

## ANALYSIS OF THE CATALYTIC FORMATION OF PCDD/Fs DURING THE SINTERING PROCESS

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### Introduction

Since the discovery of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in the flue gas and fly ash of municipal waste incinerators (MWI) by Olie and co-workers in 1977<sup>1</sup>, considerable efforts have been made to learn more about the formation and destruction of these compounds during incineration processes. Such an information was essential in order to reduce the formation of chlorinated aromatics from MWI and to apply appropriate abatement systems. Owing to the improved abatement technologies in the MWI, this process is no longer a major source of PCDD/Fs. Other processes, like metallurgical industries, become now the most important source of these pollutants. Among these, the sintering process is already recognized as the most important source of PCDD/Fs in different countries. Particular attention to this process is needed to further reduce the PCDD/Fs emissions in the environment.

The sintering process is an essential step in an integrated iron metallurgical plant. In this process, the iron ore is converted to larger fragments acceptable in the blast furnace. The sinter plant consists of a 50-100m long, 3-5m wide, horizontal strand, which supports the feed (hematite ores, cokes and lime) and is slowly moving. Burners initiate the process by igniting the feed layer on top and ambient air is sucked through the layer that moves the burning front downwards. The sinter is then cooled and broken before its use in the blast furnace. Separate chambers called wind boxes, located below the strand, collect the off-gas prior to filtering in appropriate dust collectors. Although all ingredients needed for the PCDD/Fs formation are present, the detailed mechanism as well as the place of PCDD/Fs formation in the sintering process remain unknown.

In this study, particular interest is given to the grid which supports the feed and to its potential catalytic effect on the PCDD/Fs formation during the sintering process. Composition analysis of the industrial grid has been carried out. This analysis reveals a content in chromium of about 25 wt.%. To our knowledge, no chromium catalytic activity concerning the PCDD/Fs formation has been clearly demonstrated. However, different studies on the catalytic ability of the chromium show that this element takes place in dehydrogenation reactions giving cyclisation and also in oxidation reactions<sup>2</sup>.

In a previous study<sup>3</sup>, the potential catalytic ability of the grid concerning the PCDD/Fs formation was already explored. Thermal laboratory experiments simulating a 'de novo' synthesis were carried out with fly ash collected in the electrostatic precipitator of the sinter plant and known to be very active in 'de novo' thermal experiments<sup>4</sup>.

Three kinds of experiments were carried out: i) fly ash without grid filings which serves as reference, ii) fly ash mixed with 10 wt.% grid filings and iii) fly ash mixed with 10 wt.% oxidized grid filings.

The three kinds of experiments were not significantly different, the addition of grid filings has no influence on the PCDD/Fs formation on the sinter plant fly ash. It was thus not possible to affirm from these results that the grid has a role in the PCDD/Fs formation in the industrial process.

At the industrial scale, dust sampled on the grid, at the place where it rises back to the loading

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section, presented PCDD/Fs concentrations logarithmically intermediate between the values present in the dust from the sinter cake and the values found on dust in the wind boxes. The filings ability to form PCDD/Fs, although perhaps true, can be masked by the experimental conditions used in this study. Actually, the 'de novo' activity of the fly ash is so important<sup>4</sup> that the presence or not of the filings does not influence the PCDD/Fs amounts formed.

In the present study, new thermal experiments are performed with a less active matrix: graphite. In addition, the catalytic ability of  $\text{Cr}_2\text{O}_3$  is investigated. The PCDD/Fs homologue and isomer distributions are also examined to get a better understanding of the formation mechanism of these compounds.

## Experimental section

### *Oxidized filings*

Filings of the grid which supports the feed were collected by chipping the grid. These filings were preliminary oxidized in a flow of air at 400 °C during 3h before use.

### *Graphite*

Graphite from Fluka (purum, powder < 0.1mm) was used without any pretreatment.

### *Experimental apparatus*

5g of sample was packed into a horizontal glass tube reactor (16cm long, 3cm diameter) with glass wool as plugs. The tube was placed in a furnace and the samples were heated at 400 °C under a flow of technical air (100ml/min) during 2h. Products evaporating from the fly ash were collected using two washing bottles in series (100ml toluene cooled with ice). Each experiment was performed in duplicate or triplicate.

### *Cleanup*

The slightly modified EPA-8280 method was followed for classical PCDD/Fs analysis. Detailed method has been described previously<sup>4</sup>.

### *Analysis*

All analyses were performed by HRGC/HRMS using Mat95-XL high resolution mass spectrometer and Hewlett Packard 6890 Series gas chromatograph. The GC conditions were optimized to separate most of the PCDD/Fs (see previous study<sup>4</sup>). The mass spectrometer was tuned to a minimum resolution of 10000 (10 % valley), and was operated in a mass drift correction mode using FC-5311 to provide lock masses. The two most abundant ions in the chlorine clusters of the molecular ion were recorded for each isomer of native and labeled PCDD/Fs. The source temperature was set to 270 °C.

### *Identification and quantification*

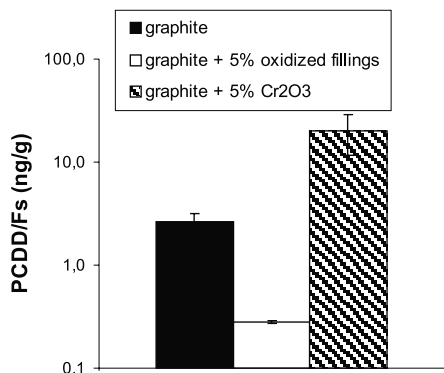
Most of the  $\text{T}_4\text{CDD-OCDD}$  and  $\text{T}_4\text{CDF-HpCDF}$  congeners were analyzed. No analyses of the species without chlorine or less than 4 chlorines were performed. Native concentration was determined by isotopic dilution using the 2,3,7,8 Cl-substituted labeled PCDD/Fs to quantify all the native isomers within homologues assuming equal response for all isomers within an isomer group and no isomer-selective losses during the clean-up. The isomers were identified according to Ryan et al<sup>5</sup>.

## Results and Discussion

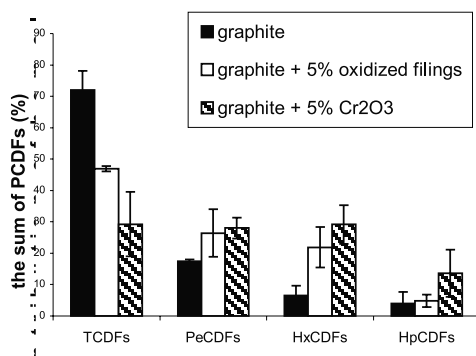
The catalytic ability of the grid in the PCDD/Fs formation was investigated by simulating De Novo synthesis. Thermal experiments with a less active source of carbon than sinter plant fly ash have been

performed at 400 °C during 2h. Graphite was mixed with 5 wt.% of oxidized filings or Cr<sub>2</sub>O<sub>3</sub>. In order to supply the necessary chlorine, 5 wt.% of NaCl was added to all the samples.

The total amounts of PCDD/Fs formed during the thermal treatment are presented in Figure 1. The graphite possesses a poor ability to generate PCDD/Fs. The addition of Cr<sub>2</sub>O<sub>3</sub> to this matrix rises the ability of the graphite to generate PCDD/Fs. Cr<sub>2</sub>O<sub>3</sub> can thus be considered as a catalyst in the De Novo formation of PCDD/Fs but seems less active than other metals like Cu<sup>2+</sup>. In another hand, the presence of the oxidized filings tends to reduce the amounts of PCDD/Fs formed from the graphite.



**Figure 1.** PCDD/Fs formation during thermal experiments, 400 °C, 2 h, air (100 ml/min), the error bars represent the mean variation between replicates.



**Figure 2.** PCDFs homologue distribution as a function of the content, 400 °C, 2 h, air (100 ml/min), the error bars represent the mean value between replicates.

Figure 2 presents the PCDFs homologue distribution obtained in the different thermal experiments as a function of the content (STCDF-HpCDF=100 %). The addition of filings shifts the distribution toward the more chlorinated species. The reduction of the amounts of PCDD/Fs observed with these filings does certainly not result from a preferential formation of less chlorinated species with fewer than 4 chlorine atoms, species which are not quantified in this study as mentioned in the experimental section. The presence of the oxidized filings leads to a no-formation or a destruction of the PCDD/Fs.

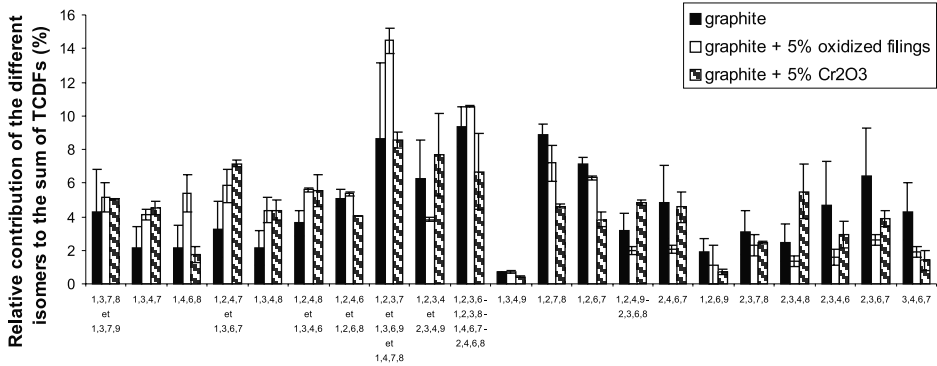
The addition of Cr<sub>2</sub>O<sub>3</sub> rises the amounts of PCDD/Fs generated from the graphite but also favors the formation of the more chlorinated species. Cr<sub>2</sub>O<sub>3</sub> acts certainly as a catalyst in the oxidative degradation of carbon, which is one step of the De Novo synthesis of PCDD/Fs, as well as in the chlorination reactions.

Full isomer distributions have also been calculated for the different experiments. The isomer distributions were calculated by setting the sum of each homologue to 100 % and calculating the relative contribution of each peak. Part of the results are presented in the Figure 3. These distributions are not influenced by the addition of filings or Cr<sub>2</sub>O<sub>3</sub> to the graphite. Actually, the differences found as a result of the different addition of filings or Cr<sub>2</sub>O<sub>3</sub> are small and in the same order of magnitude as the variation between replicates.

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**Figure 3.** Part of the TCDFs isomer distribution (400 °C, 2 h, air 100 ml/min). The error bars represent the mean variation between replicates.

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