

## VOLATILIZATION AND DECOMPOSITION OF DIOXIN FROM FLY ASH

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### Introduction

Emission control of Dioxin from municipal solid waste (MSW) incinerator has been mainly focused on Dioxin in flue gas. However, the countermeasure to decrease Dioxin in residue is also indispensable from a viewpoint of suppressing total release of Dioxin from MSW incinerator. Reduction of Dioxin in fly ash will greatly contribute to suppress the total release, because of the highest load of Dioxin in all streams from MSW incinerator. Concentration of Dioxin in fly ash should be less than 0.1ng-TEQ/g, in order to achieve the emission below 5  $\mu$ g-TEQ/ton MSW<sup>1</sup>. We have been developing volatilization and decomposition process of Dioxin from fly ash. In the present study, volatilization behavior of Dioxin from fly ash was discussed, and pilot-plant test results of volatilization and decomposition process were shown. In this process, Dioxin adsorbed in fly ash is desorbed and/or volatilized to gas phase effectively, and Dioxin in gas phase is decomposed by catalyst. This process can provide significant suppress of Dioxin reformation by de-novo synthesis in the treated fly ash, because of the simultaneous removal of other organic compounds having capability to be source for Dioxin reformation.

### Methods and Materials

#### *Volatilization and decomposition process*

Flow chart of volatilization and decomposition process of dioxin from fly ash is shown in Fig. 1. It is reported that Dioxin has boiling temperature ranging from 315°C to 537°C and vapor pressure ranging from 5.1E-4Pa to 3.2E+2Pa at 125°C<sup>2</sup>. And 94% of Dioxin was detected in gas phase, when fly ash was heated in gas flow with 10% oxygen at 350°C<sup>3</sup>. These reports imply that Dioxin adsorbed in fly ash can be effectively volatilized to gas phase by heating in gas flow. When fly ash is heated to temperature high enough to obtain high vapor pressure of Dioxin, other organic compounds that have potential to form Dioxin can be also evaporated. Thus, this process can lead significant suppress of reformation of Dioxin by de-novo

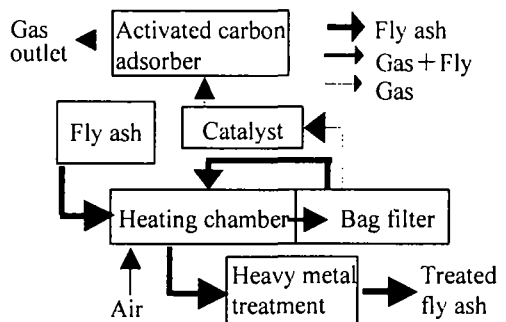


Fig.1 Flow chart of volatilization and decomposition process of Dioxin from fly ash.

synthesis in the treated fly ash. Dioxin in gas phase is decomposed by catalyst having high oxidation activity to stable compounds,  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Outlet gas from catalyst reactor is treated by activated carbon absorber to remove heavy metals evaporated in heating chamber.

### Laboratory-scale test

Fig.2 shows experimental set-up for analysis of Dioxin and organic compounds volatilized from fly ash. Fly ash was heated to  $400^\circ\text{C}$  in air flow. Organic compounds in gas phase were analyzed by FID gas chromatography. TEQ value (PCDDs/PCDFs) was measured for gas phase at  $250^\circ\text{C}$  and  $400^\circ\text{C}$  as shown in Fig.3, and for fly ashes before and after heat treatment.

### Pilot plant test

Schematic diagram of pilot plant is shown in Fig.4, and the conditions of test are listed in Table1. Cooling process of fly ash after heat treatment was not equipped with the pilot plant. Measurement of Dioxin and heavy metals were done at the sampling points (1)-(6) indicated in Fig.4. Co-PCB was quantified besides PCDDs/PCDFs, and TEQ value included Co-PCB.

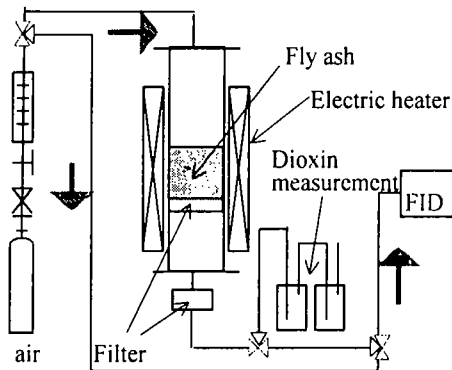


Fig.2 Experimental set-up for measurement of Dioxin and organic compounds volatilized from fly ash.

Table1 Operating conditions.

Fly ash feed rate	kg/h	50
Air flow rate	$\text{m}^3\text{N/h}$	50
Heating chamber temperature	$^\circ\text{C}$	420
Catalyst temperature	$^\circ\text{C}$	350
Activated carbon adsorber temperature	$^\circ\text{C}$	110

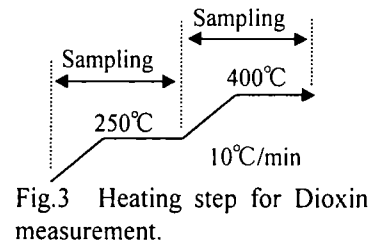


Fig.3 Heating step for Dioxin measurement.

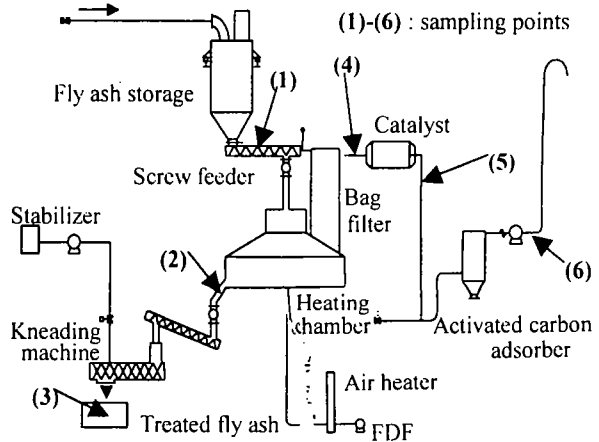


Fig.4 Schematic diagram of pilot plant.

## Results and Discussion

### Volatilization behavior of organic compounds and Dioxin from fly ash

Fig.5 shows the volatilization profile of organic compounds from fly ash at elevating temperature. Two peaks were observed at  $250^\circ\text{C}$  and  $400^\circ\text{C}$ . Lower temperature peak started at approx.  $200^\circ\text{C}$ , and FID intensity returned to zero base after 30 minutes at  $400^\circ\text{C}$ . This result implied that volatile organic compounds in fly ash can be removed by heating at  $400^\circ\text{C}$  for a certain period.

## ORGANOHALOGEN COMPOUNDS

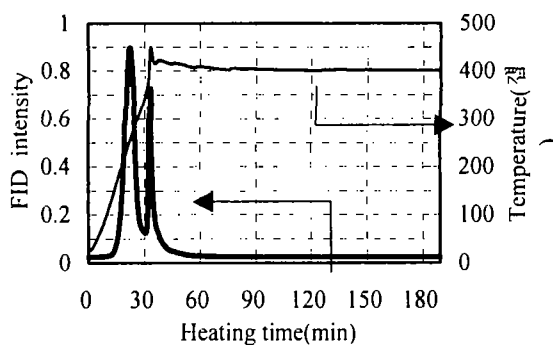


Fig.5?The volatilization profile of organic compounds from fly ash.

Volatilization behavior of Dioxin from fly ash during heat treatment is shown in Fig.6. At 200°C, small amount of Dioxin was observed in gas phase collected. On the other hand, at 400°C, most of Dioxin in fly ash moved to gas phase, and TEQ value of fly ash decreased to 0.04ng-TEQ/g with 98% removal efficiency.

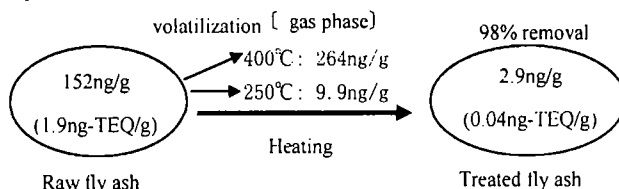


Fig.6 Volatilization behavior of Dioxin from fly ash.

### Pilot plant test

In Table2, measurement results of Dioxin and heavy metals in fly ash are shown. TEQ value at heating chamber outlet (2) was sufficiently low of 0.0044ng-TEQ/g. The slight higher TEQ value was observed at kneading machine outlet (3) in comparison with the value at (2). This was mainly caused by fluctuation of operation. The value of 0.0154ng-TEQ/g at (3) was also considerably below 0.1ng-TEQ/g. The removal efficiency of Dioxin in fly ash was 97.5%. These results showed significant suppress of Dioxin reformation by de-novo synthesis in the treated fly ash even without cooling process. Leaching test results of fly ash at (3) in Table3 indicated that heavy metals were perfectly stabilized by kneading with liquid polymer type chelating agent (NKK-A200). In addition, Pb concentration in leachate from fly ash at (2) was considerably lower in comparison with that of untreated fly ash (1). This indicated the possibility to decrease the necessity amount of chelating agent to stabilize heavy metals.

Table4 shows concentrations of dioxin and heavy metals in gas phase. Dioxin volatilized from fly ash was decomposed by catalyst to 0.0321ng-TEQ/m<sup>3</sup>N, and furthermore that concentration of Dioxin decreased to 0.0181ng-TEQ/m<sup>3</sup>N (<0.1ng-TEQ/m<sup>3</sup>N) at activated carbon absorber outlet (6). Concentrations of Heavy metals were decreased to very low level at (6).

Table2 Dioxin and heavy metals concentration in fly ash.

Sampling point in Fig.4	Dioxin	Heavy metal					
		Cr	Cd	Pb	Hg	As	Se
	ng-TEQ/g	mg/kg					
(1)	0.609	160	91	3100	7.2	3.4	0.55
(2)	0.0044	360	91	3200	0.075	1.3	0.78
(3)	0.0154	120	64	2100	0.028	0.94	0.12

Table3 Leaching test results of fly ash

Sampling point in Fig.4	Cr <sup>6+</sup>	Cd	Pb	Hg	As	Se
	mg/L					
(1)	<0.04	<0.01	45	0.0034	<0.01	0.010
(2)	0.86	<0.01	11	<0.0005	<0.01	0.018
(3)	<0.04	<0.01	<0.05	<0.0005	<0.01	0.042

Table4 Dioxin and heavy metals concentration in flue gas.

Sampling point in Fig.4	Dioxin	Heavy metal					
		Cr	Cd	Pb	Hg	As	Se
	ng-TEQ/m <sup>3</sup> N	mg/m <sup>3</sup> N					
(4)	100.9	—	—	—	—	—	—
(5)	0.0321	<0.01	0.2	4.92	0.28	<0.01	<0.01
(6)	0.0181	<0.01	0.12	3.37	0.01	<0.01	<0.01

## References

- 1.Hiraoka M., Sakai S., Sakagawa T. and Hata Y.(1997)Organohalogen Compounds,31,446.
- 2.Berchtold F. Rordorf.(1989)Chemosphere,Vol.18,Nos.1-6,783.
- 3.Elmar R. Altwicker, Yanmei Xun and Michael S. Milligan.(1994)Organohalogen Compounds,20,381.