

Formation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans on secondary combustor/boiler ash from a rotary kiln burning hazardous waste

R. Addink¹, E.R. Altwicker*

Department of Chemical and Biological Engineering, Rensselaer Polytechnic Institute, Ricketts Building, Troy, NY 12180-3590, USA

Received 15 January 2004; received in revised form 12 May 2004; accepted 22 June 2004

Available online 23 August 2004

Abstract

Ash from the secondary combustor/boiler of a rotary kiln burning hazardous chemical waste was tested in the laboratory for its potential to form polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F). The ash contained only a small quantity of “native” PCDD/F, i.e., formed on the ash in the facility. However, it produced a considerable amount of these compounds when heated in 10% O₂/N₂ under “de novo” conditions, i.e., with residual carbon (present on the ash as result of incomplete combustion) as the only organic material. The ash yielded PCDD/F for up to 90 min; gave PCDD/F yields proportional to the amount of ash used in the reaction bed; and displayed an optimum temperature range for formation (397–548 °C) higher than seen for most municipal solid waste (MSW) fly ashes. The role of copper and iron as catalytic material on the ash is discussed.

© 2004 Elsevier B.V. All rights reserved.

Keywords: De novo formation; Polychlorinated dibenzo-*p*-dioxins; Dibenzofurans; Hazardous waste; Secondary combustor/boiler ash; Rotary kiln

1. Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDD) and dibenzofurans (PCDF) can be formed in a variety of combustion processes, including incineration of municipal solid waste (MSW) and hazardous chemical waste. Although the first has received a lot of attention as a source of these toxic compounds and has been the topic of many laboratory studies [1], the latter has not been investigated as much. As with modern MSW incinerators, hazardous waste burning facilities with state-of-the-art air pollution control (e.g., electrostatic precipitator, two-stage wet scrubber, activated coke reactor, and selective catalytic reactor) can have very low PCDD/F emis-

sions (e.g., 0.01 ng TEQ/m³ [2]). Nevertheless, annual releases into the atmosphere of PCDD/F from hazardous waste incineration in the United States have been estimated between 15 g [3] and 79 g [4] TEQ per year.

Laboratory studies of hazardous waste incineration and PCDD/F formation have focused on the role of chlorine [5], metal chlorides [6], and process parameters [7]. The role of particles and deposits has rarely been explored. Work by Naikwadi et al. [8,9] was done with baghouse filter ash and bottom ash from an industrial waste incinerator, using ¹³C-pentachlorophenol as reactant at 300 °C for 60 min in air. Both ashes produced 830–950 ng PCDD/100 μg ¹³C-pentachlorophenol. H₇CDD and OCDD were the main congeners formed. Gullett et al. [10] explored PCDD/F formation in an industrial boiler co-firing hazardous waste. This co-firing was simulated by injecting a dichlorobenzene or a dichlorophenol into the boiler, combined with copper naphthenate as catalytic material. Fuel oil was used as the main feed. Other conditions were chosen so as to produce

* Corresponding author. Tel.: +1 518 276 6927; fax: +1 518 276 4030.

E-mail addresses: raddink@wadsworth.org (R. Addink), altwicker@rpi.edu (E.R. Altwicker).

¹ Present address: New York State Department of Health, Empire State Plaza, Wadsworth Center D-400, PO Box 509, Albany, NY 12201-0509, USA. Tel.: +1 518 474 7617.

sooting, leading effectively to “de novo” type PCDD/F formation from high-molecular weight material. Concentrations of PCDD/F formed were up to 2000 ng/m³. Boiler tube deposits were shown to be a particularly significant sink and source of PCDD/F, producing subsequent formation over an extended period of time.

Both of these studies illustrated the importance of particulate matter in PCDD/F formation during hazardous waste combustion. Particles originating from the rotary kiln part of a facility and carried with the off-gas into the downstream secondary combustor/boiler will obviously be carried further into the post-combustion zone and air pollution control device. When collected there these particles would likely have a residence time on a min–h scale, as do collected particles in MSW incinerators [11], and a temperature regime ($T < 600\text{ }^{\circ}\text{C}$) conducive to surface-mediated PCDD/F formation if carbon sources are present. De novo formation of PCDD/F could be feasible under these conditions, as Blaha and Hagenmaier [12] showed already significant PCDD/F yields from carbon after only 1 min and others found that this process can continue for up to several hours [1].

We used ash collected from the secondary combustor/boiler of a rotary kiln burning hazardous chemical waste and studied its PCDD/F formation potential from residual carbon. The ash was analyzed for “as received” PCDD/F (formed during combustion in the facility) and investigated for PCDD/F formation as function of reaction time, bed size, and temperature. It was also analyzed for metals and some other elements to achieve a better understanding of catalytic activity.

2. Materials and methods

Ash was obtained from the secondary combustion chamber/boiler from a facility in the United States burning hazardous chemical waste in a rotary kiln. Details on temperature and residence time at the sampling location, date of collection, and sampling method were not available to us. The ash was Soxhlet-extracted for 24 h with toluene prior to any experiment, leaving only high-molecular weight, intractable residual carbon as organic material to form PCDD/F in subsequent annealing experiments. The composition of the ash was measured with X-ray fluorescence (quantitative elemental analysis), and with X-ray diffraction plus scanning electron microscopy/energy dispersive X-ray spectroscopy for qualitative assessment of compounds. Results are listed in Table 1.

Reaction mixtures used in our experiments consisted of ash and glass beads as diluent. The materials were mixed physically by shaking and the total sample weight was 1 g for each experiment. The mixture was placed in a Pyrex glass or quartz tube against a frit with a plug of glass wool at the upstream end of the bed. It was heated in a furnace for 60 min to the desired temperature under a stream of N₂ during which formation of PCDD/F was low (0.04 nmol/g of ash). Once the

Table 1
Analysis of ash (wt.%)

Na 2.2	Cl 4.1	Mn 0.013	Sr 0.034
Mg 3.7	K 0.15	Fe 1.2	Zr 0.014
Al 0.22	Ca 0.40	Ni 0.037	Ba 0.17
Si 1.4	Ti 0.040	Cu 0.23	Pb 0.040
S 0.95	Cr 0.020	Zn 2.6	
Compounds identified on ash			
NaCl	MgO	MgFe ₂ O ₄	
CaSO ₄	ZnO	MgFe ₃ O ₄	

sample reached the reaction temperature, a mixture of 10% O₂/N₂ was passed through the bed. The flow of gases was regulated with electronic mass flow controllers. Evaporating PCDD/F were collected throughout the experiment in an ice-cooled trap containing toluene.

After each experiment the solid and gas phase (in toluene) were combined for analysis. Details have been described elsewhere [13]. T₄CDD-OCDD and T₄CDF-OCDF were measured. Blanks taken from the ash after 24 h toluene extraction and from the clean up procedure were found to contain negligible amounts of PCDD/F.

3. Results and discussion

The “as received” PCDD/F content of the ash was only 0.03 nmol/g of ash. MSW fly ash usually contains 1–2 orders of magnitude more PCDD/F. Based on these low amounts of PCDD/F, the ash could perhaps be expected to have low reactivity during subsequent annealing. On the other hand, the high temperature at the location within the facility where the ash was collected (secondary combustor/boiler, likely with $T > 600\text{ }^{\circ}\text{C}$ when sampled at the end of that zone, with T typically at 1200–1400 °C in the secondary combustor itself) may have destroyed most of the PCDD/F formed.

Results of a time study carried out at 299 °C – a typical temperature for optimum formation of PCDD/F on MSW fly ash [1] – are shown in Fig. 1. At this temperature the ash showed moderate reactivity (a typical MSW fly ash could produce up to 10× more of these compounds under these conditions). The data suggested either a linear relationship of PCDD/F formation with time ($r^2 = 0.65$) or a gradual leveling-off. Milligan and Altwicker found a linear dependency between 0 and 30 min for de novo formation on a MSW fly ash [14]. However, they did not measure longer reaction times. De novo formation typically levels off after 120 min [1]. The [PCDD]:[PCDF] ratio fluctuated between 0.20 and 0.55, i.e., <1. Such ratios are often found in de novo formation on both MSW and so-called “model fly ash” (i.e., synthetic mixtures of support (SiO₂, Al₂O₃), a carbon source, and metal chlorides) [15]. These observations might be a clue that de novo formation on ash from a hazardous waste burning facility and on MSW ash proceed in the same way. The main congeners formed were hepta- and octa-CDD/F.

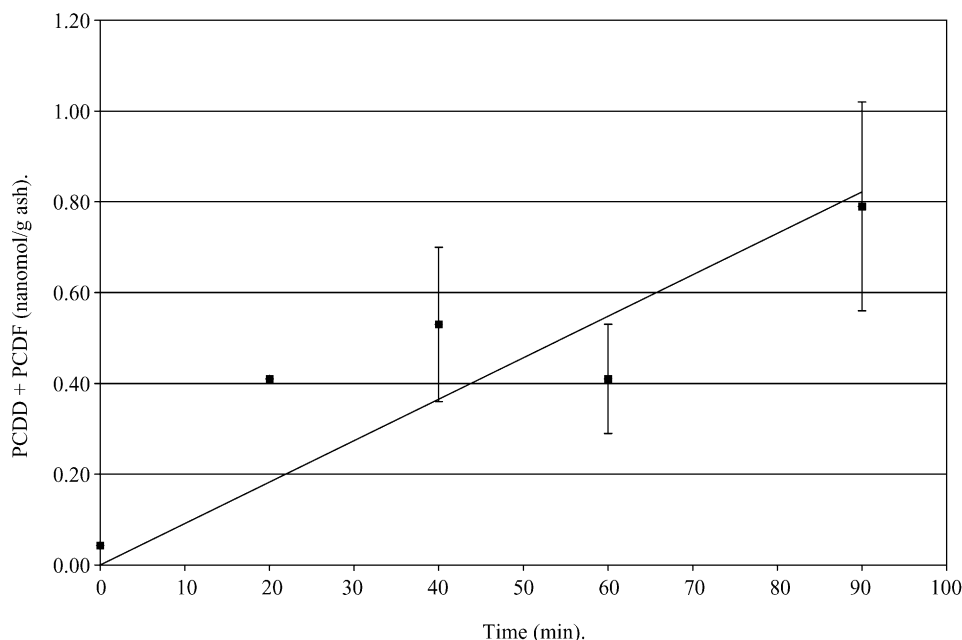


Fig. 1. Formation of PCDD/F on ash at 299 °C as function of time. Conditions: 0.50 g ash and 0.50 g beads; $T = 299$ °C; 60 min warming up in N_2 (79 ± 3 mL/min), followed by 0–90 min 10% O_2/N_2 (94 ± 4 mL/min). Data points – 0 min: $n = 1$; 20 min: $n = 1$; 40 min: $n = 2$; 60 min: $n = 5$; 90 min: $n = 2$; average \pm standard deviation shown (if $n > 1$). Regression line added as possibility.

To explore the role of the amount of ash and its homogeneity, we carried out a series of runs where the bed size was varied between 0 g (glass beads only) and 1 g (ash only). Data are shown in Fig. 2 with yields reported in nmol/g of sample (as opposed to per g of ash used for the other two graphs). A linear relationship was found with good correlation ($r^2 = 0.91$). The ash particles were very uniform by visual

appearance and seemed to be of a more homogeneous nature than MSW fly ash. This may explain the results found that a doubling or quadrupling of the bed size simply led to a proportional increase of PCDD/F yields. [PCDD]:[PCDF] ratios were 0.24 ± 0.10 (0.25 g ash); 0.35 ± 0.13 (0.50 g ash); 0.47 ± 0.23 (1.00 g ash); i.e., although the average ratio increased the margins of error in the data suggested this change was

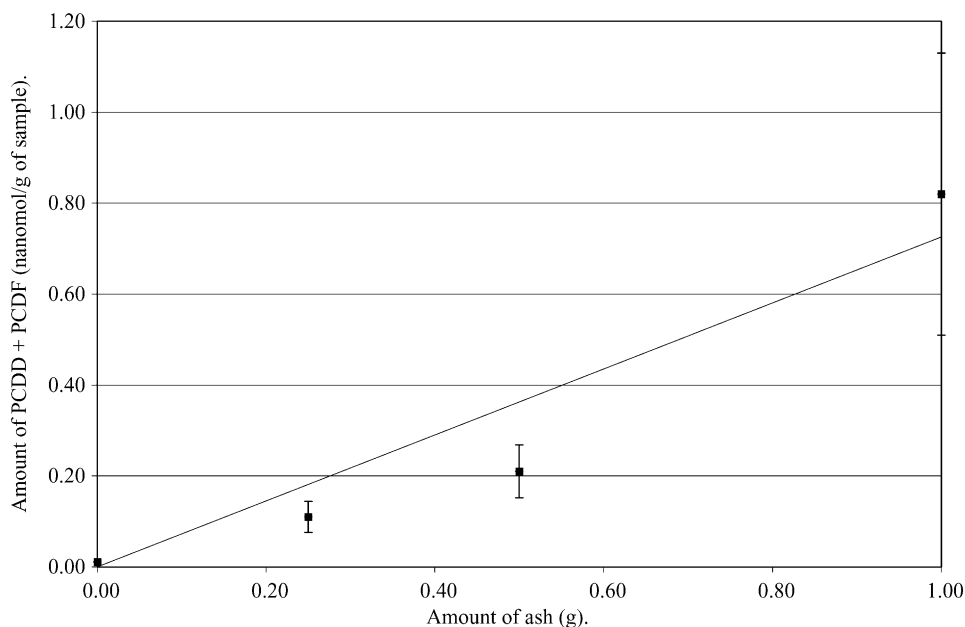


Fig. 2. Formation of PCDD/F on ash for 60 min at 299 °C as function of the amount of ash. Conditions: 0–1.00 g ash and 0–1.00 g beads; $T = 299$ °C; 60 min warming up in N_2 (77 ± 3 mL/min), followed by 60 min 10% O_2/N_2 (95 ± 2 mL/min). Data points – 0 g ash: $n = 1$; 0.25 g ash: $n = 3$; 0.50 g ash: $n = 5$; 1.00 g ash: $n = 3$; average \pm standard deviation shown (if $n > 1$). Note data here in nmol/g sample.

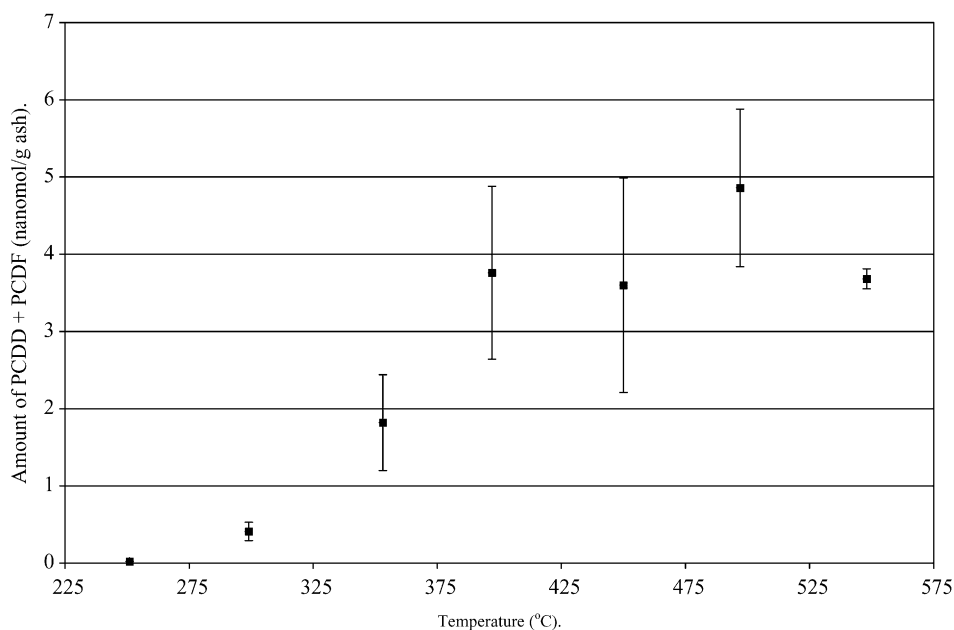


Fig. 3. Formation of PCDD/F on ash for 60 min as function of temperature. Conditions: 0.50 g ash and 0.50 g beads; $T = 251\text{--}548\text{ }^{\circ}\text{C}$; 60 min warming up in N_2 ($77 \pm 4\text{ mL/min}$), followed by 60 min 10% O_2/N_2 ($96 \pm 2\text{ mL/min}$). Data points— $251\text{ }^{\circ}\text{C}$: $n = 1$; $299\text{ }^{\circ}\text{C}$: $n = 5$; $353\text{ }^{\circ}\text{C}$: $n = 3$; $397\text{ }^{\circ}\text{C}$: $n = 6$; $450\text{ }^{\circ}\text{C}$: $n = 4$; $497\text{ }^{\circ}\text{C}$: $n = 2$; $548\text{ }^{\circ}\text{C}$: $n = 2$; average \pm standard deviation shown (if $n > 1$).

not significant. As in the other experiments mainly hepta- and octa-CDD/F were formed.

Fig. 3 shows the influence of temperature on PCDD/F formation on the ash. At $251\text{ }^{\circ}\text{C}$ formation was almost zero, increasing steadily up to $397\text{ }^{\circ}\text{C}$. Between 397 and $548\text{ }^{\circ}\text{C}$ there was considerable scatter in the data with no clear maximum. The ash was more reactive at higher temperatures than typically seen with a MSW fly ash, which gave little or no formation at $T > 450\text{ }^{\circ}\text{C}$ [13]. MSW fly ash also usually gives an inverted U-shaped plot with maximum formation within a narrow temperature range [1]. [PCDD]:[PCDF] ratios decreased from 0.29 at $251\text{ }^{\circ}\text{C}$ /0.35 \pm 0.13 at $299\text{ }^{\circ}\text{C}$ to 0.10 \pm 0.02 at $497\text{ }^{\circ}\text{C}$ /0.08 at $548\text{ }^{\circ}\text{C}$, which has also been observed with MSW fly ash [16]. H_7CDD and CDD comprised 51–100% of all PCDD formed; H_7CDF and OCDF comprised 54–100% of all PCDF.

Although the “as received” concentration of the ash was low, it showed significant formation of PCDD/F under laboratory conditions. Despite the high temperatures typically maintained in the secondary combustor ($1200\text{--}1400\text{ }^{\circ}\text{C}$), the small particle size of the ash and its fine pore structure, sufficient carbon must have survived on the surfaces to give considerable de novo synthesis of PCDD/F. In addition to potential de novo formation of PCDD/F in the post-combustion zone/air pollution control device of the rotary kiln, the off-gas of the kiln could contain precursors (such as chlorobenzenes and chlorophenols, although at lower concentrations than found in MSW off-gas) that could give PCDD/F formation on a short time scale (s) on both collected and uncollected particles [9].

Analysis of the ash suggested copper (0.23 wt.%) and iron (1.2 wt.%) as possible catalytic metal ions (Table 1),

with other metal ions unlikely to have much effect. Although [copper] was $5\times$ lower than [iron] on the ash, its concentration of 0.23 wt.% was certainly high enough to give appreciable amounts of PCDD/F. Work by Stieglitz et al. [17] showed that a synthetic fly ash composed of Mg–Al–silicate, 1 wt.% charcoal, 1 wt.% KCl, and 0.24 wt.% Cu^{++} , produced 11 nmol/g of PCDD/F when heated for 120 min at $300\text{ }^{\circ}\text{C}$ in air. Note that with [chlorine] 4 wt.% (Table 1) on this ash a sufficiently high concentration of Cl^- ions should be available so as to not be a limiting reagent. It is of interest that a MSW fly ash used in a number of studies in our laboratory contained 4–5 wt.% water-soluble Cl^- [13]. Hence, even though a rotary kiln could be expected to combust chlorinated waste and thus have a feed higher in [chlorine] than a MSW incinerator, the resulting solid residual materials (secondary combustor/boiler ash versus MSW fly ash) appeared to have very similar chlorine loads. With most likely only part of the copper present on the ash as CuCl or CuCl_2 , the effective $[\text{Cu}^+]$ or $[\text{Cu}^{++}]$ (available for PCDD/F formation) would be $<0.23\text{ wt.}\%$.

Recent work by Ryan and Altwicker [18] identified FeCl_2 , FeCl_3 , and FeOCl as possible chlorinating and catalytic agents in PCDD/F formation from carbon black. These authors found maximum formation at $400\text{ }^{\circ}\text{C}$, but formation continued at higher temperatures to some extent [19]. Although a 2% O_2/N_2 reaction mixture was used in the gas flow, PCDD/F formation occurred also with 10% O_2/N_2 [20] (the same $[\text{O}_2]$ used in our work). With 1.2 wt.% iron and 4 wt.% chlorine available on the ash, FeCl_x and FeOCl may have formed and promoted PCDD/F formation. The participation of iron compounds may explain why the ash produced significant amounts of PCDD/F between 400 and $550\text{ }^{\circ}\text{C}$. The

tendencies of FeCl_x and FeOCl to produce mainly H_7/OCDD and H_7/OCDF and low $[\text{PCDD}]:[\text{PCDF}]$ ratios (<0.12 when $T > 350^\circ\text{C}$) [18] are very similar to our own observations described above (mainly hepta- and octa-congeners formed and decreasing $[\text{PCDD}]:[\text{PCDF}]$ ratios – such as 0.1 at 500°C – with increasing T).

Copper and iron have to be considered together in explaining PCDD/F formation on this ash. Although iron was likely responsible for PCDD/F formation at the high temperature end of the range studied ($T > 400^\circ\text{C}$), the data reported by Ryan and Altwicker [18] showed that FeCl_x and FeOCl promoted PCDD/F formation even at 300°C . The temperature range between 250 and 400°C likely gave combined copper and iron catalyzed formation. Synergistic effects by complexes such as $[\text{CuCl}]^+[\text{FeCl}_4]^-$ may also be involved [21].

4. Conclusion

“As received” levels of PCDD/F on the ash used in this work were low. The high temperature typically encountered in the secondary combustor/boiler chamber of a rotary kiln (1200 – 1400°C) likely destroyed any PCDD/F on the ash. The ash was sampled upstream of the post-combustion zone, preventing re-formation of these compounds at lower temperatures ($T < 600^\circ\text{C}$). However, our work clearly showed the potential for PCDD/F formation on the ash when exposed to such temperatures in the laboratory. De novo formation of PCDD/F proved to be an effective mechanism. At $T > 400^\circ\text{C}$ formation levels on our ash approached those of MSW fly ashes at lower temperatures (300 – 350°C). The fact that formation continued up to 550°C implied that the temperature zone for surface-mediated PCDD/F formation is wider for hazardous waste facility ash than for MSW fly ash. This means that ash (when partially carried into the post-combustion zone) could be reactive at these temperatures in this zone/air pollution control device. Ash formed during the incineration of hazardous waste in a rotary kiln has to be considered as a source of PCDD/F formation when assessing emissions of these compounds from rotary kilns.

References

- [1] R. Addink, K. Olie, Mechanisms of formation and destruction of PCDD and PCDF in heterogeneous systems, *Environ. Sci. Technol.* 29 (6) (1995) 1425–1435.
- [2] P. Luthardt, J. Mayer, J. Fuchs, Total TEQ emissions (PCDD/F and PCB) from industrial sources, *Chemosphere* 46 (910) (2002) 1303–1308.
- [3] J.J. Cudahy, H.G. Rigo, National annual dioxin emissions estimate for hazardous waste incinerators, *J. Air Waste Manage. Assoc.* 48 (1998) 1107–1111.
- [4] US Environmental Protection Agency, Draft technical support document for hazardous waste combustion maximum achievable control technology standards, vol. 5, Washington, DC, 1996.
- [5] I. Halonen, J. Tarhanen, S. Ollikainen, P. Ruokojärvi, K. Tuppurainen, J. Ruuskanen, The effect of inorganic and organic chlorine on formation of highly chlorinated organic compounds during incineration – laboratory pilot-study, *Chemosphere* 28 (12) (1994) 2129–2138.
- [6] I. Halonen, K. Tuppurainen, J. Ruuskanen, Formation of aromatic chlorinated compounds catalyzed by copper and iron, *Chemosphere* 34 (12) (1997) 2649–2662.
- [7] G. Mascolo, L. Spinosa, V. Lotito, G. Mininni, G. Bagnuolo, Lab-scale evaluations on formation of products of incomplete combustion in hazardous waste incineration: influence of process variables, *Water Sci. Technol.* 36 (11) (1997) 219–226.
- [8] K.P. Naikwadi, I.D. Albrecht, F.W. Karasek, Mechanism of formation of PCDD/F in industrial waste incineration and a method of prevention of their formation, *Organohalogen Compds.* 8 (1992) 277–279.
- [9] K.P. Naikwadi, I.D. Albrecht, F.W. Karasek, Mechanism of formation of PCDD/F in industrial waste incineration and a method of prevention of their formation, *Chemosphere* 27 (1–3) (1993) 335–342.
- [10] B.K. Gullett, A. Touati, C.W. Lee, Formation of chlorinated dioxins and furans in a hazardous-waste-firing industrial boiler, *Environ. Sci. Technol.* 34 (11) (2000) 2069–2074.
- [11] R. Konduri, E.R. Altwicker, Analysis of time scales pertinent to dioxin/furan formation on fly ash surfaces in MSW incinerators, *Chemosphere* 28 (1) (1994) 23–45.
- [12] J. Blaha, H. Hagenmaier, Time dependence of the de novo synthesis of PCDD/F and potential precursors on a model fly ash, *Organohalogen Compds.* 23 (1995) 403–406.
- [13] R. Addink, F. Espourteille, E.R. Altwicker, Role of inorganic chlorine in the formation of PCDD/F from residual carbon on incinerator fly ash, *Environ. Sci. Technol.* 32 (21) (1998) 3356–3359.
- [14] M.S. Milligan, E.R. Altwicker, The relationship between de novo synthesis of PCDD and PCDF and low-temperature carbon gasification in fly ash, *Environ. Sci. Technol.* 27 (8) (1993) 1595–1601.
- [15] L. Stieglitz, Selected topics on the de novo synthesis of PCDD/F on fly ash, *Environ. Eng. Sci.* 15 (1) (1998) 5–18.
- [16] R. Addink, E.R. Altwicker, Role of copper compounds in the de novo synthesis of PCDD/F, *Environ. Eng. Sci.* 15 (1) (1998) 19–27.
- [17] L. Stieglitz, G. Zwick, J. Beck, W. Roth, H. Vogt, On the de-novo synthesis of PCDD/F on fly ash of municipal waste incinerators, *Chemosphere* 18 (1–6) (1989) 1219–1226.
- [18] S.P. Ryan, E.R. Altwicker, Understanding the role of iron chlorides in the de novo synthesis of PCDD/F, *Environ. Sci. Technol.* 38 (6) (2004) 1708–1717.
- [19] Y. Xun, Ph.D. Dissertation, Rensselaer Polytechnic Institute, 1997.
- [20] S.P. Ryan, Ph.D. Dissertation, Rensselaer Polytechnic Institute, 2001.
- [21] K.S. Brenner, Waste incineration and PCDD/F formation – problems, solutions, an essay on the chemical and technical state of the art, *Toxicol. Environ. Chem.* 47 (1995) 7–14.