PCDD/Fs AND SINTERING PROCESS: A NEW CATALYTIC ROUTE ?

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INTRODUCTION

Since the discovery of polychlorodibenzo-p-dioxins (PCDDs) and polychlorodibenzofurans (PCDFs) in the flue gas and fly ash of municipal waste incinerators by Kees Olie in 1977[1], the formation of these toxic compounds has been studied intensively. Recent reviews summarized the most important trends and results[2,3]. 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.

Although iron and steel industries are known to be an important source of PCDD/Fs in different countries[4,5], 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[6-12]. Considering the very large gas flow volumes discharged from many industrial processes, dioxin pollution by these sources seems to be a serious problem. In Belgium, it can be estimated from the data by Wevers and De Fré[13] that, in 1995, the industry sector was responsible for 34% of the total dioxin emissions; among the different industries, 24% of the dioxin emissions estimated for the industrial sector comes from the sintering.

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, 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.

In this study, particular interest is given to the grating which supports the feed and to its potential catalytic effect on the PCDD/Fs formation during the sintering process. The PCDD/Fs homologue and isomer distributions are also looked to get a better understanding of the formation mechanism of these compounds.

EXPERIMENTAL SECTION

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. **Filings.** Filings of the grating which supports the feed were collected by chipping the grating. These filings were used in the experiments just as they are or were preliminary oxidized in a flow of air at 400 °C during 3 h.

Experimental apparatus. 5 g of sample (fly ash or fly ash + filings) 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 325 °C under a flow of technical air (100ml/min) during 30 min. 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[14].

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[14]). The mass spectrometer was operated in the electron impact ionization mode using selected ion monitoring. 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 T_4CDD-OCDD and T_4CDF-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[15].

RESULTS AND DISCUSSION

In this study, particular interest is given to the grating which supports the feed and to its potential catalytic effect on the PCDD/Fs formation during the sintering process. Composition analysis of the industrial grating 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[16].

Laboratory experiments

To explore the potential grating catalytic ability concerning the PCDD/Fs formation, thermal laboratory experiments simulating a 'de novo' synthesis were carried out. Grating filings were mixed with fly ash collected in the electrostatic precipitator of the sinter plant and known to be very active in 'de novo' thermal experiments (see previous study[14]). The experiments were performed at 325°C during 30min. Three kinds of experiments were carried out: i) fly ash without filings which serves as reference, ii) fly ash mixed with 10 wt.% filings and iii) fly ash mixed with 10 wt.% oxidized filings.

The results are presented in Figure 1. Although, the presence of oxidized filings seems to rise the ability of the fly ash to generate PCDD/Fs, considering the error bars, the three kinds of experiments are not significantly different and it is thus quite hazardous to affirm from these results that the grating has a role in the PCDD/Fs formation in the industrial process.

The PCDFs/PCDDs ratios were calculated for the different experiments and are presented in Figure 2. As it can be seen on the figure, the presence of filings in the fly ash does not promote the formation of PCDDs or PCDFs.

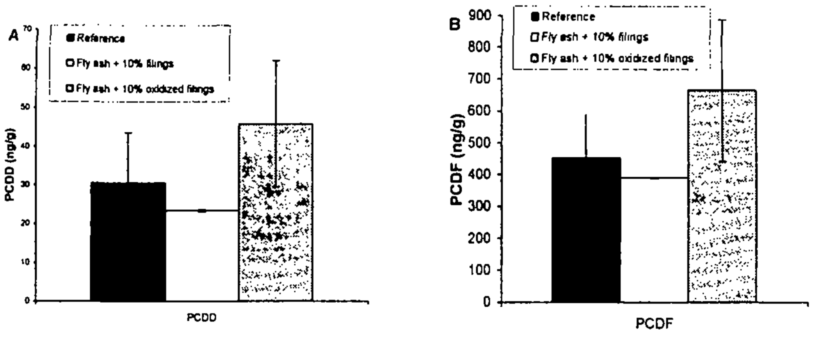
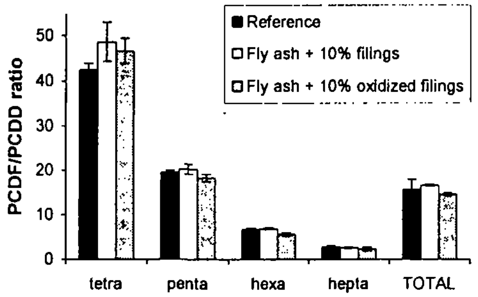


Figure 1. PCDDs (A) and PCDFs (B) formation during thermal experiments, 325°C, 30 min, air (100 ml/min), the error bars represent the mean variation between replicates.



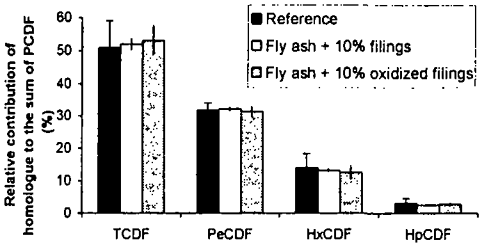


Figure 2. PCDFs/PCDDs ratios as a function of the filings content, 325°C, 30 min, air (100 ml/min), the error bars represent the mean variation between replicates.

Figure 3. PCDFs homologue distribution as a function of the filings content, 325°C, 30 min, air (100 ml/min), the error bars represent the mean value between replicates.

Figure 3 presents the PCDFs homologue distribution obtained in the different thermal experiment as a function of the filings content (ΣTCDF-HpCDF=100%). The addition of filings to the fly ash has no influence on the homologue distribution of the PCDFs. Actually, the differences found as a result of the different filings content are small and in the same order of magnitude as the variation between replicates. The same behavior was found for the PCDDs (not shown).

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. These distributions are not influenced by the addition of filings in the fly ash (not shown).

As it can be concluded form the previous results from laboratory experiments, the addition of grating filings has no influence on the PCDD/Fs formation on the sinter plant fly ash. However, it has been showed that, at the industrial scale, dust sampled on the grate at the place where it rises back to the loading 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 concerning the PCDD/Fs formation, although perhaps true, can be masked by the experimental conditions used here and not appear in these laboratory experiments. Actually, the 'de novo' activity of the fly ash is so important that the presence or not of the filings does not influence the PCDD/Fs amounts formed. New experiments with a less active source of carbon must be performed in the lab. On the other hand, the fly ash and the filings were just manually mixed together so the contact between the reagents and the catalytic sites was perhaps not good enough. Additional research has therefore to be carried out in this field.

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