FORMATION AND CONTROL OF DIOXINS OVER FLY ASHES IN A MODEL TEST USING A FIXED BED REACTOR

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1. Introduction

Regarding dioxin formation mechanisms on fly ash, many findings have been reported sinceVogg and Stieglitz[1] reported that dioxins were formed on fly ash through the heating process. However, almost none of them used fly ash ofgasification-melting processes, in which formation of dioxins (PCDDs and PCDFs and coplanar PCBs) is much less intensive than a conventional municipal solid waste incinerator. Kawamoto et al.[2] and Kanda et al.[3] have investigated the dioxin formation characteristics on fly ash of a gasification-melting process, focusing on effects of ash compositions and precursors on the formation using a fixed bed model reaction system, in order to further decrease dioxins emissions.

This report describes effects of gas compositions on dioxin formation. The effects have been deduced through analyses of experimental data that Kawamoto et al.[4] and Mabuchi et al.[5] collected in the work conducted and sponsored by the R&D committee on next generation incinerators at Japan Waste Research Foundation. Reports are also made on further experiments that were conducted using the same apparatus to examine effects of unburned carbon in fly ash of the gasification-melting process.

Experiment

Test Samples

Experiments were carried out with five samples. Ash A and Ash B are fly ashes collected in a gasification-melting demonstration furnace and a conventional stoker incinerator for municipal

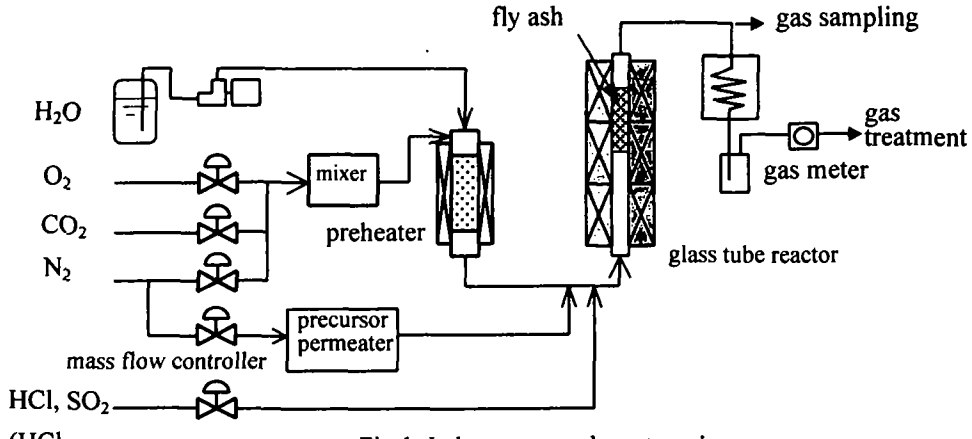

Fig.1 Laboratory-scale test equipment

solid waste (MSW), respectively. Ash A' and Ash B' are Ash A and Ash B thermally treated at 600 □C for 2 hours to deplete unburned carbon, respectively. A synthetic ash containing SiO_2 40 %, Al_2O_3 20 %, CaO 20 %, MgO 10 %, Na_2CO_3 5 %, and K_2CO_3 5 % was also tested. All samples were mixed with water and pelletized to be 1-4 mm in diameter. Compositions of prepared samples are summarized in Table 1.

Table 1 Fly ash samples used

Ash Sample	Composition (%)			
	Carbon	Chlorine	Copper	SiO2
Ash A : Fly ash of gasification-melting process	0.012	5.52	0.10	14.2
Ash A' : Treated ash of A *[1]	0.0067	-	0.093	-
Ash B : Fly ash of conventional incinerator	3.4	1.5	0.052	13.1
Ash B' : Treated ash of B *[1]	<0.01	-	-	-
Synthetic ash	0	0	0	40

*1 The ash was treated at 600°C

Experimental Procedure

Fig. 1 shows a flow diagram of the experimental apparatus used in the research. An enhanced model reaction for formation of PCDDs/DFs and coplanar PCBs proceed in a fixed bed, continuous flow reactor made of quartz. The dimension of the reactor tube is 50 mm in inner diameter and 1300 mm long and gas flows upward in the reactor. The fixed bed in the reactor was maintained at 350 □C during the experiments. Gas composition was set at N_2 80 %, CO_2 14 %, O_2 6 %, HCl 1000 ppm dry base, H_2O 20 % wet base at the standard condition in order to simulate flue gas in gasification-melting furnaces. A small amount of *o*-chlorophenol was added as a precursor in the gas phase using Permeater, GasTech Co., Ltd. The experimental parameters are summarized in Table 2.

Table 2 Set of experimental runs

Run No.	Fly ash	O_2 (%)	SO_2 (ppm)
1	Synthetic ash	6	0
2	Ash A	6	0
3	Ash A'	6	0
4	Ash B	6	0
5	Ash B'	6	0
6	Ash A	6	50
7	Ash A	6	500
8	Ash A	0.5	0

Measurements

Gas samples were collected at the gas sampling point shown in Fig. 1. Gas was sampled for four hours after the system reached at its steady-state. Ash was reclaimed from the reactor tube after each experimental run. The gas and ash samples were then analyzed to determine theirdioxins contents following the standard procedure.

Results and Discussion

Effects of Unburned Carbon on Dioxin Formation

Fig. 2 clearly shows dioxin formation in flue gas has a significant dependence on carbon contents in ash. Kawamoto et al. [4] reported that removing organic compounds in Ash A by soxhlet

extraction did not suppress dioxin formation in flue gas. Removing organic compounds in Ash A and Ash B by thermal treatment at 600 □C, however, substantially reduced dioxins concentrations by a factor of approximately 25 and 30 from those of original Ash A (gasification-melting furnace fly ash) and Ash B (conventional furnace fly ash), respectively. Dioxin concentrations in flue gas produced with Ash A' and Ash B' were as low as that produced with synthetic ash. It proved that thermal treatment at 600 □C effectively eliminated unburned carbon that contributed dioxin formation in flue gas.

Fig. 3 shows that characteristics of dioxin formation in ash resemble those in flue gas: thermal treatment of fly ash substantially reduced dioxin concentrations in ash. Figs. 4 and 5 are homologue distribution profiles of PCDDs/DFs in flue gas with Ash A (gasification-melting furnace fly ash) and Ash A', respectively. The ratios of compounds with a smaller number of chlorine is higher for Ash A' than Ash A. The shift suggests that elimination of unburned carbon from fly ash exert an influence on dioxin formation mechanisms.

In summary, dioxin formation due to unburned carbon in ash dominated dioxin formation in the investigated reaction system. Contribution of potential precursor organic compounds is considered to be small, as Mabuchi et al. [2] already reported.

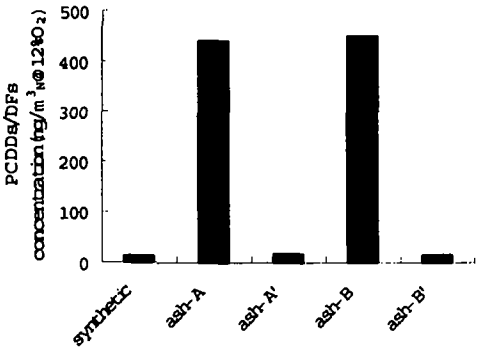

Fig.2 PCDDs/DFs concentration in flue gas from various fly ash samples

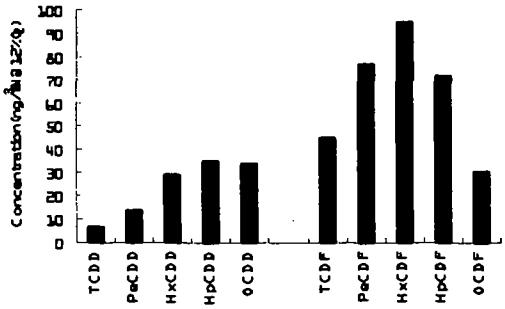

Fig.4 homologue distribution profiles of PCDDs /DFs in Run2 (Ash-A) flue gases

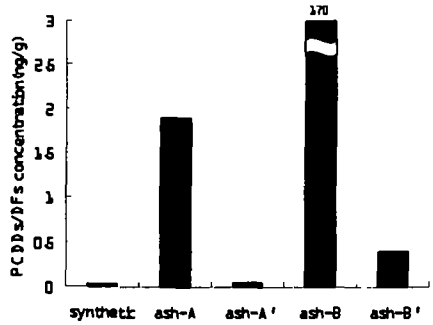

Fig.3 PCDDs/DFs concentration in various fly ash samples

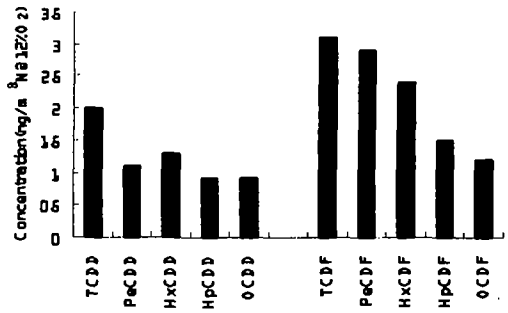

Fig.5 homologue distribution profiles of PCDDs /DFs in Run3 (Ash-A') flue gases

Effects of Sulfur Dioxide on Dioxin Formation

Table 3 summarizes effects of sulfur dioxide on dioxin formation characteristics. Existence of sulfur dioxide at concentration of 50ppm (Run 6) and 500ppm (Run 7) did not change significantly PCDDs/DFs concentrations in flue gas, while it slightly increased the concentrations in ash from 1.8 ng/g-ash (Run 2) to 5.4 and 5.9 ng/g-ash (Runs 6 and 7 respectively).
Effect of sulfur dioxide to inhibit dioxin formation[6] was not observed at S/Cl of 0.05nor 0.5 in this reaction system.

Effects of Oxygen on Dioxin Formation

Dioxin concentration at 0.5 and 6 % oxygen concentration can also be compared using Table 3. Total PCDDs and PCDFs concentrations in Run 8 at 0.5 % oxygen concentration were approximately 1/12 and 1/5, respectively, of those in Run 2 at 6 % oxygen concentration. In other words, low oxygen concentrations suppressed dioxin formation.

Table 3 Effects of SO_2 and O_2 on PCDDs/DFs concentration (ng/m^3_N at 12 % O_2) in flue gases

Run	PCDDs	PCDFs	PCDDs/DFs	Remarks
2	119	320	440	
6	113	412	525	SO_2: 50ppm
7	99	204	303	SO_2: 500ppm
8	10	58	68	O_2: 0.5%

In conclusion, unburned carbon in fly ash substantially contributed dioxin formation. Namely, dioxins formation over fly ash ofgasification-melting processes, which is much lessintnsive than that in conventional incinerators, could be suppressed by decreasing the unburned carbon. Existence of sulfur dioxide did not influence significantly dioxin formation in this model reaction system, while low oxygen concentrations suppressed dioxin formation.

Acknowledgements

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