



Potential formation of PCDD/Fs and related bromine-substituted compounds from heating processes for ashes

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ABSTRACT

Thermal experiments were conducted using real boiler ash and fly ash samples from three types of municipal or industrial solid waste incineration plants to understand the formation reactions of polychlorinated dibenzo-*p*-dioxin and furans (PCDD/Fs) and related bromine compounds that were chlorinated-brominated dibenzodioxins and furans (PXDD/Fs) and polybrominated dibenzo-*p*-dioxin and furans (PBDD/Fs). The results obtained were as follows: The formation of PCDD/Fs was clearly shown, and fly ash containing abundant carbon matter had a significant potential for *de novo* synthesis. The homologous distribution change apparently showed that the formation of PXDD/Fs occurred from the substitution of a bromine atom with a chlorine atom in the PCDD/F molecules. This suggests that PXDD/Fs are usually formed with PCDD/Fs on the ash. PBDD/Fs might be formed from any reaction mechanism different from that of PXDD/Fs. The existence of carbonaceous matters always does not mean the potential formation of PCDD/Fs. However, any addition of catalytic copper may influence the nature of ash to increase the formation potential. The findings suggest that there are many instances that result in the unintended production of trace hazardous pollutants in the incineration process and show that careful and sophisticated control is required to prevent the formation of pollutants.

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1. Introduction

Recent data have shown that the emission of dioxins from the incineration process in FY 2007 has decreased to less than 300 g-TEQ per year from more than 9000 g-TEQ per year in FY 1999 in Japan [1]. This dramatic decrease in dioxin emission is attributed to such factors as improvements in technologies for furnace combustion and flue gas-cleaning techniques. The reduction in the number of small and inappropriate incinerators might also contribute to the reduced emission. Higher temperature combustion with sufficient gas retention time can minimize the incomplete combustion that results in a significant reduction in carbon monoxide (CO) as well as dioxin formation. The use of a bag filter and activated carbon injection in a relatively low-temperature operation, for example around 170 °C, is very effective for the reduction of a variety of pollutants (other than NO_x) such as acid gases and dioxins [2].

However, PCDD/Fs may form in gas-cooling processes used in municipal solid waste (MSW) incineration plants. A typical formation mechanism of the pollutant is known to be *de novo* synthesis. Although the *de novo* synthesis pathway is too complicated to delineate clearly, it can still be understood as a critical mechanism by

which carbon and chlorine sources can be induced to react together in the presence of an effective metal catalyst such as copper (Cu) [3,4]. Therefore, for *de novo* synthesis, it should be defined that PCDD/Fs appear from a wide range of carbon sources and chlorine sources typically from ash and that related organic halogen compounds occur simultaneously. The carbon species are possibly derived from unburned components, and can play an important role in the formation of the carbonaceous structure of dioxins. However, it has been reported that ash from gasification and melting furnace plants used for the disposal of MSW can also form dioxins, probably due to *de novo* synthesis, although the carbon content is generally very low (less than 0.1 wt%), according to experimental results obtained using a thermal reactor [5,6]. The reports show that the presence of carbon is essential to the formation of dioxins and that the quantity of dioxins formed is proportional to the carbon content of the ash. Indeed, the residual carbon in MSW incinerator fly ash plays an important role in both the formation and decomposition of dioxins [7]. The type of carbon also influences the formation reactions of dioxins from various carbon sources such as graphite and coke [8–10]. Activated carbon injected into ducts for flue gas-cleaning can be a source of chlorinated organic compound formation [6,10].

On the other hand, similar formation reactions are naturally expected to be responsible for the formation of chlorinated-brominated dibenzo-*p*-dioxins and furans (PXDD/Fs) and bromi-

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Table 1
Ash samples used in the experiments.

Sample	Location of sampling or description of sample	Carbon content ^a (wt%)	Content of native dioxins (ng/g)	Content of native PXDD/Fs and PBDD/Fs (ng/g)
Ash 1: Boiler ash	Collected at the bottom of the boiler in a gasification-melting plant	0.15	21 (0.33 ng-TEQ/g)	– ^b
Ash 2: Boiler ash	Collected at the bottom of the boiler in an MSW incineration plant (Stoker furnace)	0.44	210 (1.9 ng-TEQ/g)	–
Ash 3: Fly ash	Collected at the bottom of the first bag filter equipped in a series at the same MSW plant as Ash 2	20	50 (0.62 ng-TEQ/g)	PXDD/Fs: 14 PBDD/Fs: 0.025
Ash 4: Boiler ash	Collected at the bottom of the boiler in an industrial solid waste incineration plant (kiln and stoker furnace in series)	4.7	9.5 (0.17 ng-TEQ/g)	PXDD/Fs: 1.3 PBDD/Fs: –
Ash 4': Ash 4 was fortified with reagent	Copper chloride (I) was added to the ash sample before packing.	† ^c	†	†

^a The measurement was performed three times per sample.

^b Not measured.

^c Expected to be almost the same value as Ash 4.

nated dioxins (PBDD/Fs), since ash usually contains bromine as well as chlorine. Furthermore, the widespread use, over decades, of brominated flame-retardants has resulted in the increasing likelihood of their being fed into waste combustion facilities, and the presence of PXDD/Fs and PBDD/Fs as well as dioxins has been reported [11,12].

A review paper surveyed the state of research on the formation of brominated compounds and covered four categories of thermal processes: thermal stress, pyrolysis/gasification, insufficient combustion conditions and controlled combustion conditions [13]. Of these, controlled combustion conditions may be particularly important to consider, since a huge amount of MSW is combusted daily in controlled incinerators. The presence of brominated organic compounds in flue gases, determined by a method for measuring bromine amounts in gas, was monitored at controlled incineration plants, and it was revealed that organic bromine accounts for about 2–13 mol% of the concentration of organic chlorine [14]. The available facts suggest a probable generation of brominated organic compounds, which may include *de novo* synthesis. As an attempt to investigate the *de novo* synthesis of PXDD/Fs and PBDD/Fs, Weber et al. [15] conducted experiments that used a model fly ash sample made by dry-mixing silica, copper (II) hydroxide, perylene (a polyaromatic hydrocarbon), potassium chloride and bromide. They found that bromine is incorporated in PXDD/Fs during *de novo* synthesis similarly to chlorine. However, very few studies on this subject have used real ash samples.

This study investigates the formation of PCDD/Fs and their bromine-substituted compounds by using real ash samples, from a stoker-type incineration plant and a newly introduced gasification-melting plant. Special attention is paid to studying the effect of the co-existing carbons in ash and the formation of PXDD/Fs and PBDD/Fs that may occur together with PCDD/F formation from trace bromine constituents in ash. Furthermore, mass balances and characteristics regarding congener distributions are used to understand the effect and occurrence.

2. Materials and methods

2.1. Ash sample

The ash samples used are shown in Table 1 with descriptions about sampling locations and other information including carbon and native dioxin content. The inorganic components are shown in Table 2. The real ash samples that were used were obtained from

an MSW incineration plant and an industrial waste incineration plant. Moreover, an ash sample from a gasification-melting plant that had been used in a previous paper [5] and employed fluidized bed-type gasification was also used to ascertain the reproducibility of *de novo* formation reactions. Plant processes and the locations from which the ash samples were collected are shown in Fig. 1. All the ash was sampled before lime was injected into the duct to prevent alkali components affecting the heat experiment, and the sampling locations were mainly at the bottom of the boiler because of the ease of obtaining the ash samples.

The carbon content of Ash 1 was rather low (0.15 wt%) owing to the high combustion temperature in the melting furnace. However, the ash contained metal species in relatively large quantities that may work as a catalyst [5]. Ash 2 and Ash 3 were both collected from the same incineration plant. Ash 2 was collected at the bottom of the boiler, and the carbon content was 0.44 wt%. Ash 3 was collected at the bottom of the first bag filter that was part of a two-stage bag filter flue gas-cleaning system. Ash 3 had a very high carbon content (20 wt%), and it was estimated that much of this carbon was derived from injected activated carbon powder because the carbon content of Ash 2 was low, as described above. Ash 4 was from an industrial waste disposal facility; the sample was also collected at the bottom of a boiler. However, the carbon content was fairly high (4.7 wt%), probably due to unburned constituents. All the above-mentioned types of ash were native samples; however, one artificially produced compounded sample was used. Ash 4' was prepared by adding copper chloride (I) to the original Ash 4. Copper

Table 2
Inorganic components in the ash samples.

Component (wt%)	Ash			
	1	2	3	4
Ca	11	8.1	11	9.2
Mg	1.8	1.1	3.1	1.8
Na	4.5	2.1	5.1	4.7
K	4.0	1.2	5.3	1.2
Al	5.3	10	4.8	9.2
Fe	2.0	6.1	2.7	1.2
Zn	0.84	0.34	0.81	0.31
Cu	0.42	0.13	0.34	0.053
Ni	0.0079	0.015	0.0046	–
Pb	0.15	0.032	0.16	0.11
Cl	6.2	1.4	8.9	1.7
Br (mg/kg)	320	120	1400	ND

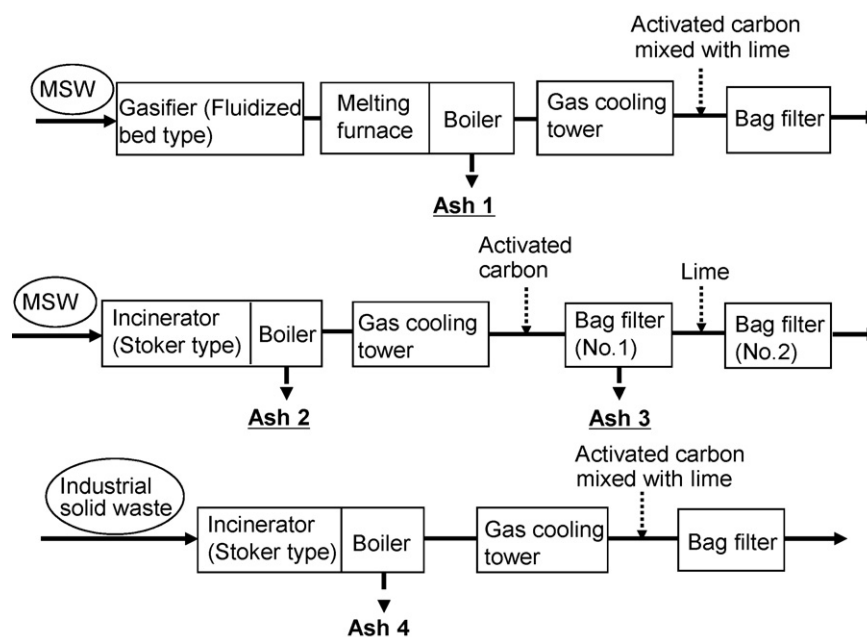


Fig. 1. Sources of ash samples in three kinds of incineration plants.

chloride was added because the ash produced a lower quantity of dioxins in the experiment. The Cu content of all these original ash samples ranged from 0.053 to 0.42 wt%, and the range was roughly usual for ash samples in incineration plants [5,16,17].

2.2. Experimental procedure and apparatus

The ash samples were made into pellets with water using a pelletizing machine before being packed into the reactor tube [5], and the pellet diameter was around 3–4 mm. This procedure was employed because the ash consisted of fine particles that posed a risk of blocking the gas flow.

Thermal experiments were conducted in the flow reactor, as shown in Fig. 2. This reactor consists of a quartz glass tube with an internal diameter of 50 mm and a length of 1300 mm. An ash sample bed is installed in the tube, and a 450-g pelletized ash sample is placed on the bed to a height of 250 mm, except for Ash 3. Because there was less of the Ash 3 sample, a 250-g pelletized sample was placed on the bed. An artificial mixed gas supply system was used, and the composition was set at 90 vol% nitrogen and 10 vol% oxygen with mass flow controlling devices. A gas sampling system was prepared at the reactor outlet to analyze the PCDD/Fs and brominated organic compounds. The experimental procedure was basically the same as that described elsewhere [5]. However, the temperature was generally set at 300 °C, which is a typical temperature for *de novo* synthesis. Furthermore, no gaseous hydrochloric acid (HCl) or organic vapors were supplied, since a previous study [5] clearly showed that trace amounts of carbonaceous matter were the source of dioxin formation, not the supplied organic vapors.

In the experiment, an ash sample was packed into a vertical quartz glass reactor at room temperature. Heating was then commenced under a flow of carrier gas. The temperature reached the desired level in about 3 h. This temperature was then further maintained for 1 h to ensure that the system had stabilized. Since the carbon content of Ash 3 was rather high, nitrogen gas and steam (17–20% in the gas) were fed into the reactor until the desired temperature had been reached to avoid any uncontrolled increase in temperature; oxygen gas was then slowly introduced to the set value of 10 vol%. Subsequently, the gas sampling of the PCDD/Fs and brominated organic compounds was initiated and continued

for 4 h. After the measurements of the dioxins and other pollutants had been completed and the experimental run had finished, an ash sample was taken from inside the reactor to determine the content of the same target compounds in the solid. Each experimental run was conducted once except with Ash 4 because this sample provided unexpected results in the first run.

2.3. Measurement method

Dioxins were measured and analyzed based on the Japanese Industrial Standard JIS K 0311; tetra-through octa-chlorodibenzo-*p*-dioxins, tetra-through octa-chlorodibenzofurans and dioxin-like polychlorinatedbiphenyls in stationary source emissions [18] were determined using high-resolution gas chromatography (HRGC)/high-resolution mass spectrometry (HRMS), and the PXDD/Fs and PBDD/Fs were analyzed based on the method described in a proposed manual for the compounds [19] using the same analytical equipment. The HRGC-HRMS system employed a JMS-700 MStation™ Double-Focusing Magnetic Sector Mass Spectrometer (JEOL Ltd., Tokyo, Japan). However, monobromo-polychloro-substituted compounds were determined in the PXDD/Fs, because standard PXDD/Fs were not obtained, and it was considered that polybromo-chloro-substituted compounds were at very low concentrations.

The analytical quality of the determination of PCDD/Fs was examined by measuring surrogate recoveries in the analytical procedure. A surrogate ¹³C-labeled mixture was added to the liquid sample in the clean-up stage and also labeled ¹³C-1,2,3,4-TeCDD was added to the XAD-2 resin adsorbent. The recoveries of the surrogates obtained were within a 50–120% range for the flue gas of the Ash 3 run. The results suggest that sufficient quality was obtained for the analysis of dioxins.

Carbon quantity was measured by using an automatic highly sensitive NC analyzer—SUMIGRAPH NC-22A (Sumika Chemical Analysis Service, Ltd., Tokyo, Japan). This equipment measures the amount of carbon based on carbon dioxide quantification with a thermal conductivity detector (TCD) for the gas components of a combusted sample. Chlorine and bromine atoms were measured by using ion chromatography for a sample solution made by aqueous extraction from a solid sample. Metals and inorganic components

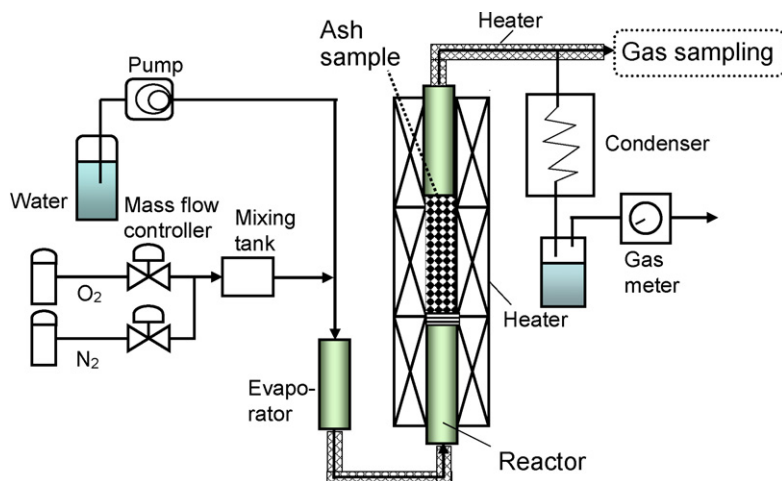


Fig. 2. Experimental apparatus used in the thermal treatment of ash samples.

were measured by using inductively coupled plasma-atomic emission spectrometry (ICP-AES VISTA-PRO, Seiko Instruments Inc.) for the liquid samples extracted with hydrochloric acid.

3. Results and discussion

3.1. Reproducibility of *de novo* synthesis from ash

To confirm the reproducibility of the experimental system, data obtained from the experiments using Ash 1 were compared to data previously obtained using the same ash sample. The results for dioxins (PCDD/Fs and dioxin-like PCBs) in flue gas obtained using the same experimental system [20] showed the gas concentration to be 230 ng/m^3 at $12\% \text{ O}_2$ (3.1 ng-TEQ/m^3). The dioxin data obtained again in this study using Ash 1 revealed a gas concentration of 180 ng/m^3 at $12\% \text{ O}_2$ (3.3 ng-TEQ/m^3). These two experimental values obtained with this system were similar, especially in terms of the TEQ value.

The congener distribution profiles were also similar, especially in terms of the distribution of PCDF, as shown in Fig. 3. The concentrations of PCDF congeners were significantly higher than those of PCDD congeners. In addition, the tetra-CDFs was the most abundant congener, and the concentrations of higher chlorinated PCDF congeners gradually decreased.

These results suggest that the reproducibility is good both in terms of the ash material and the experimental system; hence, this consideration provides a secure rationale for experiments conducted using the new materials in this study.

3.2. Formation of PCDD/Fs from boiler ash and fly ash

Table 3 shows the concentrations of PCDD/Fs, PXDD/Fs and PBDD/Fs in the flue gas and ash samples obtained in the experiments using Ash 1, Ash 2 and Ash 3 at 300°C , and the concentration at 200°C for Ash 3. Ash 3 of fly ash was sampled in the latter part of the same flue gas line as Ash 2 (Fig. 1). The PCDD/Fs concentrations in flue gas for Ash 1 and Ash 3 were almost the same, as were the results for PXDD/Fs and PBDD/Fs. The data of Ash 1 mean those described in the previous section. Very high content data were obtained for PCDD/Fs in the Ash 3 sample after the thermal treatment as well as dioxins-TEQ. This result may be caused mainly by the high carbon matter content as shown in Table 1. Further, Ash 3 contained a large amount of Cl and a relatively large amount of catalytic Cu and Fe in Table 2. These facts may comprehensively affect the high content data.

Furthermore, the results suggest that a very active *de novo* synthesis may occur on any surface site of the solid sample, and then the formed PCDD/Fs are adsorbed on the surface because the abundant active carbon is 20 wt% and a part of the formed PCDD/Fs might leave the surface. Carbon was indeed added to the fly ash in the duct. However, the chlorine and bromine content in Ash 3 were greater than in Ash 2. This was probably because gasified components containing these atoms condensed on the surface of Ash 3 at a lower flue gas temperature. Other catalytic components such as metals were also incorporated in this process and could contribute to the formation reactions.

The dioxins-TEQ content of the flue gas was 2.7 ng-TEQ/m^3 and the ratios of dioxin-like PCBs in the TEQ values were 5.9% and 1.7% for the gas and ash, respectively. Conversely, a fairly low dioxin

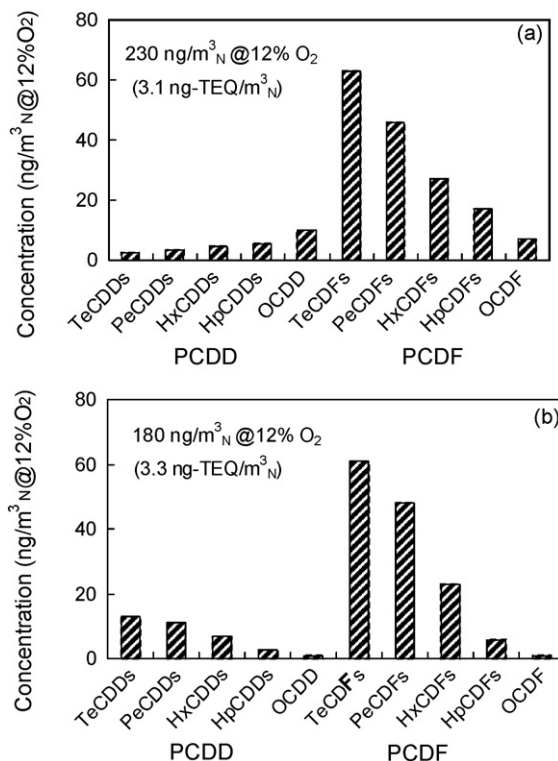


Fig. 3. Comparison of the results of thermal experiments conducted separately for Ash 1 in flue gas concentrations: (a) former and (b) this time.

Table 3
PCDD/Fs, PXDD/Fs and PBDD/Fs measured in experiments using Ash 1, Ash 2 and Ash 3 at different temperatures.

Employed ash and temperature condition	Flue gas			Ash after thermal treatment		
	PCDD/Fs (ng/m ³) ^a and dioxins-TEQ (ng-TEQ/m ³) ^a	PXDD/Fs (ng/m ³) ^a	PBDD/Fs (ng/m ³) ^a	PCDD/Fs (ng/g) and dioxins-TEQ (ng-TEQ/g)	PXDD/Fs (ng/g)	PBDD/Fs (ng/g)
Ash 1: 300 °C	170, TEQ: 3.3	25	ND	56, TEQ: 0.75	– ^b	–
Ash 2: 300 °C	48, TEQ: 0.94	5.2	(0.006) ^c	–	(0.011)	7.2
Ash 3: 300 °C	170, TEQ: 2.7	21	0.59	1700, TEQ: 43	320	0.011
Ash 3: 200 °C	0.37, TEQ: 0.0066	(0.004)	ND	–	–	–

^a Concentrations are translated to a condition of 12% O₂.

^b Not measured.

^c The parentheses indicate that figures exceeding the detection limit and below the quantification limit are included.

concentration was observed in the same Ash 3 at 200 °C, which showed a very low potential for synthesis. This comparison of results obtained at two different temperatures showed that temperature had a significant influence on the formation of dioxins, as has been reported by many researchers [21–23].

Ash 2 tested at 300 °C produced relatively low concentrations of PCDD/Fs probably because the carbon content (0.44 wt%) and catalytic copper content (0.13 wt%) were low. The difference between Ash 1 and Ash 2 can be found in the copper content, and it was 0.42 wt% for Ash 1, as shown in Table 2.

The next mass balance data and homologous distribution of PCDD and PCDF before and after the thermal treatment of Ash 3, as shown in Fig. 4, clearly demonstrate the occurrence of new reactions on the ash. The homologous distribution pattern of the compounds is helpful in understanding the new production reaction during the experiment. Further, consideration of the mass balance before and after the experiments is necessary for a discussion of *de novo* synthesis. The contents of the target compounds in the ash sample before the experiment, after the experiment and that exhausted during the measurement of the compounds (4 h) were added together.

Two significant points stand out here. Firstly, the apparent total quantities of PCDD/Fs in the ash sample were very different before and after the thermal treatment of the sample. Before the experiment, the total quantity of PCDD/Fs in the 250 g of packed Ash 3 was 23 µg, and this increased greatly to 390 µg after the thermal treatment. However, the exhaust gas from the reactor over a 4-h period contained the relatively low amount of 0.58 µg PCDD/Fs. The result strongly suggests that the formed PCDD/Fs were adsorbed on the surface of the fly ash particles because the material contained a large quantity of activated carbon, as mentioned above. The carbon content of Ash 3 after the heating experiment fell to 14 wt%, which was 70% of that in the original ash sample. A proportion of the eliminated amount of carbon may have been consumed by oxidation reactions during the heating process. Indeed, the monitored concentration of carbon monoxide during the experiment continued to be around 100 ppm in the exhaust gas. Consequently, the total mass was estimated to be reduced 6.8% compared with the original mass. Some constituents in the carbonaceous materials definitely triggered considerable production of PCDD/Fs.

Secondly, the homologous distribution patterns of PCDD and PCDF in both the ash after the experiment and the flue gas were

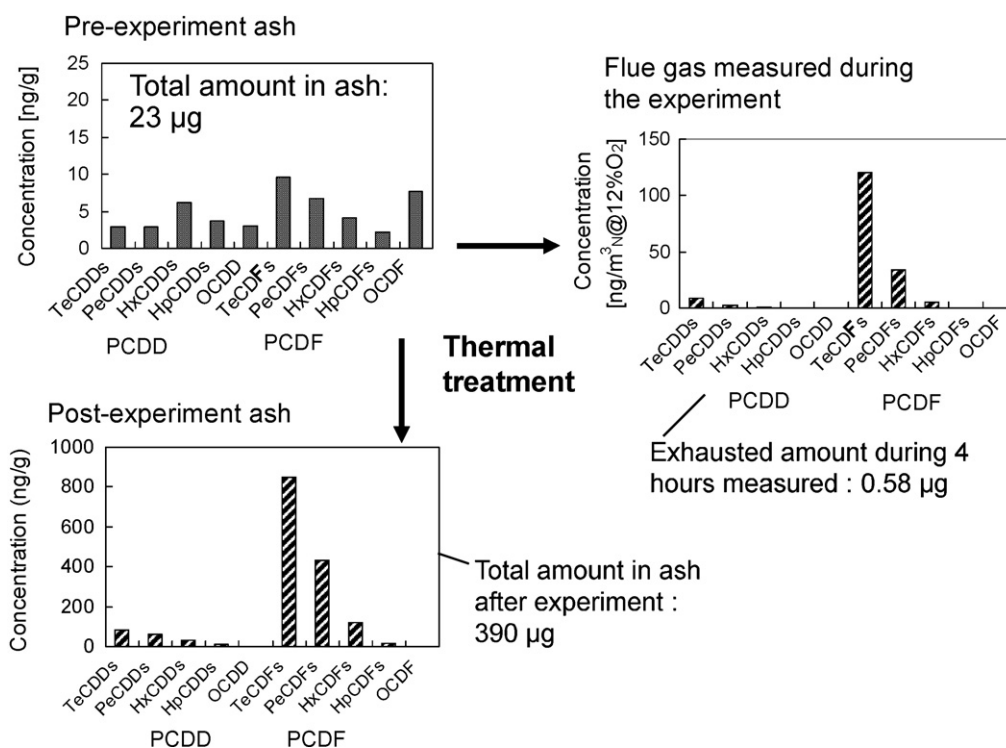


Fig. 4. Mass balance of PCDD/Fs and homologous distribution of PCDD/PCDF before and after the thermal treatment of Ash 3.

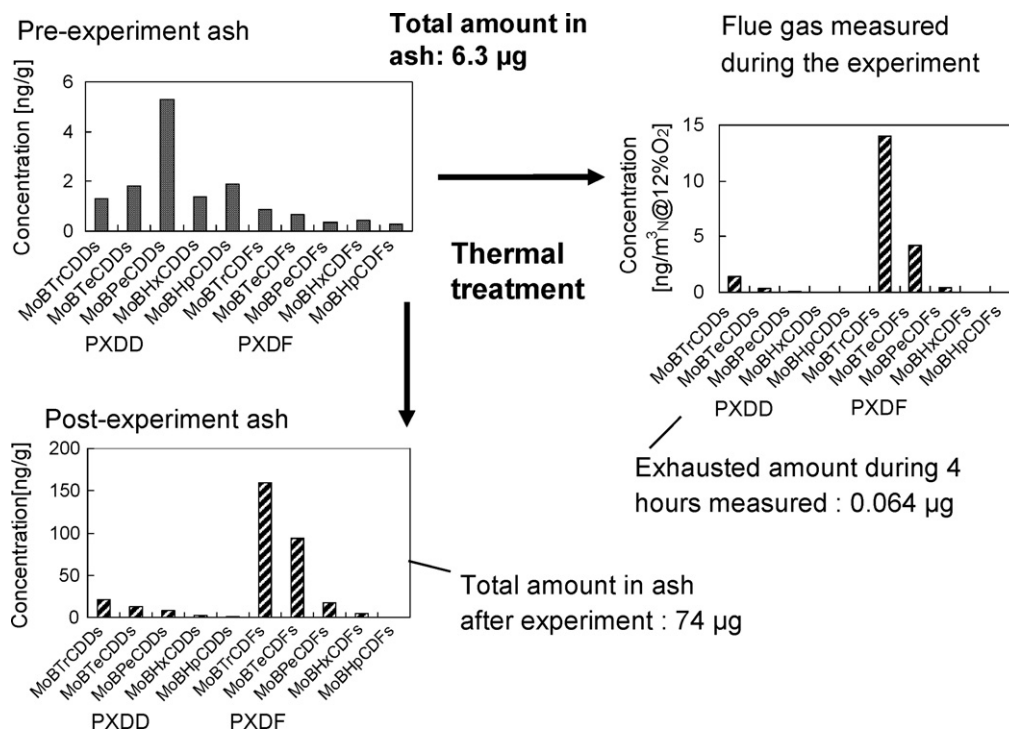


Fig. 5. Mass balance and homologous distribution of PXDD/PXDF before and after the thermal treatment of Ash 3.

entirely different from the pre-experiment ash. Low chlorinated homologues of PCDF that were TeCDFs and PeCDFs had much higher concentrations in the distribution pattern compared with PCDD, both during and after thermal treatment. These facts provide strong evidence for the occurrence of *de novo* PCDD/Fs synthesis in this experimental system.

3.3. Formation of PXDD/Fs and PBDD/Fs from boiler ash and fly ash

High concentration data for PXDD/Fs (320 ng/g) were found in the ash sample after the thermal experiment in the Ash 3 run at 300 °C as observed for PCDD/Fs, and the concentration for flue gas was determined to be 21 ng/m³@12% O₂. In contrast, very low levels of PBDD/Fs were detected in the flue gas (0.59 ng/m³@12% O₂) and the ash (0.011 ng/g). The Ash 2 run resulted in lower concentration data for both the flue gas and ash samples at 300 °C in the PXDD/Fs. However, the PBDD/Fs on this sample were a little bit higher compared with Ash 3. The native sample of Ash 2 contained a rather large amount of dioxins even compared with Ash 3, as shown in Table 1, which might be caused by *de novo* synthesis during the gas-cooling process in the incinerator. Many thermal reactions occurred on the surface of the ash between the chemical constituents, and the formation of PBDD/Fs might be a possible phenomenon.

Fig. 5 shows the results of the mass balance data and homologous distribution of PXDD/Fs, and the change in profile was quite similar to the change in the PCDD/Fs. The result also supports that the for-

mation of PXDD/Fs stems from the substitution of a bromine atom with a chlorine atom in the PCDD/F molecules. The thermal heating of the ash sample containing 6.3 µg of PXDD/Fs newly produced a large amount (74 µg) of those compounds but the composition was very different, and the exhaust gas contained 0.064 µg of that species in each 4-h period, suggesting the formation of PXDD/Fs during the thermal treatment. The clear differences in the homologous distribution patterns between the ash samples and between the original ash and the formed gas sample also provided evidence of a reaction.

The most abundant homologue was monobromo-triCDFs, followed by -tetra-CDFs, with a distribution pattern quite similar to that in Fig. 4. This characteristic significantly suggests that PCDD/Fs first generate via *de novo* synthesis, and the possible substitution of a chlorine molecule by a bromine atom among those in PCDF subsequently occurs, probably because of the presence of the active Br species [24]. Bromine may therefore be readily incorporated into PCDD/Fs during *de novo* synthesis and subsequent substitution reactions. Therefore, the *de novo* reaction was not predominant in the formation process of bromine-substituted PXDD/Fs.

3.4. Effects of added copper compound on the formation of PCDD/Fs and PXDD/Fs

Table 4 shows the results for Ash 4 collected at the bottom of a boiler in an industrial solid waste incinerator. The concentrations of generated PCDD/Fs and PXDD/Fs were rather low in spite

Table 4
PCDD/Fs and PXDD/Fs measured in experiments using Ash 4 and Ash 4'.

Employed ash	Flue gas PCDD/Fs (ng/m ³) ^a and dioxins-TEQ (ng-TEQ/m ³)	PXDD/Fs (ng/m ³) ^a	Ash after thermal treatment PCDD/Fs (ng/g) and dioxins-TEQ (ng-TEQ/g)	PXDD/Fs (ng/g)
Ash 4	2.9, TEQ: 0.025	0.099	14, TEQ: 0.36	1.5
Ash 4'	2600, TEQ: 34	96	890, TEQ: 11	58

^a Concentrations are translated to a condition of 12% O₂.

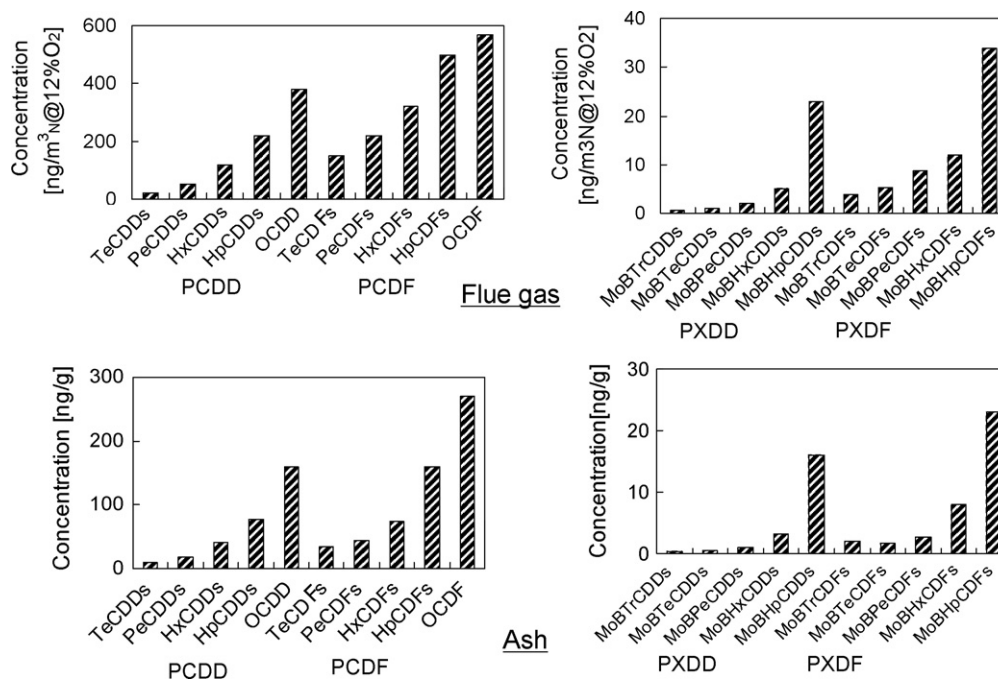


Fig. 6. Homologous distribution of PCDD/PCDF and PXDD/PXDF in flue gas and ash samples from ash fortified with copper (Ash 4').

of the moderate carbon content of the ash (4.7 wt% in Table 1), possibly suggesting that this carbon content does not always affect the *de novo* formation reactions in ash in the incineration process. Other factors, such as the type and nature of the carbonaceous matter, may influence the reaction to a greater extent. However, the contents of PCDD/Fs and dioxins-TEQ in the ash after thermal treatment were moderate, and this suggests that any reaction occurred on the surface of the ash. However, the formation of PBDD/Fs was not observed for Ash 4 in a preliminary experiment.

In the light of the above results, a test was conducted by adding copper (I) chloride that could act as a catalyst for *de novo* synthesis and as a supplier of chlorine. The compound was added to Ash 4 before it was packed into the reactor, and is named Ash 4' in Table 1. The ash sample resulted in a copper content of 0.35 wt% and a chlorine content of 1.86 wt% based on a calculation. The value of the copper content was about 6.6 times the native content and that of chlorine was 1.1 times as well.

This addition of the copper compound markedly raised the formation quantity of all chemical pollutants concerned, namely, PCDD/Fs and PXDD/Fs. The concentration of the PCDD/Fs and dioxins-TEQ in the flue gas was increased by a factor of nine hundred and one thousand and four hundred, respectively. The concentration of PXDD/Fs was also increased nine hundred and seventy times. The pollutant content in ash was increased sixty-four times for PCDD/Fs and thirty-one times for dioxins-TEQ, and a further thirty-nine times for PXDD/Fs. The copper content of the native Ash 4 was not particularly low; however, copper compounds might not be involved in any activity catalyzing *de novo* synthesis reactions. The addition of the reagent might enhance the ratio of the active copper species. As for chlorine, the native amount was fairly high, and therefore, the addition of the reagent did not increase the amount very much. However, the amount of volatile chlorine might increase due to the addition of the reagent.

These results suggest that it is necessary to pay attention to the variation of the composition of solid wastes that are incinerated, because any entering of copper into the waste may influence the composition and the nature of the ash.

The homologous distribution patterns of PCDD/Fs and PXDD/Fs, which emerged in the experiment using the ash fortified with copper (I) chloride, are shown in Fig. 6. The two homologous distribution patterns for PCDD/Fs and PXDD/Fs are clearly very similar. The results described above suggest that Ash 4, from an industrial incineration system, did not have a strong tendency toward *de novo* synthesis, but the potential was increased with certain parameter types such as the presence of a catalytic metal. The reaction characteristic whereby the concentration increases with the degree of chlorination was similar to that reported in a previous paper [5], which may show the acceleration effect that catalytic copper has on chlorination.

4. Conclusions

The thermal experiments using some kinds of ashes, including boiler ash and fly ash, clearly showed the formation potential for chlorinated and brominated organic pollutants as follows:

- (1) Formation of PCDD/Fs from boiler ash and fly ash was clearly shown by the thermal experiments at the temperature condition of 300 °C. Fly ash containing abundant carbon matters had a significant potential for *de novo* synthesis. However, boiler ash from the gasification and melting process showed a moderate formation potential even if the ash had an extremely low amount of carbon.
- (2) The homologous distribution change apparently showed that the formation of PXDD/Fs occurred from the substitution of a bromine atom with a chlorine atom in the PCDD/F molecules. This suggests that PXDD/Fs are usually formed with PCDD/Fs on the ash. PBDD/Fs might be formed from any reaction mechanism different from that of PXDD/Fs.
- (3) The existence of carbonaceous matters always does not mean the potential formation of PCDD/Fs. However, any addition of catalytic copper may influence the nature of the ash to increase the formation potential. This suggests that it is necessary to pay attention to the variation of the composition of solid wastes that are incinerated.

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References

- [1] Ministry of the Environment, Government of Japan, Dioxins Emission Inventory for 2006, 2007 (<http://www.env.go.jp/en/headline/headline.php?serial=654>).
- [2] M.B. Chang, J.J. Lin, Memory effect on the dioxin emissions from municipal waste incinerator in Taiwan, *Chemosphere* 45 (2001) 1151–1157.
- [3] L. Stieglitz, G. Zwick, J. Beck, W. Roth, H. Fogg, On the de-novo synthesis of PCDD/PCDF on fly ash of municipal waste incinerator, *Chemosphere* 18 (1989) 1219–1226.
- [4] R. Addink, K. Olie, Mechanism of formation and destruction of PCDD/F on heterogeneous systems, *Environ. Sci. Technol.* 29 (1995) 1425–1435.
- [5] K. Kawamoto, K. Mabuchi, Formation characteristics of polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans, and coplanar PCBs in fly ash from a gasification-melting process of municipal solid waste, *J. Mater. Cycles Waste Manag.* 3 (2001) 38–47.
- [6] K. Suzuki, E. Kasai, T. Aono, H. Yamazaki, K. Kawamoto, De novo formation characteristics of dioxins in the dry zone of an iron ore sintering bed, *Chemosphere* (2004) 97–104.
- [7] Y. Kakuta, T. Matsuto, N. Tanaka, T. Masuda, *Chemosphere*, Influence of residual carbon on the decomposition process of PCDD/Fs in MSWI fly ash, *Chemosphere* 58 (2005) 969–975.
- [8] C. Xhrouet, E. De Pauw, Formation of PCDD/Fs in the sintering process, *Environ. Sci. Technol.* 38 (2004) 4222–4226.
- [9] C.W. Lee, T. Imagawa, Paper fibers as a carbon source for the de novo formation of polychlorinated dioxins and furans, *J. Mater. Cycles Waste Manag.* 8 (2006) 133–139.
- [10] L. Khachatryan, B. Dellinger, Formation of chlorinated hydrocarbons from the reaction of chlorine atoms and activated carbon, *Chemosphere* 52 (2003) 709–716.
- [11] I. Watanabe, S. Sakai, Environmental release and behavior of brominated flame-retardants—an overview, *Organohalogen Compd.* 52 (2001) 1–4.
- [12] W. Chatkittikunwong, C.S. Creaser, Bromo-, bromochloro- and chloro- dibenzo-p-dioxins and dibenzofurans in incinerator fly ash, *Chemosphere* 29 (1994) 559–566.
- [13] R. Weber, B. Kuch, Relevance of BFRs and thermal conditions on the formation pathways of brominated and brominated-chlorinated dibenzodioxins and dibenzofurans, *Environ. Int.* 29 (2003) 699–710.
- [14] Y. Miyake, M. Kato, K. Urano, Emissions of semi- and non-volatile organohalogen compounds from flue gas of waste incineration facilities, *Haikibutsu Gakkaishi* (in Japanese) 16 (2005) 245–255.
- [15] R. Weber, B. Kuch, T. Ohno, T. Sakurai, De novo synthesis of mixed brominated-chlorinated PXDD/PXDF, *Organohalogen Compd.* 56 (2002) 181–184.
- [16] M. Takaoka, T. Yamamoto, A. Shiono, N. Takeda, K. Oshita, T. Matsumoto, T. Tanaka, The effect of copper speciation on the formation of chlorinated aromatics on real municipal solid waste incinerator fly ash, *Chemosphere* 59 (2005) 1497–1505.
- [17] M.C. Hsiao, H.P. Wang, J.-E. Chang, C.Y. Peng, Tracking of copper species in incineration fly ashes, *J. Hazard. Mater.* B138 (2006) 539–542.
- [18] Japanese Standards Association, Japanese Industrial Standard, Method for the determination of tetra-through octachlorodibenzo-p-dioxins, tetra-through octachlorodibenzofurans and dioxin-like polychlorinated biphenyls in stationary source emissions, *JIS K 0311* :2005, 2005.
- [19] Ministry of the Environment, Government of Japan, Tentative manual for the measurement of polybrominated dibenzodioxins and dibenzofurans, 2002.
- [20] K. Suzuki, H. Yamazaki, N. Kanda, K. Kawamoto, Dioxin formation on ash from gasification melting system (in Japanese), *Haikibutsu Gakkaishi* 15 (2004) 456–464.
- [21] H. Vogg, L. Stieglitz, Thermal behavior of PCDD/F in fly ash from municipal incinerators, *Chemosphere* 15 (1986) 1373–1378.
- [22] R. Weber, T. Sakurai, H. Hagenmaier, Formation and destruction of PCDD/PCDF during heat treatment of fly ash samples from fluidized bed incinerator, *Chemosphere* 38 (1999) 2633–2642.
- [23] E. Winkström, S. Ryan, A. Touati, B.K. Gullett, Key parameters for *de novo* formation of polychlorinated dibenzo-p-dioxins and dibenzofurans, *Environ. Sci. Technol.* 37 (2003) 1962–1970.
- [24] E. Shibata, X.-W. Li, M. Grabda, T. Nakamura, Thermodynamic behaviors of polybrominated/chlorinated dibenzo-p-dioxins in flue gas, *Organohalogen Compd.* 66 (2004) 977–982.