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# The formation of polychlorinated dibenzo-*p*-dioxins/ dibenzofurans from carbon model mixtures containing ferrous chloride

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# Abstract

The potential to form polychlorinated dibenzo-*p*-dioxins/furans (PCDD/F) was investigated in carbon model systems containing ferrous chloride tetrahydrate and a matrix representative of that found in particle emission from the catalytic extraction process (CEP) for wastes. Various types of carbons were used resulting in different PCDD/F yields but, with one exception, similar homologue distributions. Due to the similarity between the turbostratic structure of the carbon in the representative CEP dusts and the carbon blacks used in the model system, experiments were performed using two carbon blacks (termed CBA and CBB). On a mass basis, CBB was more reactive over the temperature range of 275–325°C and reaction times of 20–60 min in the formation of PCDD/F; as well as more adsorptive in terms of the desorption of PCDD/F. On a volume basis, the reactivities and adsorptivities were similar. A maximum in PCDD/F formation occurred at an oxygen concentration of 2% in nitrogen. © 2000 Elsevier Science Ltd. All rights reserved.

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# 1. Introduction

Processes other than combustion/incineration and metals other than copper have the potential for the formation of polychlorinated dibenzo-*p*-dioxins/furans (PCDD/F). Such processes include a variety of metal-lurgical and related processes (many of these operate under conditions of a low oxygen concentration in the gas phase) and metals such as iron and its compounds. In one such process, the so-called catalytic extraction process (CEP), a molten metal bath is used to transform wastes into potentially useful products (Nagle et al., 1996). This process typically operates under oxygen partial pressures between  $10^{-15}$  and  $10^{-9}$  atm. Fine particles released contain iron compounds, carbon, and inorganic salts, including oxides. The nature of the carbons depends somewhat on the reactor conditions.

A laboratory study using model compounds based on ferrous chloride tetrahydrate was initiated. In order to produce measurable quantities of PCDD/F from these model mixtures, oxygen partial pressures of  $10^{-3}$  atm or greater had to be used.

#### 2. Materials and methods

Five carbons were obtained from various sources: activated (100 mesh, Aldrich), graphic powder (Aldrich), two carbon blacks (Cabot) and Spherocarb (100 mesh, Phase Separations). These carbons were Soxhlet extracted in toluene for 24 h, vacuum dried and used in model mixtures containing ferrous chloride tetrahydrate (99.995%, Aldrich) and a support matrix of aluminum, calcium and silicon oxides (12%, 48% and 40%, respectively) (Al:Ca:SiO<sub>x</sub> powder). No additional information pertaining to the Al:Ca:SiO<sub>x</sub> powder is currently available. The ferrous chloride tetrahydrate crystals were

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ground into a fine powder under nitrogen in a glove box due to its hygroscopic nature. This ferrous chloride was physically mixed with the carbon and Al:Ca:SiO<sub>x</sub> powder in specific concentrations, as noted in Section 3. The sample mixture was then placed in an inverted glass thimble on a coarse glass frit and held in place with a glass wool plug. The reactor, a 152.4 cm long Pyrex tube of 3 cm ID, was heated using three ceramic heating elements while 0.9 l/min of nitrogen was passed through. The temperature at the center of the tube was controlled by three temperature controllers located within each heating section. When the reactor was within 50°C of the desired reaction temperature, the thimble with the sample mixture was inserted at the top of the reactor and heated to the desired reaction temperature. This heat-up time was kept constant at 30 min. Thereafter, the air flow corresponding to the desired concentration of oxygen was added to the flow of nitrogen; thus bringing the total flow through the reactor to 1 l/min. The outlet gas of the reactor exited through a side arm at the top to an ice cooled gas trap containing 250-300 ml of dichloromethane.

After the desired reaction time, the thimble was removed from the reactor and the sample was spiked with an isotopically labeled PCDD/F internal standard (CIL) and Soxhlet extracted for 24 h with toluene. This toluene extract was then labeled the solid phase sample. The dichloromethane in the gas trap was also spiked with internal standard and labeled the gas phase sample. The gas phase and solid phase samples were purified separately by fractionation on alumina, as described elsewhere (Addink and Altwicker, 1997). A sulfuric acid wash of the samples was done prior to this procedure to remove any inorganic ferrous compounds present. The  $T_4CDD-O_8CDD$  and  $T_4CDF-O_8CDF$  were quantified via gas chromatography/mass selective detection.

#### 3. Results and discussion

Initial experiments were performed with samples consisting of 21% ferrous chloride tetrahydrate on the support matrix and five different carbons (cf. Fig. 1). With the exception of Spherocarb, O<sub>8</sub>CDF was the dominant product under these experimental conditions. For the two carbon blacks (labeled CBA and CBB) and activated carbon, O<sub>8</sub>CDF accounted for approximately 85% of the total T<sub>4</sub>-O<sub>8</sub>CDD/F formed; the remainder being H<sub>7</sub>CDF and H<sub>7</sub>- and O<sub>8</sub>CDD. A slightly greater amount of H<sub>6</sub>- and H<sub>7</sub>CDF was formed with graphitic carbon, however, O<sub>8</sub>CDF was still the predominate congener. The formation of moderately chlorinated PCDF ( $P_5$ - $H_7$ ) was favored when Spherocarb was used as the carbon source. However, the [PCDD]:[PCDF] ratio of 0.05 was in agreement with the other carbon sources used.

While the congener distribution appeared to be independent of the carbon source, the amounts of PCDD/ F produced were not. Activated carbon was the most



Fig. 1. Comparison of PCDD/F Congener yields as a function of carbon source.

reactive of these carbons by a factor of 1.85 over graphitic carbon. The reactivities of CBB and Spherocarb were very similar, while carbon black A exhibited little reactivity. These results indicate that the morphology of the carbon could be important in the formation of PCDD/F.

The relative abundance of  $O_8CDF$  produced in these experiments suggests that ferrous chloride can prechlorinate carbon, as suggested by the investigations of (Stieglitz et al., 1996). The occurrence of congeners other than octa-, namely hepta- and hexa-PCDD/F, can be explained by dechlorination of  $O_8CDD/F$  on the 12% alumina support (Schoonenboom et al., 1995). The absence of lower chlorinated congeners such as T<sub>4</sub>CDD/F can then be explained by destruction on the calcium oxide support (Gullett et al., 1997).

The effect of the ferrous chloride concentration was investigated using activated carbon. A linear increase in the formation of PCDD/F on the model mixture was observed with increasing ferrous chloride concentration between 1% and 21% at 275°C. Increasing the concentration to 33% at 300°C had no further effect on the PCDD/F concentration. In the absence of ferrous chloride, no PCDD/F formation occurred in this system, suggesting that ferrous chloride is both a catalyst and chlorinating agent. The congener distribution was not a function of ferrous chloride concentration, nor was the [PCDD]:[PCDF] or the desorption of PCDD/F.

The sponsor of this work reported that the processing of some wastes yields carbons that resemble the turbostratic structure of carbon blacks in certain ways. Hence, the two carbon blacks were selected for further experiments. The effect of varying the reaction temperature on the de novo synthesis of PCDD/F with CBA and CBB in a model system at a reaction time of 60 min is summarized in Fig. 2. While a peak in solid phase PCDD/F was observed at ca. 300°C with CBA, no distinct peak occurred up to 325°C for CBB. A phase shift



Fig. 2. Solid (SP) and gas (GP) PCDD/F yields as a function of temperature with CBA and CBB.



Fig. 3. Solid (SP) and gas (GP) Phase PCDD/F yield as a function of time with CBA and CBB.

occurred between 300°C and 325°C with CBA, indicating that desorption becomes important above this temperature. Although the gas phase to solid phase ratio did increase with increasing temperature for CBB, the ratio climbed no higher than 0.26. This indicates that the adsorptivity of CBB is greater than that of CBA, thus limiting the role of desorption with CBB. The greater overall reactivity of CBB over CBA is apparent.

A comparison of the effect of reaction time at 325°C is presented in Fig. 3. A peak in overall formation with

CBA is observed at 60 min. Since the solid phase yield of PCDD/F remained relatively constant for all times studied, destruction of the gas phase PCDD/F became important after 60 min at 325°C, while the desorption rate increased up until this time. With CBB, no optimum occurred within 90 min. In both the temperature and time study, the PCDD/F congener patterns were unaffected. For the data in Fig. 3, the model system consisting of one gram samples of 8 wt% CBB or CBA, 21 wt% ferrous chloride tetrahydrate and the remainder



Fig. 4. Rastering Electron Microscopy (REM) of (a) CBA and (b) CBB surfaces.

Table 1						
Comparison	of PCDD/F	yield or	n a pe	r ml	carbon	basis

$R \times n$ Temp (°C)	PCDD/F (ng/g sample)		PCDD/F (ng/m	PCDD/F (ng/ml Carbon)		
	CBA	CBB	CBA	CBB		
275	26	57	221	249		
300	110	544	935	2380		
325	363	650	3086	2844		



Fig. 5. Effect of CBB Concentration on PCDD/F yield with ferrous chloride.

Al:Ca:Si oxides powder was reacted at  $325^{\circ}$ C in a flow of 1 l/min of 2% oxygen in nitrogen for the reaction times of 20, 40, 60 and 90 min.

From the results of the fixed bed experiments presented in Figs. 2 and 3, it is apparent that a difference exists between the two carbon blacks in terms of reactivity to form PCDD/F and their respective adsorptivity. These differences can be viewed in another light. While both carbon blacks have a similar turbostratic structure of spherical particles (cf. Fig. 4), similar to that of representative CEP dusts, they do differ in bulk density and particle size distribution.

The bulk density of CBA is nearly twice that of CBB, 0.68 and 0.35 g/ml, respectively. When this difference is



Fig. 6. (a) Solid (SP) and Gas (GP) Phase PCDD/F yields as a Function on oxygen concentration with CBB. (b) PCDD/F Congener distribution as a function of oxygen concentration with CBB.

accounted for by recalculating the PCDD/F yields on a per ml of carbon basis, a similar reactivity to form PCDD/F is evident between CBA and CBB (cf. Table 1).

In addition, the phase shift observed for CBA between 300°C and 325°C (cf. Fig. 2) was previously suggested to be evidence for a weaker adsorptivity of CBA compared to that of CBB. However, 8 wt% CBA is comparable in volume added to a 1 g model system to 4 wt% CBB. At this concentration, while the yields are perhaps too low to draw extensive conclusions, the amount PCDD/F that desorbs from the solid matrix becomes increasingly more significant. In Fig. 5, as the wt% CBB added to the sample is increased, the solid phase yield of PCDD/F increases significantly. At the lower limits of the study, between 2 and 4 wt% CBB, a phase shift occurs as was observed with 8 wt% CBA between 300°C and 325°C. Therefore, the reactivity and adsorptivity of CBA and CBB may be similar, with the apparent differences resulting from the differences in volume. These results suggest that the density differences may correspond to a larger surface area and/or a larger number of surface sites for these types of reactions, in an equivalent mass of CBB.

The effect of oxygen concentration on the system with CBB was studied for concentrations up to 5% (cf. Fig. 6a and b). A peak in formation at  $325^{\circ}$ C occurs at 2% oxygen in nitrogen, while the congener distribution and gas phase to solid phase ratio were both independent of the oxygen concentration above 0.5% oxygen in nitrogen. Recent experiments suggest that this decrease may be due to the oxidation and vaporization of the ferrous chloride; however, more work is necessary to determine the importance of this effect. At oxygen concentrations at and below 0.5%, a slight increase in lower chlorinated congeners occurs. Relating this to the chlorination mechanism reported by Stieglitz et al. (1996), it is plausible that not enough oxygen is available for the chlorination reaction.

# 4. Conclusions

A model mixture containing ferrous chloride tetrahydrate and an inorganic oxide matrix was studied using five different carbon sources. With the exception of Spherocarb,  $O_8CDF$  was the major PCDD/F congener formed via the de novo synthesis. This trend proved to be independent of the ferrous chloride concentration, perhaps suggesting that this compound is an effective chlorinating agent. Of the two carbon blacks, CBA was less reactive than CBB under all conditions studied, as well as less adsorptive on the same weight basis.

However, on a volume of carbon basis per sample, the reactivities and adsorptivities are similar. More information about the properties of these carbon blacks is necessary for a more complete analysis. The reaction temperature and time had no effect on the PCDD/F congener distribution. Furthermore, a decrease in formation with CBB was observed at oxygen concentrations greater than 2%, however, the congener distribution remained unchanged. The insensitivity of the congener distribution to these other parameters points to the possibility of a "simplified" mechanism of PCDD/F formation via catalysis and chlorination by ferrous chloride. At very low oxygen concentrations (0.5% and below), not enough oxygen may be available for the chlorination reaction thereby producing some lower chlorinated PCDD/F's.

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