CHARACTERISTIC FORMATION OF DIOXINS WHEN HEATING FLY ASH SAMPLES FROM INCINERATION PLANT

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Introduction

Kawamoto et al. have studied the formation of PCDD/Fs from gasification melting furnace fly ashes using a packed bed reactor[1]. The data of laboratory experiments suggested that de novo synthesis is the major pathway of PCDD/Fs formation compared with the precursors pathway. Further study[2] showed that unburned carbon in fly ash was a key factor for de novo synthesis of PCDD/Fs in a gasification melting furnace. In this study, we investigate the relative formation characteristics of dioxins in both a fly ash collected from a gasification melting furnace boiler which cools flue gas slowly, and a fly ash collected from a gas cooling tower which quenches flue gas. Furthermore, de novo synthesis tests using pretreated fly ash were carried out, showing the effects of carbon sources, chlorine sources, catalyst etc. on the formation of dioxins.

Materials and Methods

Fly ash samples

Fly ash samples were collected from the bottom of the boiler of a gasification melting furnace (fly ash A), the bottom of the cooling tower of a gasification melting furnace (fly ash B) and the boiler bottom of a conventional stoker type incinerator (fly ash C). Table 1 shows the composition of fly ash samples. As the samples contained fine particles, they were mechanically pelletized with water using a pelletizing machine in order to produce a good gas in a packed bed.

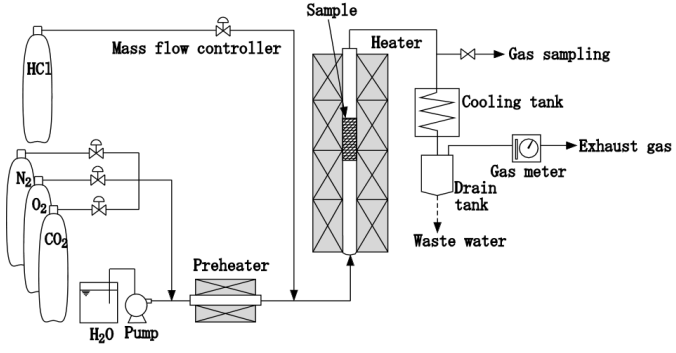

Figure 1. Experimental apparatus

Table 1. Composition of fly ash samples

Component	Fly ash A	Fly ash B	Fly ash C
Si (%,w/w)	13.1	14.2	13.1
Cu (%,w/w)	0.2	0.1	0.052
Cl (%,w/w)	1.9	5.52	1.5
C (%,w/w)	0.0099	0.012	3.4
PCDD/Fs (ng/g)	1.7	0.67	7.4
(ng-TEQ/g)	0.037	0.0081	0.14

Before conducting the experiments in which the fly ash samples were heated in a reactor, the samples were pretreated by several procedures. First, fly ash A was heated in a furnace at two temperatures of 500 ºC and 600 ºC for 2 hours. The unburned carbon content of fly ash A after this thermal treatment at 600 ºC became 0.0071 %(w/w). Using the method to remove low-molecular hydrocarbons from solids (SOF: Soluble Organic Fraction), fly ash A was soxhlet-extracted with dichloromethane for 12 hours. Fly ash A was then packed in a column (diameter: 20 mm) and 100 ml of distilled water was flowed down through the column for 4 hours for removing water-soluble heavy metals and chlorides in the fly ash. These pretreated fly ashes were used for the experiments. The experimental apparatus is illustrated in Fig. 1. Finally, the sample was packed in a quartz tube, and a synthetic gas was flowed upward through the tube at a constant flow rate of 20 l/min. The gas composition was set to N_2: 80 %; O_2: 6 %; CO_2: 14 %; HCl: 1000 ppm in a dry base and H_2O: 20 % in a wet base. In the basic condition, the fly ash was heated to 350 ºC.

Sampling and analytical methods

While the system was in the steady state, gas was sampled at the outlet shown in Fig. 1. Dioxins in flue gas were collected by four gas absorption bottles in series (water, toluene, diethylene glycol and empty bottle in this order) and XAD-2 tube according to JIS K 0311[3]. After the experiments, the fly ash sample was taken out of the reactor and part of the solids was sampled and analyzed. Analysis was performed by using HRGC-HRMS. In this study, JIS method was employed for fly ashes A, B, C and

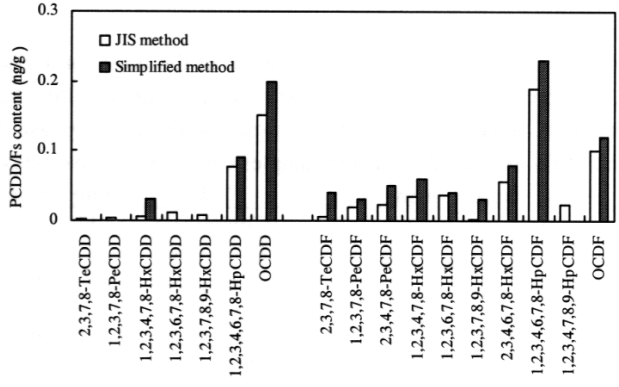

Figure 2. Comparison between JIS method and Simplified method

thermally treated ash at 600 °C. As for the other fly ashes, sampling and analysis was performed by a simplified method. Gas sampling of this simplified method was conducted using four bottles in series (water, empty bottle and 300 ml toluene×2) and GC/MS/MS was applied for this sample. Seventeen congeners of PCDDs/DFs were determined by this analysis. Figure 2 shows a comparative determination result of the PCDD/Fs homologue pattern between the JIS method and the simplified method for fly ash A. As there was no big difference, the simplified method can be applied to the evaluation of the experiments.

Results and Discussion

Formation of dioxins from fly ash from gasification melting furnace

Figure 3 shows PCDD/Fs amounts in fly ashes A, B and C. First, the PCDD/Fs amounts in fly ashes A and B were very small compared with that in fly ash C which contained abundant unburned carbon (3.4 %) as shown in this figure. Second, all three samples which were thermally treated at 600 °C exhibited a dramatic decrease. These results apparently suggested that the decrease occurred due to effective elimination of unburned carbon in fly ash. Kawamoto et al.[1] reported that unburned carbon in a fly ash sample played an important role on the formation of the dioxins. However, PCDD/Fs amount in fly ash A pre-treated at 600 °C was slightly high compared with thermally treated fly ashes B and C. This seems to be due to the difference of fly ash composition (see in Table 1), that is, the copper amount in ash had an effect on the formation of dioxins. Further research should be done focusing on copper compounds in the fly ash from the gasification melting furnace.

Homologue patterns of PCDD/Fs in fly ashes A, B and C are shown in Fig. 4. It was apparent that fly ash C depicted a distinctive pattern from other two ashes. However, fly ashes A and B depicted a similar pattern, that is, the ratio was higher with higher chlorinated PCDD homologue and the ratio of P5CDFs or H6CDFs was the highest, and was the lowest for O8CDF in the case of PCDFs. There was a big difference between fly ash from the gasification melting furnace and fly ash from the conventional stoker type incinerator as shown in Figure 4. This result shows also that there was no significant quantitative or qualitative difference between fly ashes A and B even if they had a different cooling pathway in an actual plant.

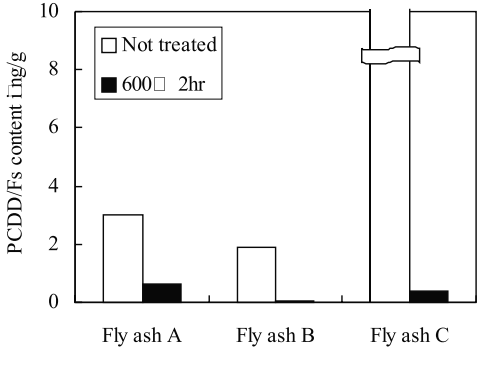

Figure 3. PCDD/Fs content in fly ash when various fly ashes were used

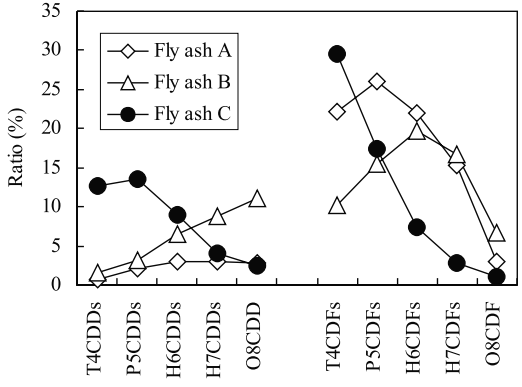

Figure 4. Homologue pattern of PCDD/Fs observed for variously fly ashes

FORMATION AND SOURCES

Comparison of dioxins formation potential for variously treated fly ashes

Figure 5 compares the dioxins formation potential for variously treated fly ashes A. The result was discussed based on the summation of 17 congeners amounts in flue gas and in fly ash after the experiment. In the case of flue gas, the amount (per g of fly ash) was calculated as the quantity of 17 congeners which flowed out with flue gas during 4 hours of the experiment.

A distinctive feature is the effect of thermal treatment. The total amounts of 17 congeners both at 500 °C and 600 °C were low compared with those of the other treatment methods. Furthermore, the amount at 600 °C was lower than that at 500 °C, which suggests that some component for dioxins formation reduced from the ash surface. Although there seemed to be no big difference in unburned carbon content between two thermally treated ashes, we assumed that the matter contained in ash would have a quantitative or qualitative influence on formation of dioxins. The amount in the case of treating with distilled water considerably decreased, the same as the case at 500 °C treatment, which showed that some constituent was removed by washing. Hence, analyses of copper and chlorine content were carried out to determine what was washed out with the distilled water. The concentration of copper was 0.22 % (W/W), which was almost the same with as that of the original fly ash A, however, chlorine concentration was 0.63 % (W/W), which was one third of the original concentration. These results show that rinsed inorganic chlorine compounds might contribute to the formation of dioxins. In contrast, the effect of suppression of dioxin formation could be seen when using fly ash that was treated by dichloromethane to remove SOF. The result suggested that soxhlet extraction could not remove any component which had dioxin formation potential, or that some impurities in the solvent contribute to the formation.

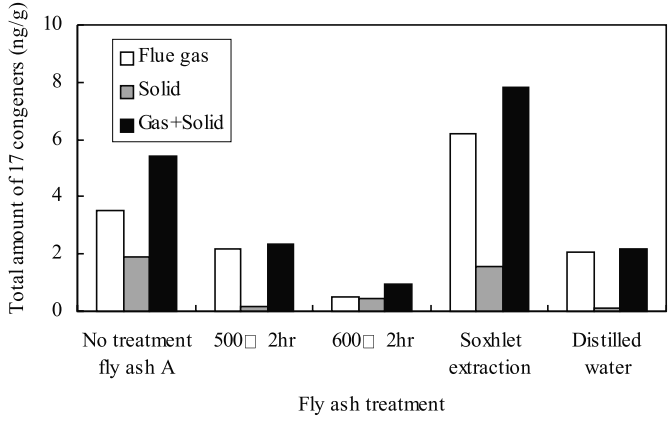

Figure 5. Comparison of dioxins formation potential between variously treated fly ashes

References

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3. Japanese Industrial Standards Committee (1999) Japanese Industrial Standard JIS K 0311, Japanese Standards Association