

## CHLORINATION PATTERNS OF POLYCHLORINATED DIBENZO-p-DIOXINS AND FURANS IN MODEL PARTICLE SYSTEMS

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### Introduction

Concentrations of iron compounds in the dust emissions from the Catalytic Extraction Process<sup>1</sup> are potentially very high, therefore, this metal's activity in polychlorinated dibenzo-p-dioxin/furan (PCDD/F) chemistry is an important issue. CEP involves the reduction/ recycling of waste streams by elemental dissociation via a molten metal bath and selective reformation to various products/ by-products. The role of iron in the formation of PCDD/F from various precursors such as hexachlorocyclohexane<sup>2</sup> and benzene<sup>3</sup> has been observed with iron as iron oxide and iron(III) chloride, respectively. Besides catalysis of these condensation reactions, it has also been proven that iron(III) chloride can chlorinate PAH's<sup>4</sup> and PCDD/F's<sup>5</sup>, perhaps via more than one mechanism. Iron can also catalyze the formation of polychlorinated dibenzo-p-dioxins/ furans (PCDD/F) via *de novo* synthesis; i.e., from native carbon<sup>6</sup>. Stieglitz et al propose that *de novo* formation is a two step process involving (i) the chlorination carbon macromolecular structure and (ii) its oxidative degradation to release "smaller" organic compounds.<sup>7</sup> The first chlorination step has been shown to be very fast relative to PCDD/F formation; therefore, the role of organic chlorine formed prior to formation has been of recent interest in PCDD/F research.<sup>8,9</sup> With this in mind the focus of this paper is on the distinct chlorination pattern observed in the PCDD/F's formed *de novo* in the presence of iron in model mixtures.

### Materials and Methods

A carbon black (Cabot Co.), labeled CBB, was chosen as a representative of carbon in actual CEP dusts for reasons discussed elsewhere<sup>10</sup>. This carbon was extracted in toluene for 24 hours, vacuum dried and used in model mixtures containing iron (II) chloride tetrahydrate (99.995%, Aldrich), iron(III) chloride hexahydrate (97%, Aldrich) or copper(I) chloride (99.995%, Aldrich) and a support matrix of aluminum, calcium and silicon oxides (12, 48, and 40%, respectively). One gram samples of various compositions of this model mixture were placed in a Pyrex reaction tube against a glass frit and held in place by a piece of glass wool, under either a nitrogen or helium flow. The reactor exit flow was bubbled through an impinger filled with toluene to collect volatile organics. When the desired reaction temperature was reached, the flow was switched to a mixture of 2% oxygen in nitrogen; reaction times were 60 minutes.

For experiments where hexane (analytical, EM Science) was added to the flow (to provide a hydrogen source), the gas flow was bubbled through a cold impinger filled with hexane and placed upstream of the furnace. The temperature of the hexane was adjusted to control the amount of hexane added to the gas stream. The actual amount added was determined by weighing the hexane trap prior to and upon completion of an experiment. The total gas flowrate for these experiments was 100 ml/min.

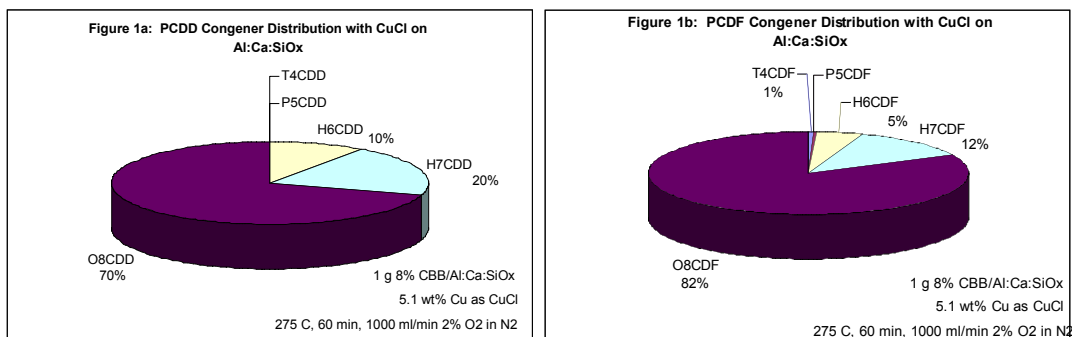
For reactions using a flowrate of 1000 ml/min, the reactor setup has been described elsewhere<sup>6</sup>. Clean-up and quantification of the gas and solid phase samples have been previously discussed<sup>6</sup>.

## Results and Discussion

This model system (with iron as iron(II) chloride tetrahydrate as the catalyst/ chlorine source) results in the almost exclusive production of O<sub>8</sub>CDD/F. O<sub>8</sub>CDD comprises 96% of the total PCDD and O<sub>8</sub>CDF is approximately 99% of the total PCDF. This congener pattern was found to be independent of all process parameters investigated.<sup>6</sup> The formation of PCDF over PCDD is strongly favored, with [PCDD]:[PCDF] ratios typically between 0.26 and 0.05; depending on reaction temperature and time.<sup>6</sup> It should be noted, while the results in ref. 6 are based on a flow of 1000 ml/min of 2% oxygen in nitrogen; the flowrate has been shown to affect only the overall yield of PCDD/F. This will be discussed further in a future reports.

The almost exclusive O<sub>8</sub>CDD/F formation is a further argument for a fast step (i) chlorination reaction of the carbon macromolecular structure prior to PCDD/F formation. Additional supporting evidence can be supplied by the fact that the H<sub>7</sub>CDD/F is characteristic of dechlorination occurring preferentially at the nine position, corresponding to the electrophilic substitution mechanism (as Schoonenboom et al. have postulated on alumina).<sup>11</sup>

A different congener pattern was produced when iron was replaced by a copper catalysts/ chlorine source, copper(I) chloride (cf. Figure 1). For these experiments, copper(I) chloride was

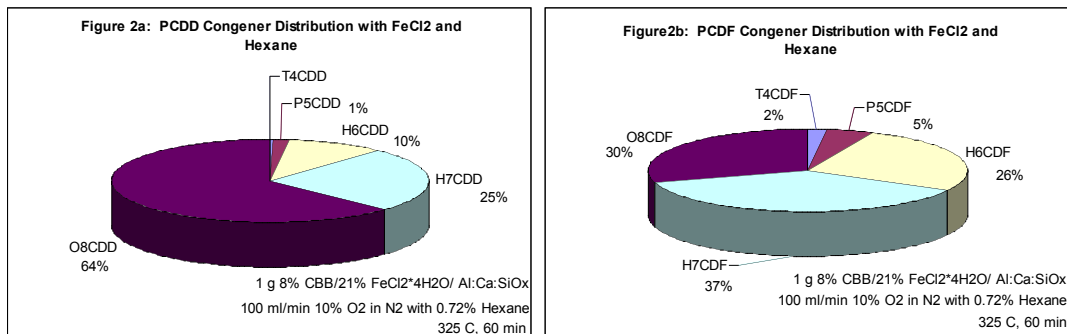


added in weight percentages of 1.5, 4 and 8 and reacted in a flow of 1000 ml/min of 2% O<sub>2</sub> in N<sub>2</sub> for 60 minutes at 275°C. For reactions at the same operating conditions with equivalent weight percentages of iron and chlorine, copper proved to be much more active in the formation of PCDD/F. However, more importantly, copper also produced lower chlorinated congeners. With iron(II) chloride, greater than 96% of the PCDD/F produced were fully chlorinated with no congeners lower than H<sub>6</sub>CDD/F present. While O<sub>8</sub>CDD/F was still the major congener (ca. 70-80%), lower chlorinated congeners were present in significant quantities; including T<sub>4</sub>CDD/F. The presence of 2,3,7,8-T<sub>4</sub>CDD/F was detected.

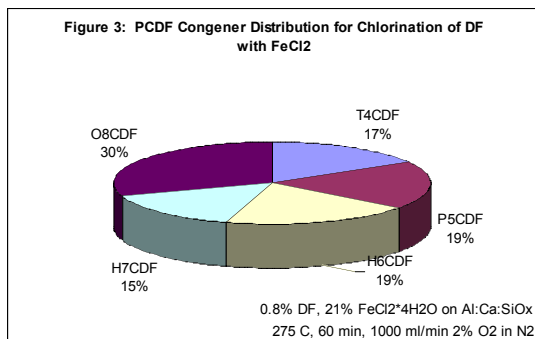
If we assume that chlorination is much faster than the formation of PCDD/F before they are released via oxidative breakdown of the carbon, then one should see exclusively O<sub>8</sub>CDD/F as is the case with iron. However, it has been shown that copper can catalyze the fast (within five minutes) dechlorination of PCDD/F to T<sub>4</sub>CDD/F with or without oxygen at temperatures of 150 to 285°C.<sup>12</sup> These authors also observed that this occurred preferentially at the nine position on the PCDD/F molecule, which is consistent with the results in this work. Hagenmaier et al found that

the hydrogen was supplied by the water in the air, which cannot be the case in this work since dry air is used. The only source for hydrogen would be hydrogen in the carbon itself.

When hexane was added to the O<sub>2</sub>/N<sub>2</sub> flow during *de novo* experiments with CBB, iron(II) chloride tetrahydrate on the Al:Ca:SiO<sub>x</sub> matrix, only the congener pattern changed drastically (cf. Figure 2). The broad congener distribution supports the hypothesis of dechlorination. It could also be due to a hydrogenation of the carbon matrix, therefore not allowing for the formation of organic chlorine (C-Cl bonds) prior to PCDD/F formation. The hexane in the flow was reacted without carbon to determine its PCDD/F formation potential. This amount (67 ng/g sample, 90-100% O<sub>8</sub>CDD/F) was then subtracted from the amount of PCDD/F formed during *de novo* experiments with hexane in the flow (6100 ng/g sample). The relative amounts and [PCDD]:[PCDF] ratios were unaffected by the hexane.



Schoonenboom et al. further showed that the dechlorination on alumina impregnated with copper(II) chloride was much faster than that of iron(III) chloride at 275°C.<sup>11</sup> In fact, iron(III) chloride showed more of a tendency toward complete dechlorination or destruction than alumina or alumina with copper(II) chloride. This could then explain the different congener patterns that develop when copper chloride is used in the system rather than iron chloride.



carbon. The congener pattern varied greatly from the pattern observed in the *de novo* experiments (cf. Figure 3). A broad distribution was observed with no one congener group dominating. While this proves that chlorination after formation is possible in this system, more work needs to be done. For PAH's, Hoffman et al.<sup>4</sup> proposed an electrophilic substitution reaction. They also concluded that iron(III) chloride is a better electrophilic chlorinator than copper(II) chloride. This could therefore explain why iron produces almost exclusively O<sub>8</sub>CDD/F. The dechlorination of O<sub>8</sub>CDD/F is slower over the iron system, however the chlorination is faster than with copper.

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### References

1. Nagle C, Chanenchuk C and Wong E; *Env. Sci. Tech.* **1996**, 30, 2155-2167.
2. Minghui Z, Zicheng B, Xiaobai X, and Keou W; *Chemosphere* **1996**, 32 (4), 595-602.
3. Nestruck T, Lamparski L, and Crummett W; *Chemosphere* **1987**, 16 (4), 777-790.
4. Hoffman R, Eiceman G, Long Y, Collins M, and Lu M; *Env. Sci. Tech.* **1990**, 24 1635-1641.
5. Beard A, Naikwadi K, Karasek F; *Env. Sci. Tech.* **1993**, 27, 1505-1511.
6. Ryan S, and Altwicker E; *Organohalogen Cmpds.* **1998**, 36, 269-273.
7. Stieglitz L, Vogg H, Zwick G, Beck J, and Bautz H; *Chemosphere* **1991**, 23, 1255-1264.
8. Addink R and Altwicker E; *Organohalogen Cmpds.* **1998**, 36, 73-76.
9. Stieglitz L, Eichberger M, Schleihauf J, Beck J, Zwick G, Will R; *Chemosphere* **1993**, 27, 343-350.
10. Ryan S and Altwicker E; submitted to *Chemosphere*.
11. Schoonenboom M, Zoetemeijer H and Olie K; *Aplied Catalysis B: Env.* **1995**, 6, 11-20.
12. Hagenmaier H, Brunner H, Haag R and Kraft M; *Env. Sci. Tech.* **1987**, 21, 1085-1088.