FEATURES OF DIOXIN FORMATION FROM VARIOUS ASHES IN GASIFICATION-MELTING FURNACE

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Introduction

In Japan, gasification-melting furnaces as a next-generation type of incinerator for municipal solid waste (MSW) have been developed and introduced. The method is expected to reduce dioxin emissions more efficiently than conventional incinerators. However, it has been reported that dioxins and PAH concentrations in flue gas increased in the gas cooling section at prototype gasification-melting plants, possibly due to de novo formation similar to that of conventional incinerators[1)]. It is considered that the de novo synthesis potential of the gasification-melting system differs from that of conventional incinerators because the composition of fly ash is very different. The fly ash produced by gasification-melting plants contains very small amounts of unburned carbon which could serve as a carbon source for the formation of dioxins, whereas volatile heavy metals such as Pb, Zn and Cu in fly ash which could serve as catalysts are enriched. In this study, experiments were performed using various fly ashes from gasification-melting plants in order to clarify the effect of unburned carbon and metal components in fly ash on de novo synthesis.

Methods and Materials

The kinds and compositions of the ash samples used in the experiments are shown in Tables 1 and 2. The ash samples collected from conventional incinerators and ash-melting furnaces were used in the experiments for comparison. These fly ash samples consisted of fine particles. As it was considered that it would be hard to make the gas flow through a reactor if it was packed tightly, the samples were pelletized by a pelletizing machine with water. Figure 1 shows the experimental apparatus. All experiments were carried out with the ash sample placed on a fixed bed in a quartz tube that was heated at 350°C. A gas stream (N_2: 80%, O_2: 6%, CO_2: 14%, HCl: 1000 ppm and water) at 20 L/min was passed through the fly ash bed. Details of the experimental procedure are described elsewhere[2)]. Evaporated dioxins were collected in a cold trap (ethylene glycol and XAD-2) during the 4 hours of the experiment. The dioxins from fly ash and the cold trap were

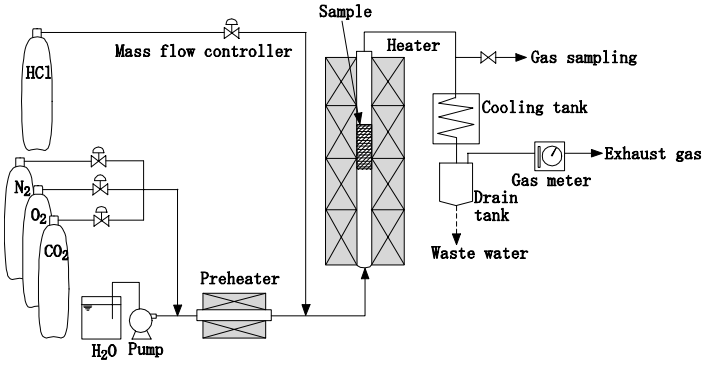

Figure 1. Experimental apparatus

cleaned up and then quantified using high-resolution gas chromatography and high-resolution mass spectrometry, respectively.

Table 1 Characteristics of ash samples

Ash	Plant type	Gasification type	Sampling location	Tempera-ture*[1]
A	Gasification melting plant (Demonstration) A	Rotary kiln	Cooling tower	500-170 °C
B-1	Gasification melting plant B	Rotary kiln	Boiler	500-300°C
B-2	Gasification melting plant B	Rotary kiln	Quenching chamber	300-170°C
C-1	Gasification melting plant C	Fluidized bed	Boiler	
C-2	Gasification melting plant C	Fluidized bed	Quenching chamber	
D	Ash melting furnace	Surface melting	EP	600-170°C
E	Conventional incinerator	Stoker	Boiler	

*1 Temperature of inlet and outlet of gas treatment equipment (sampling location)

Table 2 Elemental composition in ash used in the experiments (%)

Component	Ash A	Ash B-1	Ash B-2	Ash C-1	Ash C-2	Ash D	Ash E
Al	7.0	5.2	4.7	5.7	5.0	0.0093	11
Ca	12.5	11.1	12.5	13	12	0.086	13.5
Mg	2.1	1.8	1.6	1.9	1.7	0.0096	2.1
Na	3.8	4.8	5.9	5.2	5	12	4.8
K	3.2	3.2	4.3	3	3.4	20	1.8
Cu	0.1	0.11	0.12	0.24	0.3	0.29	0.052
Fe	1.7	1.4	1.3	1.7	1.8	0.11	3.8
Pb	0.56	0.96	0.73	0.051	0.16	0.99	0.053
Zn	1.6	1.6	1.9	0.82	0.78	5.9	0.54
Cd	0.0084	0.0077	0.0093	0.00099	0.0019	0.076	0.007
C	0.012	0.0051	0.0057	0.025	0.052	0.0039	3.4
Cl	5.5	4.3	8.4	3.3	6.8	21	1.5
S	2.9	3	2.9	3.8	3.2	-	1.5
Dioxins (ng/g)	0.67	0.53	0.39	N.D	21	6	7.4
(TEQ)	0.0081	0.00003	0	0	0.33	0.019	0.14

Results and Discussion

De novo formation potential for various kinds of ashes

Figure 1 shows the total amount of PCDD/Fs in the experiments using various kinds of ashes. The amount (ng per g-ash) is the sum of PCDD/Fs contained in flue gas and ash. The amount of PCDD/Fs in flue gas was calculated as the quantity of PCDD/Fs that flowed out with flue gas during 4 hours of measurement. The ashes of gasification-melting plants except for ash C-2 showed a considerably lower potential of dioxin formation compared with that of ash E. This result may be explained by the trace amounts of carbon in ashes except for ash E. Ashes from gasification melting plants and melting furnaces (A- C-2) contained far more heavy metals and

chlorine than ash E, however, there is a large difference in carbon content as seen in Table 2. Therefore, the carbon constituent that could be called unburned carbon may play an important role as a carbon source for dioxin formation. Figure 2 shows the concentration of chlorinated benzenes in flue gas for various kinds of ashes from gasification-melting plants. The result shows that the concentration of chlorobenzene of ash C-2 was the highest among these ashes, like PCDD/Fs.

It was observed that the metal components such as Pb and Zn in dust changed along the flue gas stream in an electric precipitator and that the nature of water solubility of the components tended to increase[3]. This observation suggests that ashes collected at different locations in an identical plant have different dioxin formation potential. We therefore carried out experiments using ashes collected from the bottoms of the boiler and quenching chamber, comparing ash B-1 with B-2, and ash C-1 with C-2. The dioxin formation potential of ashes B-1 and B-2 were almost the same, as seen in Figure 1. On the other hand, both the dioxin and chlorobenzene formation potentials of ash C-2 were significantly higher than those of ash C-1. The result suggests that the increase occurred due to the amounts of unburned carbon and copper in ash C-2. The component values of ash C-2 are the highest among the ashes of gasification-melting plants as seen in Table 2. However, it remains unknown whether the temperature change at the cooling part caused the change of ash composition.

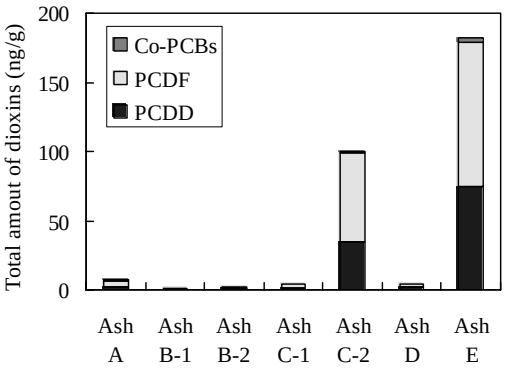

Fig.1 Total amount of dioxins for various ashes

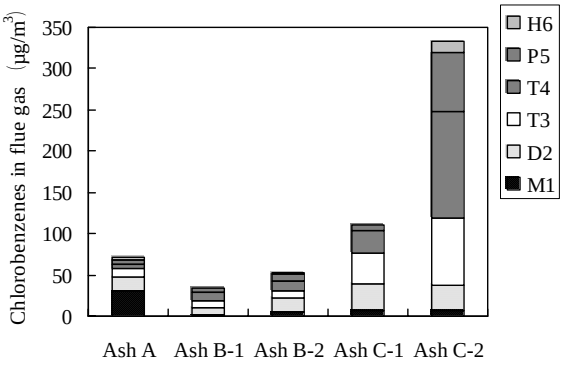

Fig.2 Concentration of chlorobenzenes in flue gas for various ashes in gasification melting plant

Influenced of unburned carbon

Figure 3 shows the relationship between the amount of unburned carbon and the total amount of dioxins among gasification-melting ashes (A- C-2) in order to confirm the effect of unburned carbon. The total amount of PCDD/Fs increased as the amount of unburned carbon increased. However, the data are scattered, which suggests that there is a difference in the quality or quantity of the catalyst metal or chlorine source. Figure 4 shows the total amount of PCDD/Fs formed per 1 g of unburned carbon in ash (μg/g-C: unburned carbon). The ratios of carbon conversion to chloroaromatic compounds (PCDD/Fs, Co-PCBs and chlorobenzenes) from unburned carbon in ashes are shown in Table 3. The dioxin formation potential of unburned carbon in ashes of gasification-melting plants was higher compared to that of conventional incinerators because of the enriched heavy metal or chlorine compounds in ash. However, the total amount of dioxins per

unit amount of fly ash is important when considering dioxin formation in actual plants. Also, it was considered that unburned carbon in ash affects the adsorption and desorption characteristics of PCDD/Fs. Figure 5 shows the percentage of PCDD/Fs in flue gas to the total amount of dioxins. The percentage decreased as the amount of unburned carbon in ash increased. This finding suggests that formed dioxin will be adsorbed on unburned carbon in ash.

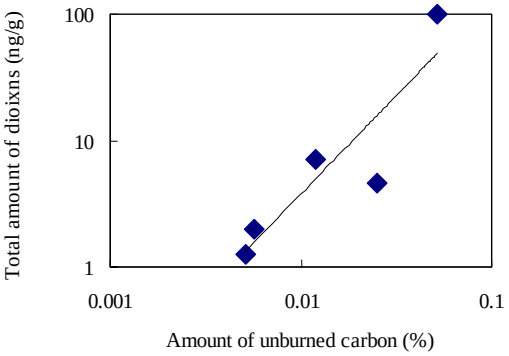

Fig.3 Relationship between total amount of dioxins and amount of unburned carbon

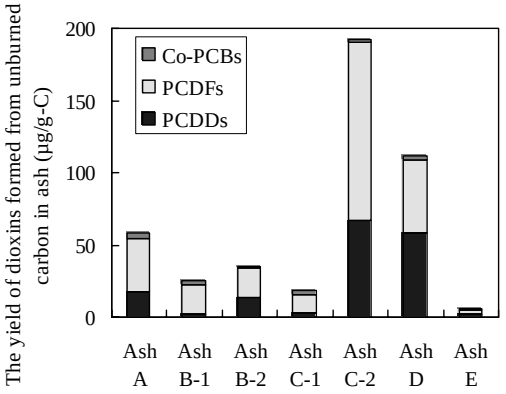

Fig.4 Yield of dioxins formed from unburned carbon in ash

Table 3 Ratio (-) of conversion to chlorinated compounds from unburned carbon in ash

	Gasification-melting ash A- C-2	Conventional ash E
CBzs	$1.9\text{-}4.1\times10^{-3}$	2.9×10^{-5}
PCDD/Fs	$0.38\text{-}1.3\times10^{-5}$	1.4×10^{-6}
Co-PCBs	$0.53\text{-}1.7\times10^{-6}$	4×10^{-8}

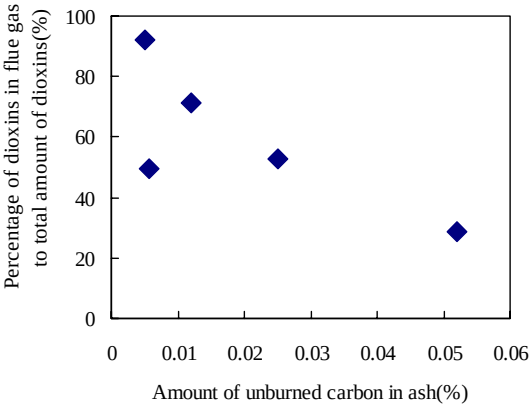

Fig.5 Relationship between percentage of dioxins in flue gas to total amount of dioxins and amount of unburned carbon

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