

Thermal Degradation of PCDD/F in Municipal Solid Waste Ashes in Sealed Glass Ampoules

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Due to their high concentrations of toxic organic compounds such as polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F), metals, and water-soluble salts, fly ashes are classified as hazardous waste in the European Union and are required to be deposited in controlled landfills. We have shown here that the tetra- to octachlorinated PCDD/F in fly ash can be degraded by thermal treatment. The temperature needed for total degradation of PCDD/F depends on the composition of the fly ash. Its concentrations of unburned carbon and alkaline compounds were found to be important in this respect. Experimental design was used to investigate the effects of varying the temperature, residence time, and atmosphere on the degradation of PCDD/F in three different types of fly ash. The results showed that the three ashes clearly showed different degradation potentials for PCDD/F during thermal treatment. The concentrations of unburned carbon, alkaline species such as CaO and Na₂O, and metals such as copper and iron strongly influenced the degradation of PCDD/F. However, the different combinations of pH and amounts of native PCDD/F, unburned carbon, metals (Cu, Fe, Sn and Na), and sulfur in the ashes made it difficult or even impossible to conclude that any single parameter was responsible for the degradation of PCDD/F in these thermal treatment experiments. The decreases observed in all of the experiments are due to dechlorination and/or destruction of PCDD/F: depending on the temperature and ash composition, either of these processes may be the more important.

Introduction

It has been known that polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F) are present in ashes from the combustion of municipal solid waste (MSW) since 1977, when Olie et al. found them in fly ash (1). PCDD/F occurs in both flue gases and ashes, but more than 95% of the total amount of PCDD/F can be adsorbed on the fly ashes (2), the ratio depending on the temperature and air pollution control device used. In the European Union (EU), fly ash from municipal solid waste (MSW) combustion is classified as hazardous waste because of its content of PCDD/F and other toxic organic compounds, metals, and water-soluble salts. Therefore, fly ash is required to be deposited in controlled landfills, which is a short-term solution as degradation of persistent organic pollutants (POP) is extremely slow in landfills and our knowledge of leaching of toxic organic compounds during long-term storage is limited. In addition,

combustion companies would like to minimize the cost of land filling.

Formation and degradation reactions of PCDD/F occur simultaneously in flue gas under normal combustion conditions between 200 and 600 °C. Two processes have been proposed for the formation of PCDD/F: de novo synthesis from the elements C, H, Cl, and O and formation from related chlorinated precursors such as polychlorinated phenols (PCPh), polychlorinated benzenes (PCBz), and polychlorinated biphenyls (PCB). After the DD/F molecule is formed, it may also be chlorinated.

Degradation can occur either via dechlorination/hydrogenation reactions, where the molecule loses one or more chlorine atoms which are replaced by hydrogen atoms, or via oxidation reactions, in which the carbon–oxygen bond is broken and the PCDD/F molecule is degraded to smaller chlorinated molecules such as PCPhs and PCBzs. Fly ash plays an important role in both formation and degradation, acting as a catalytic surface in chlorination/dechlorination reactions. Temperatures below 200 °C are too low for either formation or degradation reactions to occur, and at temperatures over 600 °C degradation reactions are favored.

When fly ash is heated, both formation and degradation occur at temperatures between 200 and 600 °C. Studies seeking to identify conditions that suppress the formation reactions have been performed over the last two decades. The original dechlorination process, by Hagenmaier et al. (3), included the following conditions: oxygen deficiency, temperature between 250 and 400 °C, residence time around 1 h, and a discharge temperature below 60 °C. The efficacy of this process was confirmed by Ishida et al. (4) in a full-scale treatment plant using a temperature of 350 °C, a residence time of 1 h, and an oxygen-deficient atmosphere of nitrogen. The total degradation of PCDD/F under these conditions was >99.7%. Neither Hagenmaier et al. nor Ishida et al. accounted for the effects of the composition of the fly ash used in these processes.

Destruction of PCDD/F in fly ash seems to be highly dependent on the composition of the fly ash. This can be seen in results from a number of studies (3, 5–7). Temperature appeared to be the most important factor determining whether formation or degradation is favored, but variables such as residence time, atmosphere, and fly ash composition have been found to be very important as well.

Degradation is also dependent on the atmosphere: in an oxidative atmosphere, higher temperatures (400–600 °C) are required for the degradation of PCDD/F (7). However, in an inert atmosphere, temperatures as low as 300–400 °C can result in degradation (6), as confirmed by Addink et al. (8). It has also been shown that the rate of formation of PCDD/F is higher in the absence of a gas flow (9), possibly because the gas flow transports away the oxygen, preventing it from participating in formation reactions. Formation is dependent on the concentration of oxygen, and even at oxygen concentrations as low as 1%, increases in PCDD/F are observed (9, 10). Further increases in oxygen concentration (up to 10%) have resulted in higher PCDD/F formation rate.

As for the composition of the ash, the concentrations of carbon, metals (Cu, Fe, Sn), and calcium (which gives the ash a high pH) have been shown to have an impact on the degradation, as well as the formation, of PCDD/F when fly ash is heated (6, 11–13). High temperatures are thought to be needed to achieve complete degradation of PCDD/F in fly ash with high concentrations of unburned carbon, since formation via de novo synthesis occurs at temperatures between 250 and 400 °C. Since most studies performed with

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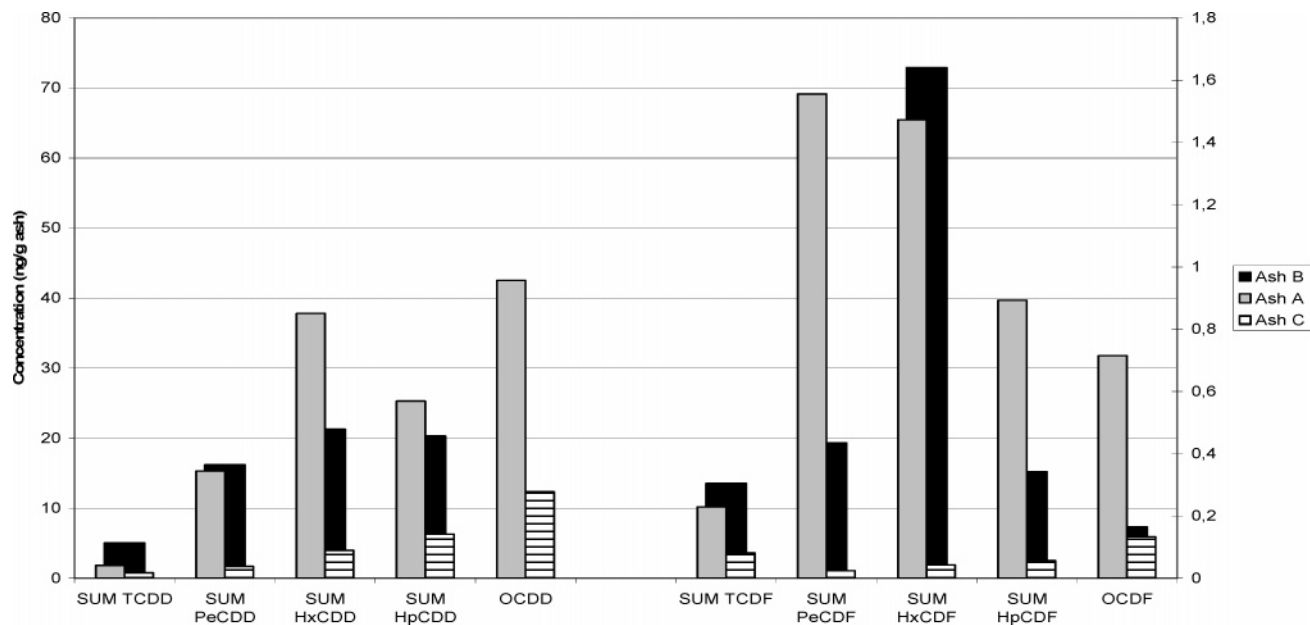


FIGURE 1. Profiles of untreated ash B (left y-axis) and ashes A and C (right y-axis). The concentration of OCDD in ash B is 11.02 ng/g of ash.

real fly ashes have included pretreatment steps that remove carbon and dioxins, or have not reported the carbon content, it is difficult to evaluate how carbon content affects the destruction potential of fly ashes.

The effect of high calcium content on PCDD/F degradation has been studied by Weber et al. (11), who analyzed fly ash taken before and after injecting $\text{Ca}(\text{OH})_2$ into flue gas and showed that $\text{Ca}(\text{OH})_2$ disfavors the formation of PCDD/F. In another investigation, the effects of $\text{Ca}(\text{OH})_2$, copper compounds (elemental Cu, Cu_2O and $\text{Cu}(\text{OH})_2$), Fe_2O_3 , ZnO, PbO, and SnO were studied (13). The results showed that a model fly ash containing $\text{Ca}(\text{OH})_2$ had considerable destruction potential, even at a temperature as low as 260 °C in an inert atmosphere. Cu_2O was found to exhibit the highest dechlorination potential, while elemental Cu and $\text{Cu}(\text{OH})_2$ were less effective. Fe_2O_3 and SnO were also tested and showed dechlorination potential (13). The similarities between the isomer patterns from experiments with model fly ash and fly ash from an incineration process indicate that the dechlorination can be assigned to the effects of various metal oxides/compounds.

Differences between the degradation process of dioxins and furans have been observed (12–14). The mechanisms of degradation reactions obviously depend on the composition of the fly ash, and since this is seldom reported, it is difficult to determine the causes of different degradation patterns observed with these fly ashes. It has been proposed that iron and copper are involved in dechlorination reactions and that other degradation reactions are facilitated by the alkalinity of the ash (13). The question of whether dechlorination precedes degradation of PCDD/F or whether the two processes occur simultaneously has also been considered (3), and it has been shown that either of these two possibilities may occur (12).

In summary, the net formation/destruction of PCDD/F observed at any given temperature is dependent on the catalytic properties of the fly ash in question. At temperatures over 400 °C together with a long residence time, the concentration of PCDD/F can be reduced to very low levels in all fly ashes, regardless of the atmosphere.

The aim of this study was to investigate the influence of temperature, residence time, and atmosphere on the degradation of PCDD/F in fly ashes with different composition. In addition, since sealed systems are cheaper than flow

TABLE 1. Characteristics of the Three Ashes

	ash A	ash B	ash C
facility	BFB	grate	BFB
type of ash	filter ash	ESP ash	cyclone ash
C (% by weight)	1.9	11.1	0.58
carbonate (% by weight)	1.9	0.86	0.52
CaO (% of dry substance)	10.4	11.7	17
Na_2O (% of dry substance)	30.6	3.82	5.59
Fe_2O_3 (% of dry substance)	1.96	5.48	4.25
SiO_2 (% of dry substance)	6.61	27.7	41.4
Cl (% of dry substance)	22	5.8	1.7
Cu (mg/kg of dry substance)	9470	1010	3840
Cd (mg/kg of dry substance)	98.3	184	14.3
Sn (mg/kg of dry substance)	207	164	72.9
Ni (mg/kg of dry substance)	59.9	158	159
Pb (mg/kg of dry substance)	6800	7720	1140
Zn (mg/kg of dry substance)	8930	23600	5930
S (mg/kg of dry substance)	35500	11700	7930
pH	11.5	7.5	11.5

systems, we wanted to investigate the degradation of PCDD/F in ashes in a sealed system.

Experimental Section

The three ashes used in this study originated from two different plants, one with a fluidized bed (ashes A and C) and one with an old grate incinerator (ash B). The fluidized bed was a 15 MW unit of the bubbling type (BFB), built in the middle of the 1980s. The flue gas cleaning system consisted of a cyclone and a textile filter. Ashes A and C were obtained in October 2000. Ash A is a filter ash and was taken from the apparatus after filtration, while ash C was taken from the cyclone prior to filtration. Ash B was obtained in January 1986 from a 20 MW grate incinerator built in 1984 and was taken from the electrostatic precipitator. The only flue gas cleaning used at this time was an electrostatic precipitator working at 150 °C, and the process used no additives. Profiles of the PCDD/F content of all three ashes (A, B, and C) can be seen in Figure 1 and the characteristics of the ashes in Table 1. Both plants were incinerating MSW at the time of sampling.

The study was divided into three parts: a screening study, the main study, and finally four additional experiments (Table

TABLE 2. Experimental Matrix Showing the Ashes and Conditions—Temperature, Residence Time and Atmosphere (N₂ or Air)—Used in Each Experiment

	study	ash	T (°C)	t (h)	atmosphere	no. of samples
1	screening	A	150	2	N ₂	1
2	screening	A	150	2	air	1
3	screening	A	300	2	N ₂	1
4	screening	A	300	2	air	1
5	screening	A	450	2	N ₂	1
6	screening	A	450	2	air	1
7	main	B	150	1	N ₂	2
8	main	B	300	1	N ₂	2
9	main	B	150	2	N ₂	2
10	main	B	300	2	N ₂	2
11	main	B	150	1	air	2
12	main	B	300	1	air	2
13	main	B	150	2	air	2
14	main	B	300	2	air	1
15	main	B	225	1.5	N ₂	2
16	main	B	225	1.5	N ₂	2
17	main	B	225	1.5	N ₂	2
18	main	C	150	1	air	2
19	main	C	300	1	air	2
20	main	C	150	2	air	2
21	main	C	300	2	air	2
22	main	C	150	1	N ₂	2
23	main	C	300	1	N ₂	2
24	main	C	150	2	N ₂	2
25	main	C	300	2	N ₂	2
26	additional	B	450	1	N ₂	1
27	additional	B	450	1	air	1
28	additional	B	600	1	N ₂	1
29	additional	B	600	1	air	1

2) in which the three fly ashes were used. The screening study (experiments 1–6, single samples) was performed with ash A and investigated the effects of temperature (150, 300, and 450 °C) and atmosphere (nitrogen or air), with a constant residence time of 2 h. On the basis of the screening study, the main study (experiments 7–25, mean values from two samples presented, with one exception), in which ashes B and C were used, utilized a full factorial design (CCF) at two levels with three factors (2³). The three factors were temperature (150 and 300 °C), residence time (1 and 2 h), and atmosphere (nitrogen or air). Additional experiments (nos. 26–29, single samples) were performed on ash B, which was heated to 450 and 600 °C under atmospheres of nitrogen and air for 1 h (Table 2).

Approximately 3 g of ash in soda glass ampules (volume, 25 mL) were used in all experiments, except those at 600 °C, in which quartz glass ampules were used. The ampules were sealed with atmospheres of either nitrogen or air. Once the predetermined temperature (150, 300, 450, or 600 °C) was reached in the furnace, a sealed glass ampule was placed in the furnace separately, and treated under conditions shown in Table 2. After the thermal treatment, the glass ampule was left to cool to room temperature without any quenching. The treated ashes were then analyzed for tetra- to octachlorinated PCDD/F. For a more detailed description, see Liljelind et al. (15). A Soxhlet–Dean–Stark extractor was used for extracting the PCDD/F. For this, approximately 3 g of ash was mixed with 20 g of toluene-washed sand treated with acetic acid and then extracted over 48 h with two portions of toluene (400 mL in total). Labeled internal standards were added before the addition of acetic acid. The PCDD/F was purified by applying the extract to a multilayer silica column and eluting with *n*-hexane directly onto an alumina oxide column, which was eluted with cyclohexane:dichloromethane (49:1) followed by cyclohexane:dichloromethane (1:1). The latter fraction contained the PCDD/F and was concentrated

and then further purified on a column with a mixture of carbon and Celite eluted with *n*-hexane, cyclohexane: dichloromethane, and toluene. The toluene fraction contained the PCDD/F and was concentrated to 40 μL of tetradecane after addition of recovery standard. The PCDD/F were analyzed by GC–MS, using a VG 70 250 S instrument. Untreated ash was analyzed twice and the mean value of the two analyses was used in the evaluation.

Results

Ash A. Ash A was a BFB filter ash that was low in carbon, with a pH of 11.5 due to high Na₂O content. At 150 °C, thermal treatment left the concentration of both PCDD/F (~7.6 ng/g of ash) and TCDD equivalents (0.23 ng TEQ/g of ash) unchanged. The dioxin fraction (DF = (PCDF + PCDD)/PCDF) was 0.36 at 150 °C, i.e., the concentration of PCDF was greater than that of PCDD. At 300 and 450 °C, however, the treatment reduced the PCDD/F concentration to below 0.45 ng/g of ash, a decrease of approximately 95% (Figure 2). The reduction in concentration of TCDD equivalents was between 93 and 96% at 300 and 450 °C (see Figure 3). DF was increased to ~0.80 at these higher temperatures. The furan concentration was reduced by more than 96% in all congener groups, but the dioxin concentration was not reduced to the same extent. The octachlorinated dioxins were almost completely eliminated, but concentrations of tetra- and pentachlorinated dioxins were only reduced to between 0.12 and 0.21 ng/g of ash. No obvious difference was observed between the samples treated under the nitrogen and air atmospheres; the degree of reduction was approximately the same both in total amounts and TCDD equivalents. In addition, no differences were found between them with respect to individual congener groups or isomers.

Ash B. Ash B was a cyclone ash that was rich in carbon and low in Na₂O and CaO, with a pH of 7.5. At *T* = 150 °C, the total amounts of both PCDD/F and TCDD equivalents were practically unchanged (Figures 2 and 3). However, at 300 °C, the total concentrations of PCDD/F were reduced, while the TCDD equivalents were only reduced when the residence time was 2 h (Figures 2 and 3). DF increased slightly, indicating that PCDF concentrations were reduced to a greater extent than PCDD concentrations. With a residence time of 1 h, the tetra- and pentachlorinated dioxins increased in concentration, while the tetra- and pentachlorinated furan concentrations decreased. In the case of hexa- to octachlorinated congeners, the concentrations of dioxins and furans decreased. No significant differences in degradation were observed under the different atmospheres. Increasing the residence time to 2 h resulted in further formation of tetra and penta-PCDD/F and a decrease of all other congeners, the greatest reduction occurring in air. At 300 °C both residence time and atmosphere had an impact on the PCDD/F concentration after treatment, with degradation being favored by longer residence times and the presence of oxygen. The degradation rate increased with increases in chlorination level, and PCDF decomposed faster than PCDD. At temperatures of 450 and 600 °C (Table 3), all PCDD/F were degraded. Following these treatments, their concentrations were lower than 0.7 ng/g of ash, i.e., decreased by >99%, in terms of both total amount and TCDD equivalents (see Table 3). The total concentrations (0.7 ng/g of ash) were made up of approximately the same amount of PCDD and PCDF and were equally distributed between the tetra, penta-, hexa-, hepta- and octachlorinated homologues. With such high temperatures, 1 h was enough to degrade practically all PCDD/F. Little difference was observed among the results obtained under the different atmospheres at 450 and 600 °C.

Ash C. Ash C was a cyclone ash, with low carbon, Na₂O, and CaO contents. The PCDD/F concentration in the untreated ash was very low; for several isomers the con-

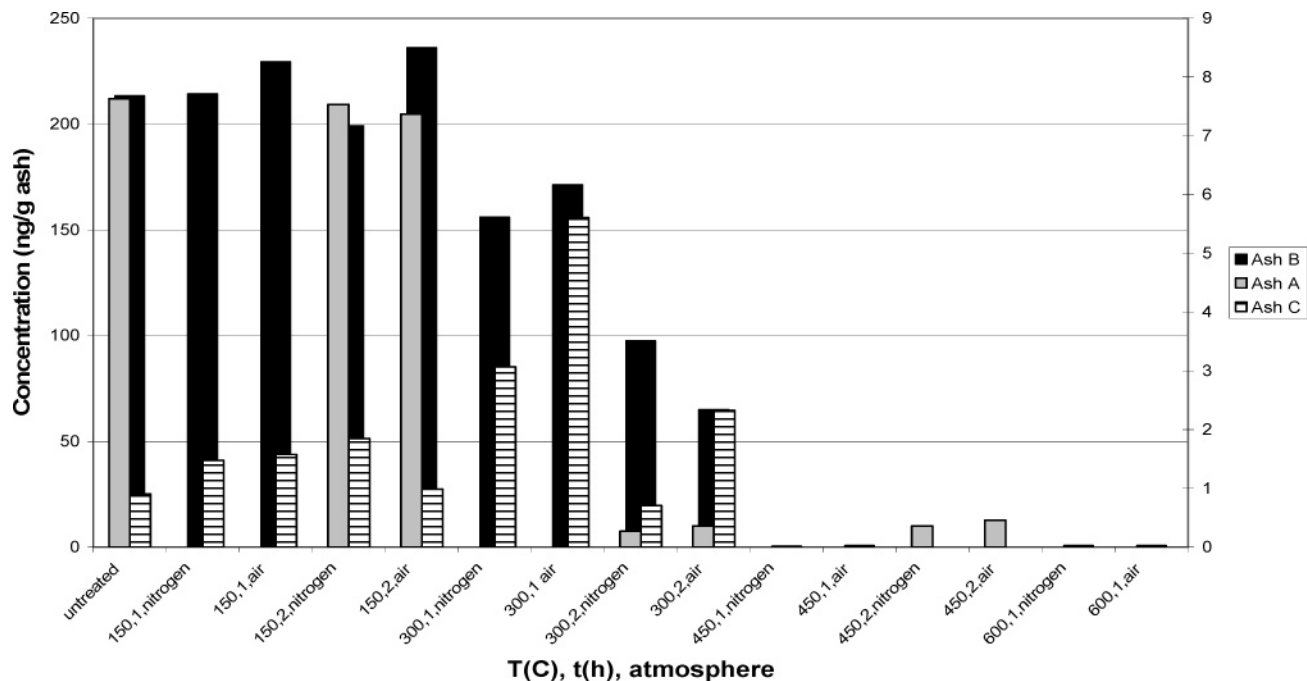


FIGURE 2. Total concentration of PCDD/F after treatment in ash B (left y-axis) and ashes A and C (right y-axis): ash A, no experiments with $t = 1$ h or at $T = 600$ °C; ash B, no experiment at $T = 450$ °C when $t = 2$ h; ash C, no experiments at $T = 450$ or 600 °C.

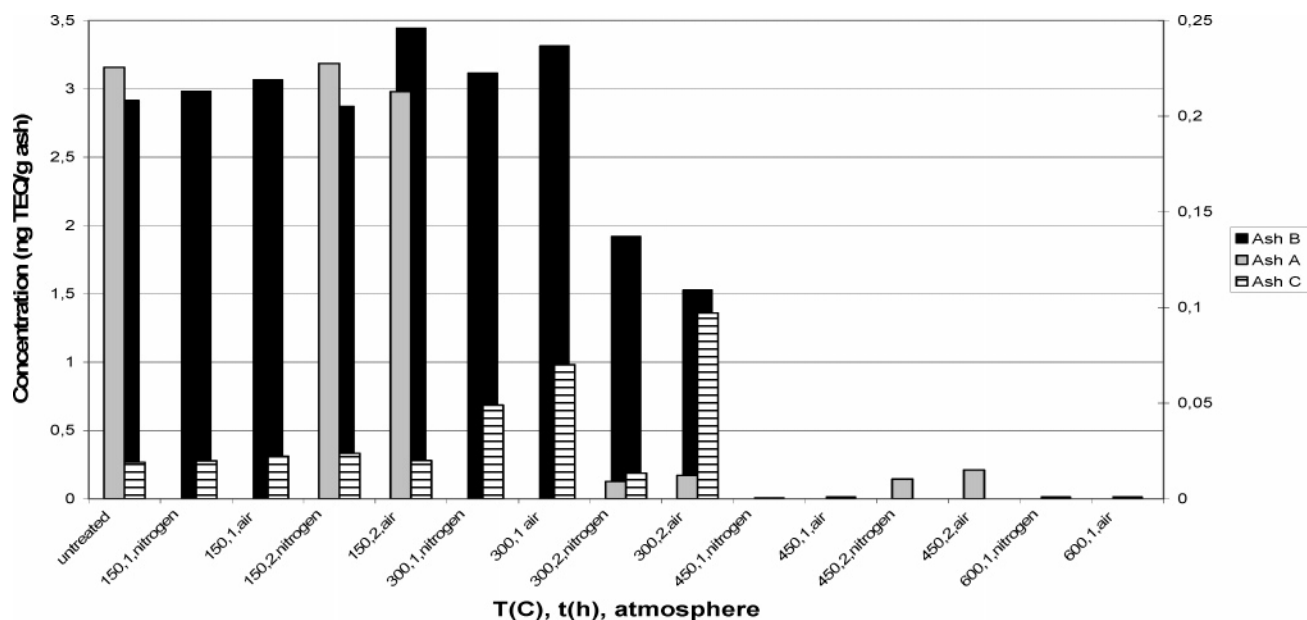


FIGURE 3. Post-treatment concentrations of PCDD/F in TCDD equivalents for ash B (left y-axis) and ashes A and C (right y-axis): ash A, no experiments with $t = 1$ h or at $T = 600$ °C; ash B, no experiment at $T = 450$ °C when $t = 2$ h; ash C, no experiments at $T = 450$ or 600 °C.

TABLE 3. Results of the Additional Experiments at 450 and 600 °C with Fly Ash B after Treatment

T (°C), t (h), atmosphere	450, 1, N ₂	450, 1, air	600, 1, N ₂	600, 1, air
PCDD/F, total amount (ng/g of ash)	0.37	0.65	0.64	0.65
reduction in total amount (%)	99.9	99.8	99.8	99.8
TCDD equivalents (ng TEQ/g of ash)	0.01	0.01	0.01	0.01
Reduction in TCDD equivalents (%)	99.9	99.7	99.8	99.7

centration was too low even to be detected. This made the results of treatment at 150 and 300 °C for specific isomers and TCDD equivalents uncertain, but the results obtained for total amounts remained valid. Significant increases in concentration were observed at both 150 and 300 °C (Figure 2), as was an increase of up to 400% in TCDD equivalents (Figure 3). A reduction in PCDD/F content was achieved

only at 300 °C with a residence time of 2 h under a nitrogen atmosphere and even then it was relatively minor (22%, with a 30% decrease in TCDD equivalents).

Discussion

The three ashes clearly showed different degradation potentials for PCDD/F during thermal treatment. For all three

ashes the decrease in PCDD/F concentrations was very low or negligible at 150 °C, in accordance with a previous study (7), in which temperatures below 200 °C had no effect on PCDD/F concentration. The differences appeared at temperatures of 300 °C, where the total concentration of the tetra- to octachlorinated dioxins and furans in ash A was reduced from 7.63 to <0.45 ng/g of ash, a reduction of >95%. In ash B, the total concentration was reduced from 213 to 65 ng/g of ash, and for ash C, an increase in total concentration was observed, from 0.90 to 5.6 ng/g of ash at 300 °C. This was in accordance with previous findings (6, 7, 11, 16). Somewhere between 300 and 350 °C, formation (in the presence of oxygen) reaches a plateau, while degradation increases exponentially with increasing temperature (11), as shown by Vogg and Stieglitz in experiments where fly ash was heated to temperatures between 120 and 600 °C (7). The cited authors found that at 300 °C PCDD/F are formed, but at temperatures over 400 °C, they are degraded. In a later publication, Stieglitz and Vogg showed that degradation is favored at temperatures above 350 °C (6). However, if the residence time is long enough, degradation of PCDD/F may be favored at temperatures around 300 °C (11) or even 260 °C (16), although this depends on the composition of the fly ash, since formation may also occur at these temperatures in some cases (6).

When the temperature was increased to 450 or 600 °C efficient degradation of the PCDD/Fs occurred in ash B; both the total amounts and TCDD equivalent concentrations decreased by >99% (Table 3). However, in our experiments, the nature of the atmosphere was not as important as indicated in previous studies (6), in which almost all of the experiments were performed under a flow of either air or an inert gas. We observed a decrease in total concentration with oxygen present at 300 °C in ash B. In a sealed glass ampule, the oxygen can oxidize the carbon and other compounds present in the ash and then degradation under oxygen-deficient conditions can take place, which may explain the reduction in PCDD/F concentrations in our experiments with ash B.

The differences in degradation potential in these three ashes were due to differences in the composition of the ashes. The concentrations of unburned carbon, alkaline species such as CaO and Na₂O, and metals such as copper and iron strongly influenced the degradation of PCDD/F. However, the different combinations of pH and amounts of native PCDD/F, unburned carbon, metals (Cu, Fe, Sn, and Na), and sulfur in the ashes made it difficult or even impossible to conclude that any single parameter was responsible for the degradation of PCDD/F in these thermal treatment experiments. This was especially true for ashes A and C, which had similar pH values, but differed in other respects. Previous studies have shown that high alkalinity promotes the main degradative route of the PCDD/F molecule (11, 13, 14). Furthermore, experiments in which Ca(OH)₂ and CaCO₃ were added to model ash have indicated that high pH, rather than the presence of Ca²⁺ ions, is responsible for the high destruction potential of alkaline ashes with high Ca contents, since the addition of CaCO₃ (pH around 8–9) had a much weaker effect than adding Ca(OH)₂ (pH > 13) (11). This effect was further investigated by Weber et al. (12), who found that alkaline fly ash exhibits a higher potential for the destruction of polychlorinated aromatics. Thus, since ashes A and C had similar, high pH values (> 11), they should have had similar destruction potentials, but the results proved otherwise. The total amount of PCDD/F decreased at 300 °C for ash A, while amounts of PCDD/F in ash C increased. The reason for the difference in degradation behavior could be that ash A had more Cu, Cl, C, and S and more native PCDD/F than ash C. Ash A is richer in copper, implying that it should have a higher potential for formation of PCDD/F, but the concen-

tration of sulfur is extremely high and this may inhibit the Deacon reaction, allowing degradation to dominate. Sulfur has been shown to inhibit PCDD/F formation in flue gases by reacting with the copper catalytic sites, altering their form and presumably their ability to produce Cl₂ through the Deacon reaction, which is important in PCDD/F formation (17). The role of sulfur in thermal degradation will be further investigated. The precise cause of this difference in degradation behavior between ash A and C could not be established from our experiments.

The high concentration of unburned carbon in ash B may contribute to the degradation behavior of PCDD/F in this ash, but it is unlikely to be the main reason for the effect. The effect of carbon has been studied by Weber et al. (11), who found that the addition of 2% activated charcoal to a fly ash with low PCDD/F concentrations resulted in a 50% increase in PCDD/F levels when heated at 310 °C for 1.5 h in a stream of 10% oxygen. However, Stieglitz and Vogg have reported that treating a fly ash with low initial concentrations of PCDD/F at 300 °C for 2 h in an air stream caused the PCDD/F concentrations to rise (6). In our experiments with ash C, in which the concentrations of carbon and PCDD/F are low in the untreated ash, an increase in concentration of PCDD/F was observed at 300 °C. However, this did not apply to fly ash A (Figure 2), which also had a low concentration of carbon. Since the pH of both ashes A and C is > 11, this finding implies that variables other than the concentration of carbon contributed to the high degradation potential in ash A. In addition, our experimental setup differed from those of Weber et al. (11) and Stieglitz and Vogg (6) because we did not use flow reactors. Since active carbon is added to absorb PCDD/F in an operating incinerator, it is important to clarify the fate of unburned carbon and its potential effects on the degradation process of PCDD/F.

Our study also showed that ash composition influences the relative extent of degradation of PCDD and PCDF. Dechlorination rates are similar for both of these groups of compounds, but the first dechlorination step has been found to be faster for OCDF than OCDD (12), and no preference for dechlorination at the 2-, 3-, 7-, or 8-position was found. Experiments on model fly ashes have also suggested that OCDF are dechlorinated to a greater extent than OCDD (13). However, the opposite was found to be the case in another study on real fly ash in which the PCDD:PCDF ratio was between 0.12 and 0.15 after treatment, compared to 0.85 in the untreated fly ash (14). This implies that PCDD are more prone to degradation than PCDF (14). In our experiments with ash A, PCDF is degraded to a greater extent than PCDD, while in ash C the opposite was true. The cause of this difference is not yet known.

The decreases observed in all of the experiments are due to dechlorination and/or destruction of PCDD/F: depending on the temperature and ash composition, either of these processes may be the more important. Since we have only analyzed the tetra- to octachlorinated PCDD/F, it is impossible to say which of the two reactions is dominant.

Acknowledgments

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