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Understanding the Role of Iron Chlorides in the De Novo Synthesis of Polychlorinated Dibenzo-*p*-dioxins/Dibenzofurans

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The formation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F) was investigated for mixtures of carbon black and iron chloride supported on a ceramic glass powder matrix in a low (2%) oxygen environment. Three iron chloride types (iron(II) chloride tetrahydrate, iron(III) chloride hexahydrate, and iron(III) oxychloride) were studied to gain some insights into their role in de novo formation. The importance of iron(II) and iron(III) chlorides both as chlorinating agents and promoters of low-temperature carbon gasification was observed. Iron(III) oxychloride was shown to be a very effective promoter at 325 °C and above; its conversion to iron(III) chloride was suggested as a key step. The predominant product was octachlorodibenzofuran. The oxide support matrix was found to be an important parameter.

Introduction

The formation of polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) from many anthropogenic sources has been studied since the 1970s because of the extreme toxicity of certain isomers. Dioxins (PCDD/F), as these compounds are often referred to collectively, are formed as trace byproducts from processes such as incineration, combustion, chloro-chemical production, pulp and paper manufacturing, and metallurgical industries such as smelting and sintering. Olie et al. (*1*) first identified municipal solid waste incinerators (MSWI) as a significant source of PCDD/F, sparking a major focus on control. Over the past quarter century, major strides have been made in controlling and reducing such emissions. Among sources other than incineration, metal processing such as iron ore sintering has been identified as one of the most significant primary source sectors in the United Kingdom (*2*).

The formation of PCDD/F during MSWI has been proposed to occur predominantly heterogeneously, catalyzed by fly ash. Two types of reactions have been extensively studied: (i) the formation from chemically similar precursors such as chlorophenols (*3*−*8*) and chlorobenzenes (*9*−*11*) and (ii) the formation from particulate carbon in fly ash involving the chlorination and subsequent oxidation of the macromolecular carbon matrix to release chlorinated organic compounds, including PCDD/F (*12*). The latter has been termed the de novo synthesis, based on fixed bed studies on MSWI and model fly ashes (*13*); laboratory fixed bed experiments involving native carbon in fly ash or particulate carbon in model fly ash have often been referred to as de novo experiments. Similarities between field levels and patterns of PCDD/F have been used to support both mechanisms.

In both types of reactions, metals in the fly ash play an important role in PCDD/ F formation (*14*, *15*). Copper(II) chloride has proven to be very active in promoting this formation by either (i) (*16*) or (ii) (*12*, *17*, *18*) as stated previously. Iron has also been shown to be active in catalyzing the formation of PCDD/F from precursor reactions and via chlorination of dibenzo-p-dioxin/dibenzofuran (*9*, *19*). Iron(III) chloride participates in or promotes formation via de novo synthesis, albeit less efficiently than copper(II) chloride (*20*). This cited study was done at one concentration of iron (ca. 1 wt %) and at one temperature (300 °C). Typical concentrations of iron in MSWI can be 10−100 times greater than those of copper (% vs ppm levels, respectively); thus, iron may be of comparable importance in PCDD/F formation. The concentration of iron is much higher in processes other than MSWI incineration, such as metallurgical processes. For example, a fly ash from an iron ore sintering process contained 49.9 wt % iron (and 9.5 wt % chlorine) (*21*). Brenner (*22*) noted a high correlation between iron content and PCDD/F formation; the author also indicated that the iron/copper redox pair was a very active synergistic composition in corrosion tests. Although often found together, any potential synergistic effects of these metals in promoting PCDD/F formation has not been specifically reported.

The present work was initially motivated by the investigation of the potential for PCDD/F formation in the Catalytic Extraction Process (CEP), developed by Molten Metal Technologies, Inc. (*23*). In this process, a waste stream (including hazardous waste) is dissociated into its respective elements by using the catalytic and solvent properties of a molten metal bath (i.e., iron). PCDD/F emissions were reported to be very low or nondetected (*23*); however, the high levels of iron in the particulate byproduct warranted investigation into potential de novo formation. In addition to high levels of iron and carbon, a support matrix of alumina, calcium oxide, and silica was typical of CEP particle emissions. The oxygen concentrations in the CEP were very low (ca. 10^{-15} to 10^{-9} atm) during normal operation (*23*).

The present paper discusses the formation of PCDD/F in a model system of carbon black, promoted by iron chlorides supported on a matrix consistent with that of actual CEP emissions. The reason for using carbon black has been noted elsewhere (*24*). The role of different iron chloride compounds as well as the influence of the support matrix was investigated as a function of temperature and time in a low (2%) oxygen environment. The components of the support matrix were also studied separately.

Experimental Procedures

The de novo formation of PCDD/F on model mixtures was investigated using Pyrex or quartz fixed bed reactors (0.5 m in length, 1 cm i.d.) containing a coarse ground glass frit in the axial center. Typically, 1 g of model mixture was loaded into the reactor and held against the frit by a plug of quartz or glass wool. The quartz reactor and wool were used for the higher temperature experiments of this study (400 °C) as well as in some lower temperature experiments. No differences in formation occurred as a result of the different reactor materials. The reactor was placed in an 800 W Lindbergh

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clamshell ceramic oven with a J-type thermocouple (0−400 °C set point range) placed in the bed through a silicon-based septum; the temperature was controlled (±1.0 °C) using an Omega CN9001 digital PID controller. The flows of nitrogen (N_2) (Matheson, Ultrahigh Purity) and/or 10.1% oxygen (O_2)/N_2 (Matheson) were controlled by a Hastings Mass Flow Controller (MFC) Model 202 and/or Tylan MFC Model FC-260, respectively. The total flow rate was 100 mL/min, unless otherwise noted. The exhaust from the reactor passed through an impinger filled with toluene kept in an ice water bath. Flow rates were adjusted and measured before the start of each experiment using a bubble flow meter to ensure that the correct atmosphere makeup was used, typically 2% O_2/N_2; a lower oxygen mole fraction did not produce reasonable quantities of PCDD/F in the reaction times employed here.

The reactor was heated from ambient to the desired bed temperature in a nitrogen flow (80−100 mL/min) for a period of 45 min. After this heat-up time, the experiment was started by adding O_2 to the flow. For the experiments in only nitrogen, the reaction time (0−90 min) was also taken after the heat-up period. After the desired reaction time, the O_2 flow was stopped, and the reactor was cooled quickly by removing it from the clamshell furnace. The bed was removed and placed in a pre-extracted (with toluene, for 1−2 h) cellulose extraction thimble. A 10 μL internal PCDD/F standard spike (Cambridge Isotope Laboratories, EDF-4053) was added to the bed, and the sample was Soxhlet extracted with 250 mL of toluene (99.98%, EM Science) for 24 h. This sample was termed the solid phase (SP) fraction. The toluene from the impinger, referred to as the gas phase (GP) fraction, and solvent rinses of the reactor were combined with the toluene of the solid-phase extraction for most experiments. Where a phase distribution (GP/SP) is reported, the samples were cleaned up and analyzed separately. Details of the cleanup and analysis can be found in Ryan and Altwicker (*24*) and Addink and Altwicker (*15*).

In addition to PCDD/F analysis, the change in total organic chlorine (C−Cl) in the model mixture after reaction was also investigated as a function of temperature and time. This analysis was performed at the Forschungszentrum Karlsruhe (Germany) under the direction of Dr. L. Stieglitz according to the protocol for adsorbable organic halogen (AOX) (DIN 38409). Briefly, 10−50 mg of the sample was extracted with a dilute nitric acid solution (pH = 2) at 70 °C for 30 min followed by a rapid quench. After 60 min of mixing via a mechanical shaker, the sample was filtered and washed with a nitrate solution to displace inorganic chlorides. The filter, containing the sample plus 50 mg of activated carbon added prior to the extraction step, was then combusted at 1000 °C in oxygen/argon. A EUROGLASS AOX/EOX/VOX analyzer was used to quantify the C−Cl via a coulometric titration of the chloride from the combustion gas captured in an electrolytic cell (signal in mC) that was then converted to μg C−Cl/g sample. The thermal behavior of model mixtures (cf. below) was investigated by differential scanning calorimetry (DSC-404) in the temperature range of 20−700 °C with a heating rate of 4 °C/min. In a few auxiliary experiments, the gas stream exiting the reactor was passed through a water-filled impinger. These samples were analyzed for the presence of iron using an AAnalyst 300 model Perkin-Elmer Atomic Absorption Spectrometer (AAS).

The model mixtures used in these studies consisted of physically ground mixtures of particulate carbon black, metal chloride, and a support matrix. The particulate carbon black was obtained from Cabot Corp. in two lots, labeled CBA and CBB. Both lots were investigated as carbon sources (after toluene extraction to remove adsorbed organics) for de novo PCDD/F (*24*), and more details on the properties of each are discussed elsewhere (*25*). Preliminary experiments indicated a much greater facility of PCDD/F formation using CBB; hence, it was used in all subsequent experiments. CBB had no measurable amount of C−Cl, as determined by the AOX analysis described previously. Therefore, all C−Cl that was measured on the CBB in the model mixtures after being reacted was due to conversion from the inorganic chloride added into the mixture. To investigate the potential for preexisting C−Cl to be incorporated as chlorine in PCDD/F, soot was prepared from the combustion of *o*-dichlorobenzene according to the procedure described in Van Dell et al. (*26*). This combustion was done at an equivalence ratio of 1.8 with a flame temperature between 700 and 740 °C. After extracting the *o*-dichlorobenzene (ODB) soot with toluene (Soxhlet, 24 h) and drying, the amount of C−Cl was determined to be 15 mg/g soot (*27*).

The metal chloride sources were iron(II) chloride tetrahydrate (99.995%, Aldrich), iron(III) chloride hexahydrate (>97%, Fisher Scientific), and iron(III) oxychloride (cf. below); these were used without further purification. Iron(III) oxide (J. T. Baker) was used in a few select experiments as noted within the text. Iron(III) oxychloride was not available commercially; it was prepared according to the method of Schafer (*28*). Briefly, iron(III) chloride hexahydrate (1.92−3.90 g) was added to a Pyrex boat that was placed in the axial center of a 0.5 m long (2 cm i.d.) Pyrex glass tube. Glass wool plugs were placed on both sides of the boat, and a 50 mL/min flow of nitrogen was initiated. The tube was heated to 250 °C in the Lindbergh clamshell furnace over a period of 25−30 min. Once the set-point temperature was reached, the outside of the tube was cooled with forced air while the sample was still under inert gas flow. The outlet of the reactor was connected to an impinger filled with deionized water to scrub out any volatilized iron compounds (i.e., iron(III) chloride) and/or Cl_2/HCl gas from the exhaust stream. The dark blackish-red product in the boat was rinsed with deionized water and scraped into a Buchner funnel lined with filter paper. This product (a mixture of iron(III) oxychloride and iron(III) oxide) was rinsed with deionized water followed by acetone, transferred to a small (ca. 5 mL) round-bottom flask, and dried under a vacuum in a 60 °C water bath (Buchi Rotovap). The purity of the mixture, in terms of % as iron(III) oxychloride, was between 77 and 91% (85% average) as determined by a chloride titration using *n*-methyldiphenylamine red as an indicator (*29*).

The support matrix for the mixtures used in the PCDD/F formation experiments was a fine glass powder consisting of alumina (12 wt %), calcium oxide (48 wt %), and silica (40 wt %) (CAS matrix) furnished by Molten Metal Technologies, Inc. specifically for this work. For comparison purposes, alumina (acidic, J. T. Baker), silica (Alltech), and calcium oxide (technical grade, Mallinckrodt) were used individually or in combination in some experiments.

Results and Discussion

The focus of this work was on a very specific system that might simulate the potential formation of PCDD/F in low oxygen environments in the presence of iron chlorides. This atmosphere favored iron(II) chloride. An extensive study was completed to develop an understanding of PCDD/F formation in such a system.

1. Formation from Iron Chlorides. It did not matter whether the iron(II) chloride was mixed physically with the particulate carbon and the support matrix or placed separately upstream at 325 °C, a typical experimental temperature. When iron(II) chloride tetrahydrate (21 wt % in a 1 g sample) was mixed with CAS matrix and placed upstream of a 1 g bed of 8 wt % CBB/CAS matrix, the PCDD/F yields and homologue profiles were identical to a mixed, combined bed of CBB with those same components. With a low vapor pressure at 325 °C and a high melting temperature, it was apparent that iron(II) chloride was converted to a more volatile and mobile

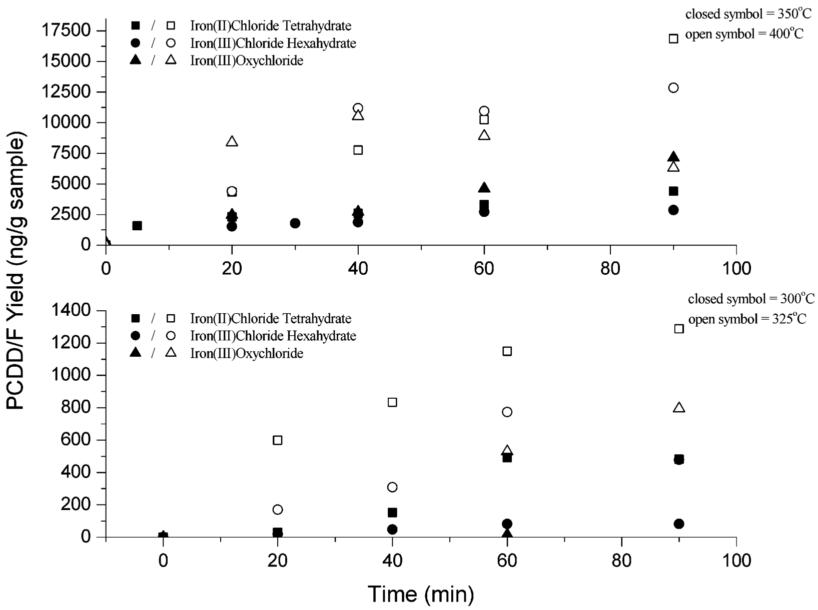


FIGURE 1. PCDD/F formation as a function of temperature and time on model mixtures containing different iron chlorides.

species in the separated bed experiment. Direct evidence for this conversion and subsequent mobility was the presence of crystals consistent in appearance to those of iron oxide and iron(III) chloride downstream of the glass frit. AAS analysis of a water impinger following heating of the model mixture at 325 °C added further evidence for the proof of iron compounds migrating downstream of the bed.

According to the literature, iron(II) chloride reacts with oxygen at temperatures above 250 °C via the four reactions (R1−R4) listed below (*30*):

$$2\mathrm{FeCl}_{2(s)} + \frac{1}{2}\mathrm{O}_{2(g)} \xrightarrow{>250\ ^\circ\mathrm{C}} \mathrm{FeOCl}_{(s)} + \frac{1}{2}\mathrm{Fe}_2\mathrm{Cl}_{6(g)} \quad \text{(R1)}$$

$$2\mathrm{FeOCl}_{(s)} + \frac{1}{2}\mathrm{O}_{2(g)} \xrightarrow{>250\ ^\circ\mathrm{C}} \alpha\mathrm{Fe}_2\mathrm{O}_{3(s)} + \mathrm{Cl}_{2(g)} \quad \text{(R2)}$$

$$3\mathrm{FeOCl}_{(s)} \xrightarrow{>320\ ^\circ\mathrm{C}} \alpha\mathrm{Fe}_2\mathrm{O}_{3(s)} + \frac{1}{2}\,\mathrm{Fe}_2\mathrm{Cl}_{6(g)} \quad \text{(R3)}$$

$$\mathrm{Fe}_2\mathrm{Cl}_{6(g)} + \frac{3}{2}\mathrm{O}_2 \xrightarrow{>370\ ^\circ\mathrm{C}} \eta\mathrm{Fe}_2\mathrm{O}_{3(s)} + 3\mathrm{Cl}_{2(g)} \quad \text{(R4)}$$

In R4, iron(III) oxychloride (FeOCl) was also noted as a product depending on the Fe/O_2 ratio. No conversion or decomposition of iron(II) chloride occurred in a nitrogen environment up to its melting temperature of 674 °C.

A. PCDD/F Formation as a Function of Temperature/Time and Iron Chloride. The individual iron chlorides mentioned previously were used in model mixtures (8 wt. % CBB/5.9 wt % iron as iron(II) chloride tetrahydrate, iron(III) chloride hexahydrate, or iron(III) oxychloride/CAS matrix), and the PCDD/F formation was studied as a function of temperature (300−400 °C) and time (0−90 min). All three iron chlorides behaved similarly with respect to time at temperatures of 325 °C and above (cf. Figure 1). At 400 °C, the amount (ng/g sample) of PCDD/F formed with iron(III) oxychloride decreased from 60 to 90 min. Since >90% of the amount of PCDD/F formed was found in the impinger at this temperature, this decrease is most probably due to factors other than destruction. The net formation rate with both iron(III) chloride and iron(III) oxychloride was initially high and leveled off with time; this was the case at the lower temperatures (300−350 °C) for all iron chlorides. The net formation is defined as the difference between the total formation and the total destruction, thus resulting in the total amount and product distribution observed in each experiment. Results for iron(II) chloride are reported separately in Figure 2 and more clearly show the decreasing net formation rate with time up to 350 °C. The results at 400 °C are not as clear since a linear fit (i.e., constant formation rate) up to 90 min may be suggested from the data (Figure 3, top). Excluding the 90 min data results in a fit that was more closely related to that observed at the lower temperatures; however, no evidence suggests that this point is an outlier. An experiment at 350 °C and 5 min revealed that nearly half of the total amount at 60 min was already formed. Replicates were performed at 300 (two experiments) and 325 °C (four experiments) for a reaction time of 60 min with iron(II) chloride. The average values are plotted in Figure 2. All duplicates were less than ±8.6% from the average PCDD and PCDF values.

The increase in amount with temperature is illustrated in Figure 3, shown for iron(II) chloride with CBA and CBB. The difference in formation between the two lots of carbon black is dealt with in a prior publication (*24*, *25*). The focus of this work was on CBB due to its high formation potential and more similar size distribution to some actual CEP particulate (*24*). The net formation from mixtures containing either carbon black increased almost exponentially with increasing temperature up to 400 °C, which was also the optimum formation temperature reported by Xun (*31*) on a similar model mixture (using activated carbon and iron(II) chloride). Some experiments (noted by closed symbols in the figure) were performed in a larger vertical fixed bed reactor capable of handling higher flow rates. The 10-fold increase in flow rate did not change the amount or product distribution.

The total net formation with iron(III) chloride was consistently lower than that from either of the other two iron chlorides (cf. Figure 1). Kanungo and Mishra (*32*) reported the decomposition of iron(III) chloride hexahydrate in nitrogen to iron(III) oxychloride, water, and hydrogen chloride at a temperature of 250 °C. Since the samples were preheated in nitrogen to the reaction temperature before the addition of oxygen at the start (cf. Experimental Procedures), this decomposition might explain the apparent lower activity of iron(III) chloride. Although such decomposition was likely to increase at higher temperatures, the activity of the promoter to form PCDD/F also increased. This resulted

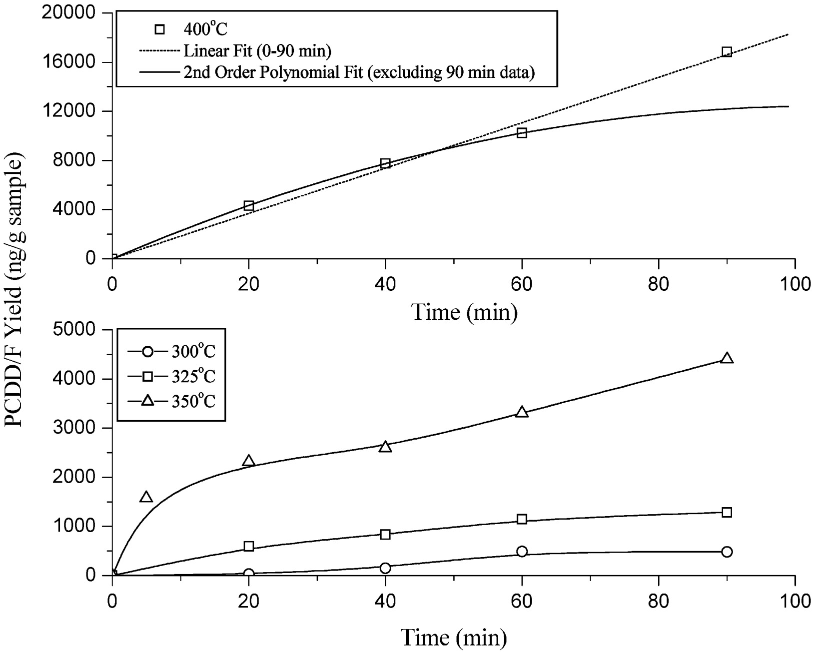


FIGURE 2. PCDD/F formation as a function of reaction temperature, time, and 21 wt % iron(II) chloride tetrahydrate.

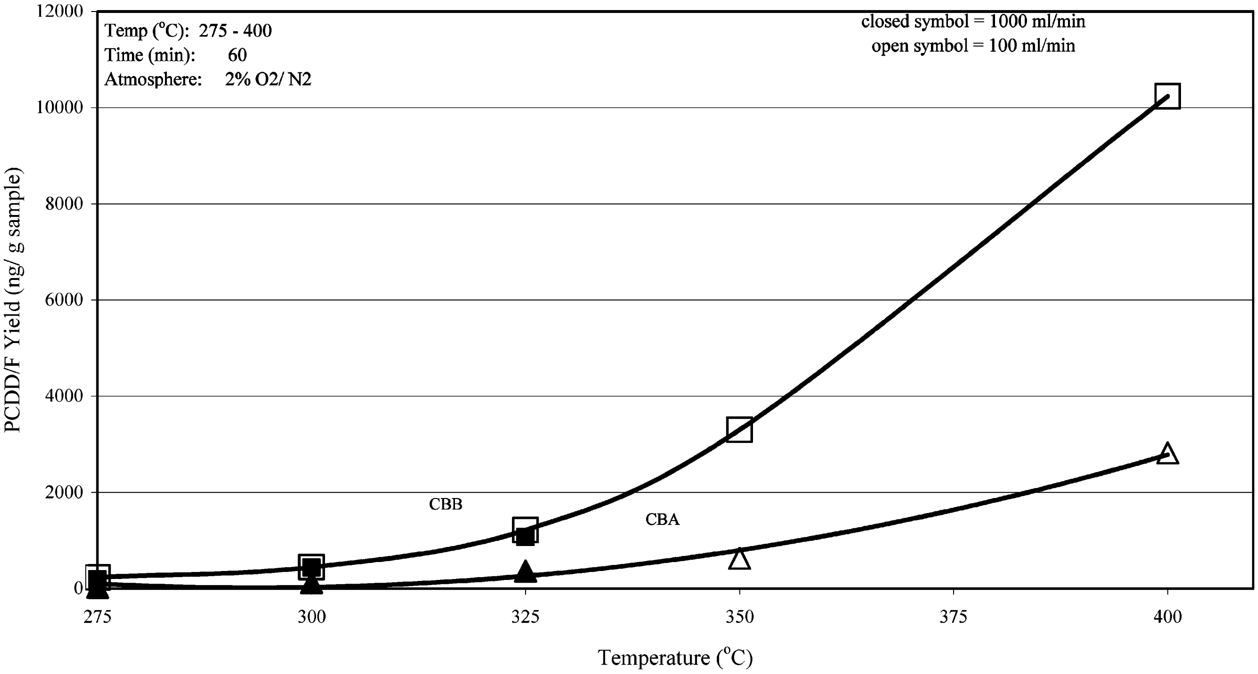


FIGURE 3. PCDD/F formation from carbon black (A and B) and iron(II) chloride tetrahydrate as a function of temperature.

in the net increase with temperature that was observed even if concentrations of iron(III) chloride in the reaction mixture at the start of the experiment might have been lower at the higher temperatures. Insignificant amounts of PCDD/F were formed in a nitrogen-only environment.

Formation on all three model mixtures was very dependent on the amount of iron chloride added to the bed (up to about 4 wt % iron). An almost linear increase with iron concentration was observed below this value; thereafter, PCDD/F formation became largely independent of the iron amount. When the amounts of PCDD/F were plotted as a function of chloride concentration, a definite dependence was observed albeit at different iron concentrations (cf. Figure 4). At equivalent chloride concentration in the samples, those containing iron(II) chloride had around half the amount of iron as samples containing the oxychloride. Since the net formation with iron(III) chloride was consistently lower than with the other two, they are omitted from this comparison.

Formation of PCDF was greatly favored over that of PCDD. Proof of this can be found in Table 1, listing the ratio of PCDD to that of PCDF as ([PCDD]:[PCDF]). Replicates run at two specific experimental conditions with iron(II) chloride (discussed previously) showed insignificant changes (<0.01) in the [PCDD]:[PCDF] ratio. This ratio decreased with increasing temperature and time, a result directly related to greater PCDF amounts at higher temperatures; PCDD formation was not strongly dependent upon temperature. At 325 and 350 °C, the total PCDD formed did not increase after 20 min.

No formation of PCDD/F was observed at 300 °C with iron(III) oxychloride. This might be indicative of the importance of iron(III) chloride in the formation of PCDD/F,

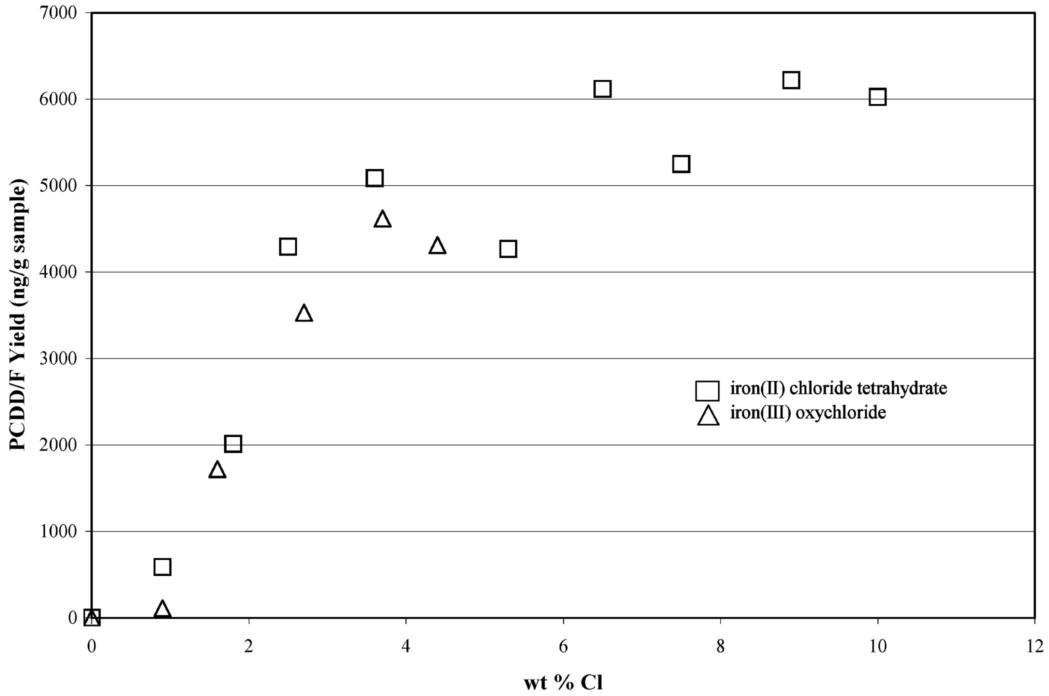


FIGURE 4. PCDD/F formation as a function of inorganic chloride concentration 1 g samples of 8 wt % CBB/× wt % chloride as listed/CAS matrix reacted at 350 °C for 60 min in 100 mL/min 2% O_2/N_2.

TABLE 1. [PCDD]:[PCDF] Ratios for De Novo Formation on Model Mixtures as a Function of Iron Chloride

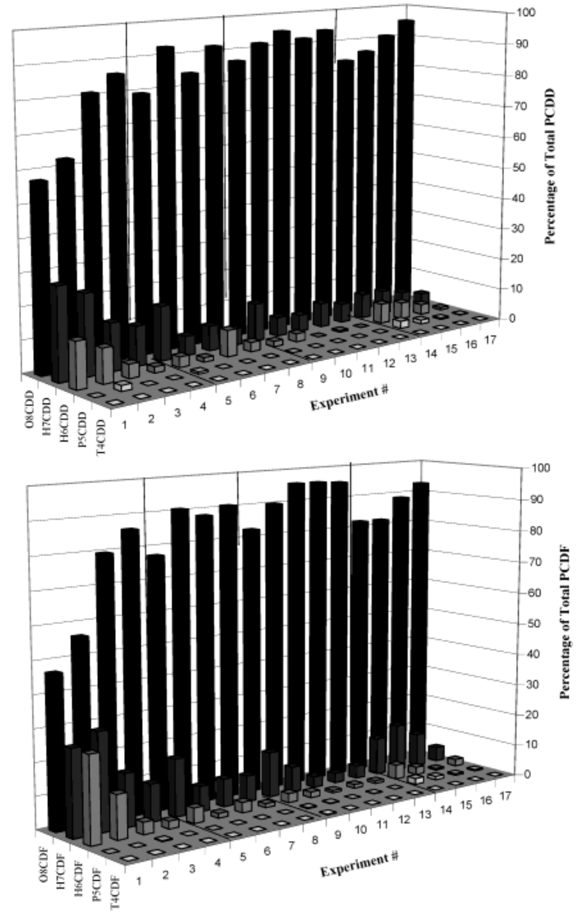
	time (min)			
300 °C	**20**	**40**	**60**	**90**
iron(II) chloride	0.93	0.58	0.31	0.28
iron(III) chloride	0.14	0.13	0.12	0.12
iron(III) oxychloride				
325 °C	**20**	**40**	**60**	**90**
iron(II) chloride	0.35	0.22	0.20	0.15
iron(III) chloride	0.10	0.06	0.05	0.07
iron(III) oxychloride			0.34	0.28
350 °C	**20**	**40**	**60**	**90**
iron(II) chloride	0.18	0.06	0.06	0.04
iron(III) chloride	0.02	0.04	0.03	0.03
iron(III) oxychloride	0.19	0.15	0.10	0.10
400 °C	**20**	**40**	**60**	**90**
iron(II) chloride	0.14	0.12	0.12	0.13
iron(III) chloride	0.03	0.08	0.05	0.05
iron(III) oxychloride	0.14	0.13	0.11	0.13

formed via R3 from iron(III) oxychloride at temperatures above 320 °C. When iron(III) oxide was used in place of the iron chlorides (5.9 wt % Fe), no formation was observed at 350 °C after 60 min. This result was not unexpected, considering that CBB had no measurable amount of organic chloride (C−Cl), and no additional chlorine was added to the system.

B. Homologue Distributions as a Function of Temperature/Time and Iron Chloride. The homologue distributions of PCDD/F were a function of both temperature and time (cf. Figure 5 for mixtures with iron(II) chloride tetrahydrate). The octa-CDD/F (OCDD/F) were the most abundant congeners, followed by hepta-CDD/F (H7CDD/F) and hexa-CDD/F (H6CDD/F). Only very minor amounts, if any, of penta-CDD/F (P5CDD/D) and tetra-CDD/F (T4CDD/F) were observed. With increasing temperature, the time required for the OCDD/F to reach their maxima (ca. 95%) in terms of percentage of total PCDD/F formed decreased drastically. At 300 °C, this percentage increased from 45 to 55% at 20 min to 85% at 90 min; above 300 °C, the time to maximal degree of chlorination dropped considerably. The formation of predominately OCDD/F (OCDD ≪ OCDF) was consistent with that observed by Xun (*31*) on actual bag house dusts collected from the CEP process.

The homologue distribution was a function of the iron chloride concentration (Figure 6) up to 4.2 wt % iron as iron(III) oxychloride; corresponding to 2.7 wt % Cl. The homologue pattern as a function of weight percent iron, presented in Figure 6, was representative of the other iron chlorides. However, the level of chloride addition at which point no significant change in the homologue pattern occurred was a function of the iron chloride type. On this basis, iron(III) oxychloride was the most effective chlorinating agent. For example, at 1.6 wt % chloride, the degrees of chlorination at 350 °C were 6.29, 7.50, and 7.74 for mixtures containing iron(III) chloride hexahydrate, iron(II) chloride tetrahydrate, and iron(III) oxychloride, respectively. The net formation was comparable for all three mixtures (as indicated by Figure 1 for the results at 5.9 wt % Fe), ranging from 1224 ng/g sample for iron(III) chloride hexahydrate to 2013 ng/g sample for iron(II) chloride tetrahydrate. However, the decomposition of iron(III) chloride hexahydrate in the inert atmosphere during heat-up may have diminished its apparent effectiveness both in terms of PCDD/F amounts and in terms of degree of chlorination. At the lowest iron concentration, a broader homologue pattern was observed with a maximum now shifted to H6CDD/F; the isomer patterns within each homologue were largely unaffected.

C. Mechanistic Implications. The importance of the conversion of iron(II) chloride to iron(III) chloride and iron(III) oxychloride (via R1) is evident from the split bed experiment and physical property data of iron(II) chloride. The only iron chloride that could have been transferred to



1 = (300,20) 2 = (300,40) 3 = (300,60) 4 = (300,90)
5 = (325,20) 6 = (325,40) 7 = (325,60) 8 = (325,90)
9 = (350,5) 10 = (350,20) 11 = (350,40) 12 = (350,60) 13 = (350,90)
14 = (400,20) 15 = (400,40) 16 = (400,60) 17 = (400,90)

FIGURE 5. PCDD and PCDF homologue profiles (in %) as a function of temperature and time experiment numbers correspond to (temperature, time).

the carbon containing bed in the split bed experiment was iron(III) chloride, due to the reaction temperature of 325 °C and iron(III) oxychloride being formed as a solid in R1. The lack of conversion of iron(III) oxychloride to iron(III) chloride below 320 °C (via R3) and the minimal formation with iron(III) oxychloride at 300 °C further suggests the importance of iron(III) chloride for PCDD/F formation. The similarity between iron(II) chloride and iron(III) oxychloride on a chloride basis at least indicates that they have similar steps for promoting PCDD/F formation. Whether this is via formation of iron(III) chloride or by the oxychloride itself cannot be answered definitively. The importance of iron(III) oxychloride for the catalysis of carbon oxidation, deemed an important step in the de novo synthesis, has been postulated by Mul et al. (*33*).

The increase in PCDD/F seems to parallel the increase in iron(II) chloride catalyzed carbon oxidation as a function of temperature; both exhibit an onset around 300 °C and nearly exponential behavior to 400 °C. The peak oxidation temperature for a CBB/iron chloride/CAS mixture was found to be ca. 410 °C by differential scanning calorimetry (DSC). Iron chloride has been shown to significantly lower the carbon gasification temperature of flame soot (*34*). A possible link between low temperature oxidation of carbon and PCDD/F formation has been previously reported (*35*−*38*). Both Stieglitz et al. (*38*) and Collina et al. (*35*) have reported similar comparisons between the peak oxidation temperature as determined by DSC and the maximum temperature for PCDD/F net formation on MSWI fly ashes. Up to that peak temperature the net difference between formation and degradation of PCDD/F increases with increasing temperature.

Although usually discussed together, formation of PCDD and PCDF probably occur, at least in part, via different mechanisms. Direct evidence for this from the present work can be found in the behavior of the [PCDD]:[PCDF] ratio with temperature and time. This behavior was consistent with that observed for laboratory de novo formation on fly ash from a waste wood incinerator (*39*) and MSWI fly ash (*40*). The difference in dependence on temperature may be related to the stability differences of the two classes of compounds or the temperature dependences of the different formation pathways. The fact that PCDF is less prone to oxidative degradation than PCDD has been discussed by Luijk et al. (*17*). Hell et al. (*41*) concluded that PCDD can be formed at equal rates via heterogeneous condensation reactions and direct release from the carbon structure during de novo formation on MSWI fly ash doped with isotopically labeled amorphous carbon. But PCDF was found to form completely intact (i.e., no mixture of labeled and unlabeled carbon rings). Additional work by Wikström et al. (*42*) has added further support to the previous conclusions.

The increase in net formation of PCDD/F diminished with time, as observed in many other de novo studies (*12*, *18*, *20*, *39*, *43*). Weber and Sakurai (*44*) reported very high initial rates of formation within the first 10 s of reaction, followed by a significant decrease at longer times. A decreasing rate of net PCDD/F formation was also accompanied by an increase in the degree of chlorination in the present work. Changes to the carbon structure may account for these results and are probably linked. Stieglitz et al. (*38*) and Milligan and Altwicker (*45*) reported a decrease in the rate of carbon oxidation with time on a MSWI fly ash. The increase in the degree of chlorination suggests that the carbon structure is increasingly chlorinated, as confirmed by the measurement of C−Cl bonds (cf. below). This increase in C−Cl likely makes oxidation increasingly more difficult, thus slowing the rate of low temperature carbon oxidation. As carbon is oxidized, it has been reported to become more structured (*46*), potentially making further oxidation increasingly more difficult.

Chlorine is undoubtedly incorporated into the carbon structure at some step during PCDD/F formation; however, at which step in a mechanism this occurs remains a question. In an attempt to understand this important mechanistic step, the change in the amount of organic chlorine (C−Cl) on the carbon matrix (CBB/ iron(II) chloride tetrahydrate/CAS powder) was investigated. An increase in C−Cl on CBB, initially containing no measurable amount of C−Cl, occurred along with the increase in the degree of chlorination of PCDD/F as a function of temperature. For example, the amount of C−Cl on the reacted sample increased from 1799 to 4331 μg/g sample over the temperature range of 275−365 °C and the degree of PCDD/F chlorination increased from 7.76 to 7.93 between 300 and 350 °C. These results suggest that the chlorination of the carbon macromolecular structure and/or secondary chlorination of PCDD/F to form OCDD/F was increasingly more effective with increasing temperature between 275 and 350 °C. The behavior of carbon chlorination (C−Cl bond formation) with respect to temperature agreed with findings of Boehm (*47*) concerning the uptake of gas phase chlorine by carbon black. Hydrogen substitution by chlorine on carbon black increased nearly exponentially before leveling off between 400 and 550 °C and decreasing sharply at higher temperatures. Although uptake by carbon of gas-phase chlorine may be relatively significant in terms of amount, this route to C−Cl bonds was not investigated in

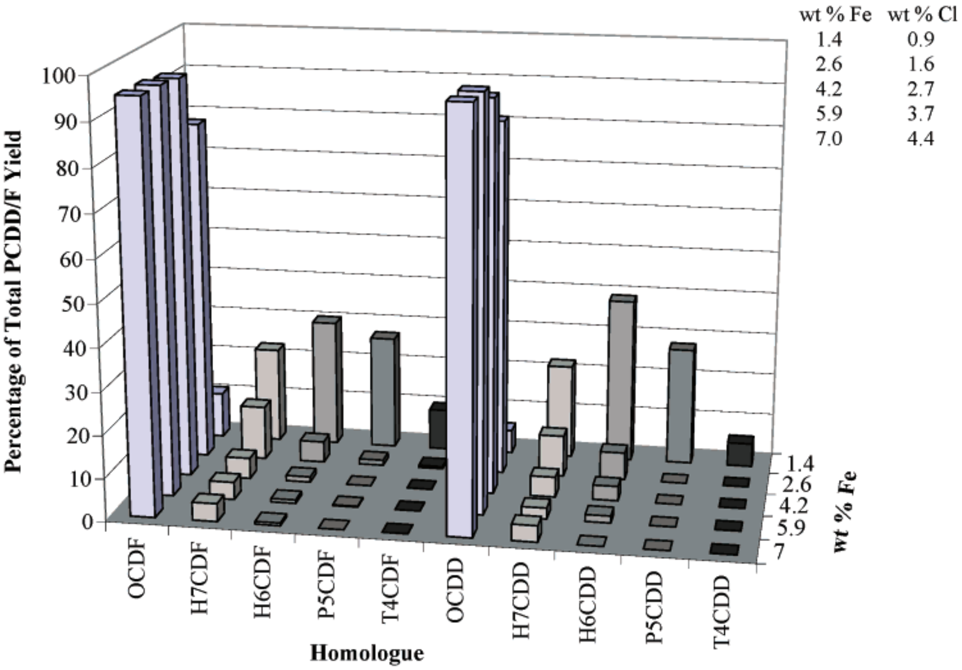


FIGURE 6. PCDD/F homologue distribution on model mixtures as a function of iron(III) oxychloride concentration.

this work; hence, its importance for PCDD/F formation could not be assessed. As shown below, the existence of C−Cl bonds per se in soot cannot account for PCDD/F formation.

The formation of C−Cl bonds via metal chlorides has been observed to be fast in both this study (>650 μg C−Cl/g sample within 5 min) and by Stieglitz et al. (*48*). Stieglitz (*13*) suggested that this may be evidence that the chlorination of the carbon structure can precede the oxidative degradation of the macromolecular carbon resulting in the release of chlorinated organic compounds. Luijk et al. (*17*) surmised that the chlorination of the carbon structure could prevent local burnoff via oxidation and promote the release of chlorinated aromatic compounds, including PCDD/F.

Although the formation of C−Cl was shown to be quite fast, the extent to which such C−Cl bonds may be incorporated into PCDD/F has not been determined (*49*). To further test the potential for the incorporation of existing C−Cl bonds into PCDD/F, a mixture of ODB soot (0.8%)/ iron oxide (8.4% Fe_2O_3) and CAS matrix was reacted in air at 350 °C for 60 min. Although this mixture contained a 120 ug/g sample of C−Cl, no PCDD/F formation was observed. Addink and Altwicker (*50*) reported a similar finding with copper oxide. Organic chlorine alone apparently is not a sufficient source to form PCDD/F via the oxidative breakdown of the chlorinated particulate carbon structure; rather, this suggests the importance of metal chlorides. A link between chlorination and oxidation leading to PCDD/F formation perhaps indicates the importance of surface complexes formed on the carbon during its low-temperature catalytic oxidation, considered to be a function of metal type (*34*).

2. Dibenzofuran Chlorination and OCDF Dechlorination. To investigate the question of whether chlorination occurred simultaneously with formation and release (from the carbon macromolecular structure) of PCDD/F or in sequence, chlorination of unchlorinated dibenzofuran (DF) and dechlorination of OCDF were investigated. Although the conversion of DF to PCDF (T4-O8CDF) was relatively high (1.78% at 350 °C in 10 min), the homologue and congener distributions were considerably different from those observed with carbon black. DF yielded T4CDF (79%) from chlorination with iron(II) chloride, perhaps indicating that successive chlorination of PCDF became increasingly more difficult as suggested by Beard et al. (*19*) in experiments with iron(III) chloride. The chromatogram peak representing several coeluting isomers of T4CDF on the DB-5 chromatographic column, including the 2378 substituted, accounted for almost 85% of the total T4CDF. This peak was most likely predominately 2378-T4CDF since further chlorination at the 1 position resulted in the 12378-P5CDF that was the dominant P5CDF product. Chlorination then occurred at the 4 position, resulting in 88% of H6CDF as the 123478 isomer. The addition of a seventh chlorine atom to 123478-H6CDF at the 6 position was favored 2:1 over the 9 position. This order of halogenation was identical to that reported by Luijk et al. (*51*) in a copper-(II) halide/ hydrogen halide (bromide and chloride) system for unchlorinated dibenzo-*p*-dioxin (DD) and DF. The 12378-P5CDF accounted for almost 85% of the total P5CDF formed, while our de novo experiments produced a much broader pattern with no isomer accounting for more than 18% of the total P5CDF amount; 12378-P5CDF was less than 5% of the total P5CDF in carbon black experiments. The competition for chlorine might initially be a plausible explanation for the different homologue profiles observed; however, this likely cannot explain the different congener patterns produced. Unlike the homologue profiles, the congener patterns from the de novo formation were found to be largely independent of temperature and time.

The lack of agreement between the congener distributions of DF chlorination by iron(II) chloride and PCDF formation on CBB suggests initial formation and release of PCDF from carbon black with some degree of chlorination. Support for this comes from the similarities between the congener profile from the dechlorination of OCDF and that from the de novo experiments. Dechlorination of OCDF on the CAS matrix occurred preferentially at the 9 position (>60%), with the remainder of the H7CDF products equally distributed. The H6CDF isomer pattern from dechlorination was, therefore, much more evenly distributed as compared to the pattern from chlorination of DF, with no one peak contributing more than 21% to the total amount. As was the case for the isomer patterns within the other homologues (T4CDF−H6CDF), the H7CDF pattern from de novo formation was very similar to that of OCDF dechlorination. These results seem to fit the dechlorination-controlled isomer pattern theory proposed

TABLE 2. Effect of the Amount of the CAS Matrix on PCDD/F Formation[a]

yield (ng/g sample)	amount of CAS matrix (mg) per sample				
	0	355	710	710[b]	1065
T_4CDD	0	0	0	0	0
P_5CDD	12	0	0	0	0
H_6CDD	27	0	0	0	0
H_7CDD	64	28	9	24	7
OCDD	1685	972	267	289	249
ΣPCDD	1788	1000	276	313	256
T_4CDF	0	0	0	0	0
P_5CDF	0	3	1	0	1
H_6CDF	172	109	34	59	22
H_7CDF	603	251	100	189	88
OCDF	28584	1439 1	4839	3128	4988
ΣPCDF	29359	1475 4	4974	3376	5099
ΣPCDD/F	31147	1575 4	5250	3689	5355
PCDD:PCDF	0.06	0.07	0.06	0.09	0.05

[a] 1.355 g samples of 80 mg CBB/210 mg of iron(II) chloride tetrahydrate/0−1065 mg of CAS matrix reacted at 350 °C for 60 min in 100 mL/min 2% O_2/N_2 values normalized per sample for 60 min in 100 mL/min 2% O_2/N_2 values normalized per sample weight (ng/g total sample). [b] Glass beads (100−150 mesh) were added in place of the CAS matrix.

by Iino et al. (*52*). The initial release of highly chlorinated PCDF that then undergo dechlorination and/or further chlorination is suggested by the present results. Thus, the formation of C−Cl bonds by the metal chlorides is an important step in the de novo synthesis, and this PCDF formation process results in PCDF with a high degree of chlorination. Subsequent chlorination and reactions on the support matrix can then contribute to the final product composition depending on reaction conditions.

3. Effect of the Support Matrix on Formation and Product Distribution. The amount of PCDD/F was a strong function of the support matrix. The CAS matrix used in this work was furnished by Molten Metal Technologies and prepared in a high-temperature process (>1500°) in a way thought to be consistent with particle formation and emission from this CEP-reactor (*53*). It should be noted that formation of PCDD/F from activated carbon (*31*) or carbon black (this work) combined with iron(II) chloride and the CAS-matrix were in excellent agreement with laboratory formation on actual CEP-solids emissions in terms of specific [PCDD]:[PCDF] ratios and homologue and congener profiles. This observation is of considerable importance; the body of evidence suggests that the support matrix component of model fly ashes can influence PCDD/F amounts, homologue and congener profiles, and [PCDD]:[PCDF] ratios (*12*, *54*−*57*).

In all experiments where the concentration of carbon or iron chloride was investigated, the amount of CAS matrix was adjusted to keep the total sample weight at one gram in all experiments discussed previously. Thus, before any conclusions could be drawn regarding the effect of carbon, iron, or chloride concentrations on PCDD/F formation, the influence of different amounts of the matrix needed to be known. Different quantities (0−1065 mg) of the CAS matrix were mixed with 80 mg of CBB and 210 mg of iron(II) chloride tetrahydrate and reacted at 350 °C for 60 min in a flow of 100 mL/min 2% O_2/N_2. For comparison, an experiment was performed with a one gram sample using glass beads (100−150 mesh) in place of the CAS matrix. Previous experiments have shown the glass beads to be inert in PCDD/F formation (*58*). Final sample weights were between 0.29 and 1.355 g for this aspect of the study. The amount of PCDD/F formed was normalized to a per gram of sample basis. Varying the amount of the matrix seemed to mainly have a dilution effect, similar to that of glass beads (cf. Table 2) on PCDD/F amounts. The formation was highest on the unsupported samples, in terms of total (ng) and normalized (ng/g) amount, consistent with the findings of Luijk (*17*). The congener distribution and [PCDD]:[PCDF] ratios were unaffected. It can be inferred that the typical variations in the amount of CAS matrix added (650−920 mg), to keep the weights consistent at one gram when different amounts of carbon or iron chloride were used, did not significantly affect the net amount of PCDD/F formed.

It was obviously important to determine if one particular component or combination of any two components of the CAS matrix dominated the overall properties of the support in terms of PCDD/F formation. Hence, each component was used individually at 325, 350, and 400 °C for 60 min. Two additional experiments at 350 °C were performed with a physical mixture of alumina and silica (1:3.33) and a synthetic CAS matrix. The latter was prepared by physically mixing all three CAS-components in the same ratio as the original (see Experimental Procedures).

At 350 °C, no formation occurred on calcium oxide, while alumina and silica supported samples exhibited less than 1/4th of the reactivity, respectively, of those containing the CAS matrix (cf. Table 3). The major products in all cases were OCDD/F, with OCDF ≫ OCDD. The Al:Si mixture reduced amounts further; the synthetic CAS matrix was obviously dominated by calcium oxide since no net formation was observed. The lack of formation on the basic calcium oxide appeared consistent with the results of Gullet et al. (*59*), who reported rapid decomposition of T4CDF in the same tem-

TABLE 3. PCDD/F Formation as a Function of the Support Matrix at 325, 350, and 400 °C [a]

	CAS matrix	alumina (acidic)[b]	silica	calcium oxide	Al:SiOx matrix[c]	syn CAS matrix[d]
325 °C						
ΣPCDD (ng/g sample)	195	49	14			
ΣPCDF (ng/g sample)	953	872	368			
av degree of chlorination	7.80	7.95	7.88			
350 °C						
ΣPCDD (ng/g sample)	223	27	20	0	18	0
ΣPCDF (ng/g sample)	4243	1068	1034	0	759	0
av degree of chlorination	7.95	7.88	7.94		7.91	
400 °C						
ΣPCDD (ng/g sample)	1127	19	33			
ΣPCDF (ng/g sample)	9110	882	1203			
av degree of chlorination	7.87	7.90	7.73			

[a] 1 g samples of 8 wt % CBB/21 wt % iron(II) chloride tetrahydrate/ remainder support matrix as shown reacted at the temperature indicated for 60 min in 100 mL/min 2% O_2/N_2. [b] Notes: CAS matrix is alumina (12%), calcium oxide (48%), and silica (40%) powder furnished by MMT, Inc. [c] Al:SiOx matrix: physically combined mixture of alumina and silica in the ratio of 1:3.33. [d] Syn CAS matrix: physically combined mixture of alumina (12%), calcium oxide (48%) and silica (40%).

perature window.

At 325 °C, the net formation on the CAS matrix and alumina were in agreement; those on silica were lower by ∼1/4. At 400°, a 4-fold increase in amount was observed on the silica supported sample from its value at 325 °C, which, however, was more than eight times less than the formation in the presence of the CAS matrix.

It is evident that the time and temperature history of the support matrix could be very important in determining the reactivity of the sample. The CAS matrix gave an aqueous slurry with pH 8.4. For comparison, the water slurry pHs of alumina, silica, and synthetic CAS solids were 5.8, neutral, and 12.4, respectively. Some physical properties of the CAS batch used for this work were determined directly in the laboratory or furnished by MMT. The average particle size was 1 μm. The average range of particle diameters of the acidic alumina and silica were 50−200 and 70−150 μm, respectively (i.e., more than 1−2 orders of magnitude greater than CAS). In light of the inhibitory nature reported for calcium oxide (*59*), the dechlorination/destruction on alumina (*57*), and the agreement observed in this present work, it is clear that the in situ formed support matrix (an apparently intimate mixture of these three compounds) exhibits properties different from a matrix prepared by physically combining the individual components.

A direct comparison between PCDD/F formation with copper (II) chloride, copper (I) chloride, and iron(II) chloride in the present CBB/CAS matrix at their respective reported maximum net formation temperatures (275 °C for the copper chlorides and 400 °C for iron chloride) was performed. The copper(II) chloride containing samples produced approximately 5 times more total PCDD/F than the iron(II) chloride mixtures in the 2% oxygen atmosphere over 60 min at equivalent metal concentrations (0−5 wt % metal). Mixtures with iron(II) chloride were slightly more active (1.2−1.5 times) in producing PCDD/F over this metal concentration range than those samples containing copper(I) chloride. It should be noted that the concentrations of iron in MSWI has been reported as being 10−100 times greater than those of copper, thus perhaps counterbalancing iron's slightly lower propensity to promote PCDD/F formation in such. In iron ore sintering fly ash, iron concentrations of nearly 50% have been reported (*21*). Synergistic activity between copper and iron chlorides and the modeling of these systems has been reported (*25*) and will be the subject of forthcoming papers.

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