EFFECT OF SOOT, TEMPERATURE, AND RESIDENCE TIME ON PCDD/F FORMATION

Grandesso E[1], Ryan S[2], Gullett B[2], Touati A[3], Tabor D[2].

[1]Universita' degli Studi di Milano Bicocca, Piazza della Scienza, 1 20126 Milano, Italy; [2]U.S. Environmental Protection Agency, Office of Research & Development, E305-01, Research Triangle Park, NC 27711, USA; [3]ARCADIS G & M, Inc., 4915 Prospectus Drive, Durham, NC 27713, USA.

Introduction

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are formed during thermal processes in the presence of fly ash that acts as an oxidation catalyst as well as a carbon and chlorine source (e.g., metal chlorides or chloride complexes in the fly ash)[1,2]. Recent laboratory studies[3-5] pointed out the importance of soot as a persistent carbon source, as well as fly ash. This may provide a partial explanation of the high PCDD/F yields in waste incinerators during shut-down and start-up[6] operation when high soot levels are likely. Despite numerous qualitative examinations on the key parameters affecting PCDD/F formation, more investigations are needed to predict PCDD/F emissions in real combustion (e.g., incineration) facilities by simulating operational modes such as shut-downs and start-ups. Kinetic studies can be used to correlate PCDD/F formation/destruction rates to those of the reactants (e.g., carbon degradation). Some kinetic models were developed on the basis of the mechanism of carbon gasification in fly ash and model mixtures [7,8]. Collina et al. [7], studied the kinetics of the gasification of carbon by measuring the total organic carbon (TOC) in fly ashes and proposed that this reaction was the result of two simultaneous processes leading to the formation of surface oxygenated complexes (SOCs) as reaction intermediates. SOCs can be precursors of PCDDs/Fs via the *de novo* synthesis.

In this work we studied PCDD/F formation in a laboratory system. The testing conditions applied during this study were chosen to simulate the post-combustion zone, transition conditions (i.e., start-ups/shut-downs), and memory effects (persistently higher emissions for a period after a transient event) in full-scale incinerators. We optimized the parameters, which according to the literature and real facility conditions, lead to higher PCDD/F production levels. The main variables in this study were sampling time and temperature in order correlate PCDD/F formation rates with particulate carbon (e.g., soot) chlorination/oxidation rates in fly ash deposits.

Methods and Materials

A multi-temperature system (MTS) was used to study PCDD/F formation at different temperatures and times. In this system four beds could be treated simultaneously at four different temperatures using the same inlet gas flow. Experimental conditions were chosen in order to simulate the post-combustion zone, start-up and shut down operations in municipal solid waste incinerators (MSWI). The reaction beds were comprised of 0.005g of chlorinated-soot (Cl-soot), 0.5g of oxidized fly ash (OX), and 1.5 g of glass beads. The Cl-soot was produced using a diffusion flame at equivalence ratio (Φ) of 0.86 and adding 200 ppm of Cl_2 to the flow; OX was a C-free fly ash produced as reported in by Wikström [9]. The gas mixture fed to the MTS for all experiments was $8.0 \pm 0.1\%$ of O_2, 211 ± 2ppm of Cl_2, $6.0 \pm 0.8\%$ of water vapor (H_2O) and N_2. The water was added to the flow using a water bath at 55 °C and a flow of N_2 of 4 L/min. The H_2O and N_2 were then mixed with Cl_2 and passed through a reactor maintained at 800 °C. In this way different chlorine species (Cl_2, HCl, Cl·) were present in the gas flow [10]. The flow was split and passed through four parallel quartz or Pyrex tubes (51 cm in length, 8 mm ID) which were heated using a clamshell oven with four separate temp control zones. The exhaust gas stream from each reactor was sampled separately and analyzed for mono- to octa-PCDD/F according to a modified U.S. EPA Method 0023a [11]. A pump and a gas meter box were used for coupled beds. The flow through each reactor, controlled using rotameters, was 0.6 ± 0.1 L/min in each experiment. Experiments were conducted at four different temperatures (280, 320, 350,

380 °C) and five reaction times (10, 30, 60, 120, 180 min). A heating time of 6 minutes with only a N_2 flow was used before starting the experiments.

Results and Discussion
The analysis of the bed materials (soot and OX) prior to treatment resulted in non-detectable PCDD/F values. When soot and OX were treated separately, not combined, at 280 °C for 30 min, only low concentrations close to the detection limit (2.5 ng/run for each compound) were measured. However, the addition of soot into the OX bed led to significant PCDD and PCDF formation. The formation of PCDD and PCDF from OX and soot is shown in Figure 1 as a function of time (t) and temperature. In the cases in which replicate experiments were run, the average value and the relative errors bars are reported. The values represent the sum of the amounts in the solid phase (adsorbed in the reaction bed) and in the gas phase (trapped in the sampling train XAD). Separate analysis of the beds and sampling trains showed that the compounds studied were mainly adsorbed in the XAD. The percentage of PCDDs/Fs in the gas phase increased with increasing temp and decreasing t. The highest desorption from the reactant bed to the gas phase was found for the experiment at 380 °C with a reaction time of 10 minutes: only 10% of the total was found in the bed. Due to the high desorption from the bed, the contribution of desorption and destruction of PCDDs/Fs can not be distinguished: Figure 1 values represent the net formation.

PCDF concentrations were around 10 times higher than those of PCDD at all conditions. Although the overall amounts formed were significantly different, PCDD and PCDF formation vary in a similar way with temp and t. PCDD and PCDF formation was shown to be controlled by different pathways [12,13]; however, our results suggest a common step in the mechanisms, such as oxidation and chlorination of the carbon matrix to produce SOCs.

The net formation of PCDDs/Fs generally increased with temp and t. Our data suggest an increase in the reaction rate with time (Table1) for the first 60 min at the temperature of 280 and 320 °C and for the first 30 min at 350 °C. At 380 °C the reaction rate seems to decrease at 30 min and longer. Therefore, depending on the temperature, an induction period could be identified (evident for the 280-320 °C range). This could be due to the time needed for the chlorine and the oxygen to react with the solid phase causing surface oxychlorination. The rate increase with time for the experiment at 280-350 °C seems to suggest that the reaction was not controlled by the reactant concentrations. The reactants may be considered to be surface structures in the carbon matrix ($>C_{12}$)[11,14,15], high molecular weight PAHs[16,17], or perhaps monoaromatic compounds[15,18]. In the presence of metal catalysts, the reactants likely form biphenyl and chloro-biphenyl substructures with ambient oxygen and specific chlorine sources. The chlorine sources may be gas-phase chlorine or metal chloride complexes (e.g., copper or iron chlorides or oxychlorides). At longer reaction times, the PCDD/F net formation rates decreased and tended towards zero. This decreasing reaction rate with increasing time was shown also by Stieglitz et al[14] at 300 °C after reaction times of 2 h. The rate decrease is probably due to the decrease in the reactant concentrations. The reactant concentrations are directly dependent on the amount of soot remaining in the bed at the different reaction times and temperatures.

To investigate the relationship between soot gasification and the PCDD/F formation rate, CO_2 and CO emissions were measured during the experiments and used to calculate the soot degradation (in nmols) as a function of time. The data were fit with a first order equation as:
$$C \text{ (nmol)} = C_0\, e^{-kt}$$
where C is the total carbon, C_0 is the initial carbon (440 nmol) and t is the reaction time. The kinetic constants, k, and the R^2 values (always > 0.99) for the fitting were calculated for each of the four temperatures studied (data not shown). As seen in Figure 2, the carbon gasification as a function of t appears to complement the PCDD/F net formation with time (cf. Figure 1). After the first minutes of experiment (30-60 min for 280-350 °C) the decrease in carbon concentration in the bed could have led to a decrease in the formation of PCDDs/Fs (i.e., the formation reaction became dependent on the limiting concentration of carbon). It must be noted that at the temp of 380 °C, corresponding to the higher carbon gasification rate, the decrease in PCDD/F rate results in total amounts formed

Thermal processes

lower than at 350 °C. This result suggests that a maximum in net formation is achieved below 380 °C for the soot/OX fly ash mixture, although more experiments are required to clarify this point. The maximum in formation might be a function of time (cf. 350 and 380 °C for PCDFs in Figure 1).

Reaction temperature and time both impacted the PCDD and PCDF homologue patterns. Since PCDD and PCDF homologue distributions were similar at the same experimental conditions, only PCDF values are reported (Figures 3a and 3b for 10 and 60 min of experiment). As the reaction temperature was increased, the percentage of higher chlorinated congeners decreased and the percentage of lower chlorinated congeners increased. The reaction time also influenced how the homologue chlorination was affected by temperature: at different times we could identify a compound, as a separation point, that seemed to distinguish between two homologue groups. The amounts of one group increased with the temperature rise and the amounts of the other one decreased with the temperature rise. For example, at one hour HpCDFs and OCDFs decreased while MCDF thru PeCDFs increased; the percentage as HxCDF (separation point) seemed relatively unaffected by temperature. At 10 minutes, the homologue separation point shifted to PeCDF. As the reaction time increased at a constant temperature, the homologue profile also shifted towards higher percentages of higher chlorinated congeners. In the experiment at 10 min, low chlorinated compounds were predominant at 350 and 380 °C and decreased going from MCDF thru OCDF. After 60 min, the PeCDF thru OCDFs comprised at least 80% of the total PCDF formation at these temperatures.

PCDD/F formation from the soot may be considered the result of competitive chlorination and oxidation reactions on the carbon matrix [19], catalyzed by the metals in the OX fly ash after reaction with the gas-phase chlorine (creating metal oxide - chloride complexes). This competition is likely reflected in the observed homologue distribution. With increasing time, the metals in the fly ash and carbon matrix become increasingly more chlorinated [19] and the degradation of highly chlorinated SOCs leads to formation of higher chlorinated PCDDs and PCDFs. In the first minutes of the reaction, soot oxidation of less-chlorinated SOCs leads to a higher percentage of lower chlorinated homologues than in subsequent measurements. This effect was more evident for the 350 and 380 °C experiments, where the PCDD/Fs formation rate was higher than at the lower temperatures. After a transition time of 30-60 min, the chlorination of the soot reached an equilibrium — the surface-bound chlorine (e.g., in a metal chloride complex involved in soot chlorination and oxidation) consumed in PCDD/F formation was replaced with the reacting atmosphere and the homologue pattern in the 1 h and 2 h experiments was consistent (shifted to higher chlorinated compounds). This equilibrium was a function of temperature and, therefore, the homologue profile was also observed to be a function of temperature (in addition to time).

References
1. Stieglitz L, Vogg H. *Chemosphere* 1987;16:1917.
2. Vogg H, Stieglitz L. *Chemosphere* 1986;15:1373.
3. Ryan S, Wikstrom E, Gullett B K, Touati A. *Organohalogen Comp* 2004;66:1119.
4. Iino F, Imagawa T, Takeuchi M, Sadakata M. *Environ Sci Technol* 1999;33:1038.
5. Lee C W, Kilgroe J D, Raghunathan K. *Environ Eng. Sci* 1998;15:71.
6. Gass H, Lüder K, Sünderhauf W, Wilken M. *Organohalogen Comp* 2004;66:920.
7. Collina E, Lasagni M, Tettamanti M, Pitea D. *Environ Sci Technol* 2000;34:137.
8. Huang H, Bukens A. *Chemosphere* 2001;44:1505.
9. Wikstrom E, Ryan S, Touati A, Tabor D, Gullett B K. *Environ Sci Technol* 2004;38:3778.
10. Wikstrom E, Ryan S, Touati A, Telfer M, Tabor D, Gullett B K. *Environ Sci Technol* 2003;37:1108.
11. Wikstrom E, Ryan S, Touati A, Gullett B K. *Environ Sci Technol* 2003; 37:1962.
12. Wikstrom E, Ryan S, Touati A, Gullett B K. *Environ Sci Technol* 2004; 38:2097.

13. Hell K, Stieglitz L, Dinjus E. *Environ Sci Technol* 2001;35:3892.
14. Stieglitz L, Zwick G, Beck J, Bautz H, Roth W. *Chemosphere* 1989;19:283.
15. Hell K, Altwicker E R, Stieglitz L, Addink R. *Chemosphere* 2000;40:995.
16. Fullana A, Nakka H, Sidhu S. *Organohalogen Comp* 2004;66:1126.
17. Wilhelm J, Stieglitz L, Dinjus R, Will R. *Chemosphere* 2001;42:797.
18. Stieglitz L. *Environ. Eng Sci* 1998;15:5.

Table 1 – PCDF (F) and PCDD (D) instantaneous formation rates (Δ yield/ Δ time) in nmols/min at each temperature (^{o}C) studied

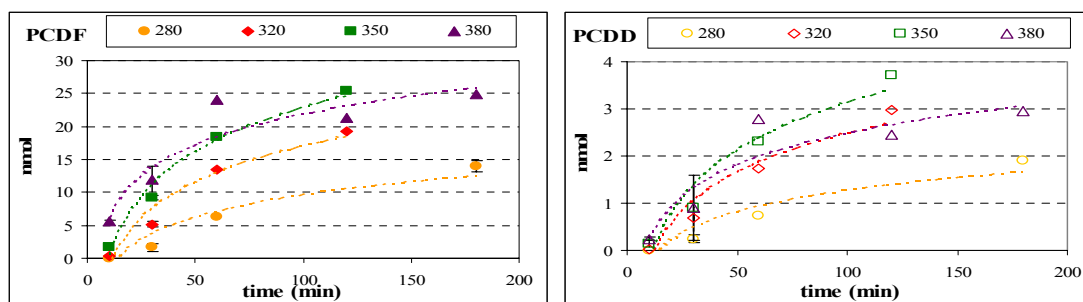| Time (min)	*F 280*	*F 320*	*F 350*	*F 380*	*D 280*	*D 320*	*D 350*	*D 380*
10	7.00E-03	3.07E-02	1.77E-01	5.68E-01	1.19E-03	2.80E-03	1.32E-02	2.44E-02
30	8.20E-02	2.42E-01	4.57E-01	3.19E-01	1.18E-02	3.34E-02	3.81E-02	3.31E-02
60	1.54E-01	2.79E-01	2.52E-01	3.98E-01	1.61E-02	3.48E-02	4.72E-02	6.23E-02
120		9.69E-02	1.14E-01	-4.46E-02		2.07E-02	2.32E-02	-5.41E-03
180	6.37E-02			5.81E-02	9.85E-03			8.18E-03

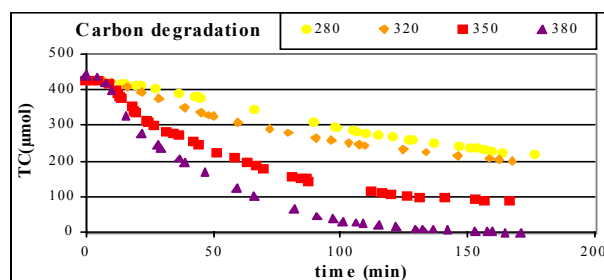**Figure 1** - PCDD/Fs total formation with time (min) and temperature (^{o}C)

Figure 2 – Carbon degradation as a function of reaction temperature (^{o}C) and time (min)
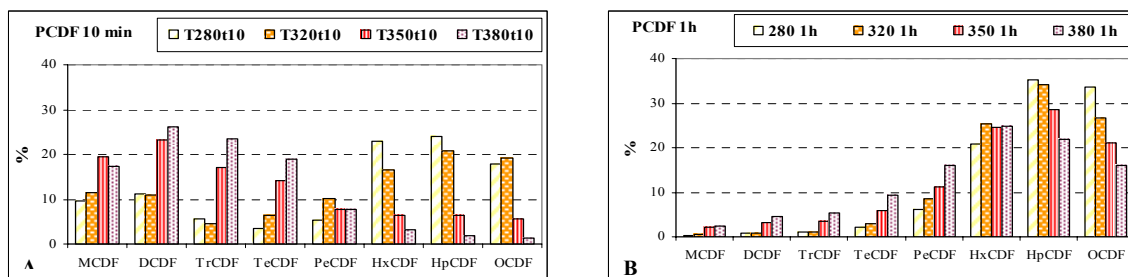

Figure 3 – PCDD/F homologue percentage distribution in 10 minutes (a) and 1 hour experiments (b)