable due to its composition in metal oxides like those of Al2O3, CaO, Fe2O3, P2O5 or SiO2, and also in a lower amount MgO, TiO2, Cr2O3, ZnO, CuO. Yamada et al. indicate that the continuous injection of Fe2O3-based catalysts is an efficient method for the elimination of dioxins and furans and their precursors, and also those catalyst based on Fe2O3/CaO where the oxidation power is increased due to the presence of CaO [10,11]. The cement raw material has these oxides as major constituent, and, although its more efficient temperature range is 400-450 ºC, the effectiveness is also due to other basis constituent, forming a material that is able to produce dechlorination and destruction reaction on the material surface, where organic volatiles could be retained due to the high alkalinity of the medium [12].

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