

# FORMATION AND SOURCES II -POSTER

## PCDD/Fs AND SINTERING PROCESS: POSSIBLE INFLUENCE OF THE COKE MORPHOLOGY.

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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 by Kees Olie in 1977<sup>1</sup>, the formation of these toxic compounds has been studied intensively. Recent reviews summarized the most important trends and results<sup>2,3</sup>.

Two different pathways have been proposed to explain the presence of PCDD/Fs in the emissions of incinerators or other combustion processes: the synthesis from precursors and the *de novo* synthesis. The *de novo* synthesis consists of the PCDD/Fs formation from macromolecular carbon present in the fly ash. It concerns heterogeneous reactions between the gas phase and the fly ash catalyzed by some constituents of the fly ash such as copper and iron chlorides. The *de novo* formation of PCDD/Fs is supposed to be strongly correlated with the metal catalyzed oxidation of carbon in the fly ash<sup>4</sup>. The oxidative degradation of the carbon structure gives mainly gaseous products CO<sub>2</sub> and CO as well as, in a minor pathway, some small aromatic compounds including PCDD/Fs.

Although iron and steel industries are known to be an important source of PCDD/Fs in different countries<sup>5,6</sup>, most studies concerning the formation of these highly toxic compounds deal only with municipal waste incineration. Relatively few data are available for industrial and metallurgical processes, in particular for sintering plants<sup>7-13</sup>.

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 50-100 m long, 3-5 m 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 and located below the strand collect the off-gas prior to filtering in appropriate dust collectors.

The detailed mechanism as well as the place of PCDD/Fs formation in the sintering process remain unknown although all the necessary ingredients are present: carbon from the coke, oxygen in the air sucked through the cake, chlorine and catalytic metals available in the ores.

The coke added in the feed is the major source of carbon in the process for the *de novo* synthesis of PCDD/Fs. Different authors<sup>4,14-16</sup> have shown that the carbon morphology (amorphous-graphitic structure) is an important factor in the *de novo* synthesis of PCDD/Fs: the crystal lattice of graphite is obviously resistant to an attack of chlorine/oxygen to a greater extent than the other carbon samples which consist in part of amorphous carbon and of microcrystalline carbon with a degenerated graphitic structure of disoriented layers. The way of preparation of the coke (temperature and coking time) can certainly influence the structure of the cokes and thus perhaps their ability to produce PCDD/Fs by *de novo* synthesis.

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This study takes an interest in this fact and describes the thermal behavior of one graphite and two cokes differing by their coking time (9 or 15h at 1325°C) relating to the *de novo* synthesis of PCDD/Fs. The homologue and isomer distributions are also looked at to get a better understanding of the formation mechanism of these compounds.

## EXPERIMENTAL SECTION

**Cokes.** Two different cokes and one graphite were used in the different experiments. The two cokes differ by their coking time: 9h or 15h at 1325°C.

**Fly ash.** Fly ash was collected in the electrostatic precipitator of a Belgian sintering plant. All experiments were conducted with extracted fly ash in order to minimize potential interferences from adsorbed organic precursors and native PCDD/Fs. Prior to experiments, all fly ashes were Soxhlet extracted with toluene (2x24h), rinsed with hexane, and air-dried at room temperature. Only trace amounts of PCDD/Fs were found in the extracted fly ash.

**Experimental apparatus.** Around 5 g of sample (graphite, coke or mixture) 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 flasks in series (100ml toluene cooled with ice). The toluene from the cold traps was used for the Soxhlet extraction. Each experiment was performed in duplicate or triplicate.

**Clean-up.** The slightly modified EPA-8280 method was followed for classical PCDD/Fs analysis. Detailed method has been described before<sup>17</sup>.

**Analysis.** All analyses were performed by HRGC/HRMS using Mat95-XL high-resolution mass spectrometer and Hewlett-Packard 6890 Series gas chromatograph. Detailed analysis method, concerning the GC conditions and the mass spectrometer tuning, has been described before<sup>17</sup>.

**Identification and quantification.** Most of the T<sub>4</sub>CDD-OCDD and T<sub>4</sub>CDF-HpCDF congeners were analyzed. 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>18</sup>.

## RESULTS AND DISCUSSION

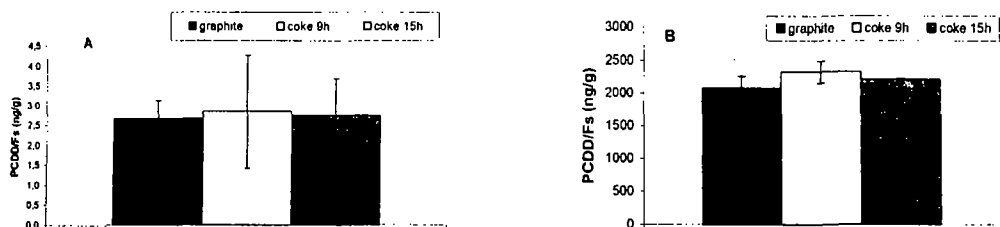
### Graphite and cokes examination

The graphite and the two cokes were examined for their PCDD/Fs content. The amounts found were very low: between 0.12 and 0.15 ng/g for the PCDDs and between 1.15 and 1.74 ng/g for the PCDFs. The PCDFs/PCDDs ratios, as well as the homologue and isomer distributions do not differ for the three types of samples.

### Comparison of the graphite and the two cokes relating to *de novo* synthesis of PCDD/Fs

Laboratory experiments were carried out with the three types of samples to simulate a *de novo* synthesis of PCDD/Fs. The experiments were performed at 400 °C during 2 h. In a first set of experiments, the samples were used directly and in a second set of experiments, the samples were preliminary mixed with 10 wt.% of extracted fly ash collected in the electrostatic precipitator of a sinter plant. This fly ash, known to be very active in *de novo* synthesis<sup>17</sup>, was added to the samples to bring the necessary catalysts. The results are presented in Figure 1.

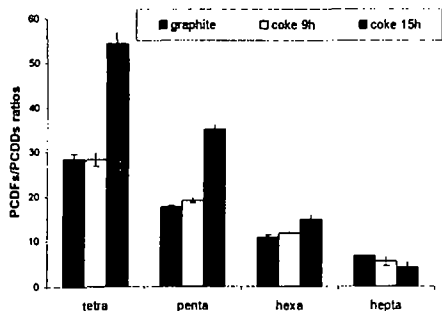
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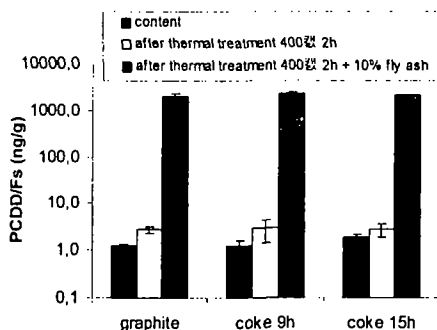
**Figure 1.** Total amounts of PCDD/Fs measured in the different experiments (A: 400°C 2h; B: 400°C 2h + 10 wt.% fly ash), mean value  $\pm$  range.

The nature of the carbon source has no influence on the global amounts of PCDD/Fs formed in the different experiments. The three samples present the same ability to produce PCDD/Fs by *de novo* synthesis.

Figure 2 presents the PCDFs/PCDDs ratios calculated for the different homologues in the case of the experiments performed at 400°C, 2h in the presence of fly ash. The graphite and the coke 9h present a same trend. For the coke 15h, the proportion of PCDFs produced is much higher, especially for the lower chlorinated families. A possible difference in the concentration of chemically-bound oxygen of three samples may be responsible for these different PCDFs/PCDDs ratios.



**Figure 2.** PCDFs/PCDDs ratios for the different chlorofamilies as a function of the carbon source (400°C 2h + 10wt.% fly ash), mean value  $\pm$  range



**Figure 3.** Global amounts of PCDD/Fs produced as a function of the thermal treatment, mean value  $\pm$  range

The homologue distributions obtained for the different experiments are dependent on the carbon source (not shown). The PCDD/Fs profiles for the coke 9h are always more oriented towards the lower chlorinated species than the profiles of the two other samples, resulting perhaps from less chlorine available on this carbon source. The isomers distributions (not shown) are not influenced by the nature of the carbon source for the experiments performed without fly ash, but when fly ash is added to the samples, some particular isomers are produced in a much higher proportion.

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In conclusion, concerning the global PCDD/Fs amounts produced, the three kinds of samples do not present important differences. Nevertheless, the PCDD/Fs produced during the thermal treatment present differences in the fingerprint and thus a deeper study of the results has to be carried out and will perhaps bring information concerning the mechanism of formation of the PCDD/Fs by the *de novo* synthesis.

### Effect of the addition of sinter plant fly ash

The effect of the addition of the fly ash to the samples is presented in Figure 3 (note the logarithmic scale). The PCDD/Fs content of the three samples, as well as the PCDD/Fs produced with the pure samples during the thermal treatment are very low in comparison with the huge amounts of PCDD/Fs produced when fly ash is added to the carbon sources. The amounts are multiplied by a factor greater than 1000 because of a simple addition of extracted fly ash collected in the electrostatic precipitator of a sinter plant. These results should caution against the recycling of the fly ash in the feed of the sintering process.

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