

Volatilization and Decomposition of Dioxin from Fly Ash

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The dioxin volatilization and decomposition process was developed to remove dioxin from fly ash in MSW (Municipal Solid Waste) incinerators. In this process, dioxin adsorbed on the surface of fly ash is volatilized to the gas phase and then decomposed by catalytic or high temperature treatment. This process significantly suppresses dioxin reformation by de-novo synthesis in the treated fly ash because of the simultaneous removal of other organic compounds that may be sources for dioxin reformation.

1. Introduction

The control of dioxin emissions from MSW incinerators has primarily focused on the dioxin in flue gas. However, measures to decrease dioxin in the residue are also critical for reducing the total release of dioxin from MSW incinerators. Reductions of dioxin in the fly ash will greatly lower the total amount released because dioxin are more concentrated in the fly ash than in any other stream from a MSW incinerator. The concentration of dioxin in fly ash should be less than 0.1ng-TEQ/g to achieve emissions below $5 \mu\text{g-TEQ/ton MSW}^1$. We have been developing a process for the volatilization and decomposition of dioxin from fly ash.

The volatilization behavior of dioxin from fly ash was evaluated, and pilot-plant tests of the volatilization and decomposition process were performed in the present study. In this process, dioxin adsorbed in fly ash is effectively desorbed and/or volatilized to the gas phase. The gas phase dioxin is then decomposed by catalyst. This process can significantly suppress the reformation of dioxin by de-novo synthesis in the treated fly ash because of the simultaneous removal of other organic compounds that can provide sources for dioxin reformation.

2. Volatilization and decomposition process

A flow chart for the volatilization and decomposition process of dioxin from fly ash is shown in Fig.1. Dioxin has a boiling temperature ranging from 315°C to 537°C and a vapor pressure ranging from 5.1E-4Pa to 3.2E+2Pa at 125°C². When fly ash was heated in a gas flow with 10% oxygen at 350°C, 94% of the dioxin was detected in

the gas phase³). These reports imply that the dioxin adsorbed in fly ash can be effectively volatilized to the gas phase by heating in a gas flow. Other organic compounds that have the potential to form dioxin are also evaporated at the temperatures needed to provide a sufficiently high dioxin vapor pressure. Thus, this process can significantly suppress the reformation of dioxin by de-novo synthesis in the treated fly ash. Dioxin in the gas phase is decomposed by catalyst with high oxidation activity to the stable compounds CO₂ and H₂O. An activated carbon adsorber treats the outlet gas from the catalyst reactor to remove heavy metals evaporated in the heating chamber.

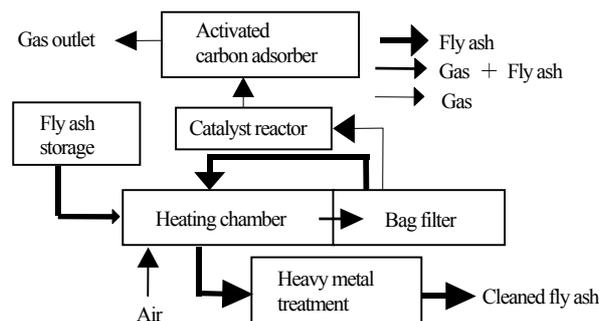


Fig.1 Flow chart of volatilization and decomposition of dioxin from fly ash

3. Experiment

3.1 Laboratory-scale test

Fig.2 shows the experimental set-up for analyzing the dioxin and organic compounds volatilized from fly ash. Fly ash was heated to 400°C in an air flow. Organic compounds in the gas phase were analyzed by FID gas chromatography. The TEQ value (PCDDs/PCDFs) was

measured for the gas phase at 250°C and 400°C, as shown in Fig.3, and for fly ash before and after heat treatment.

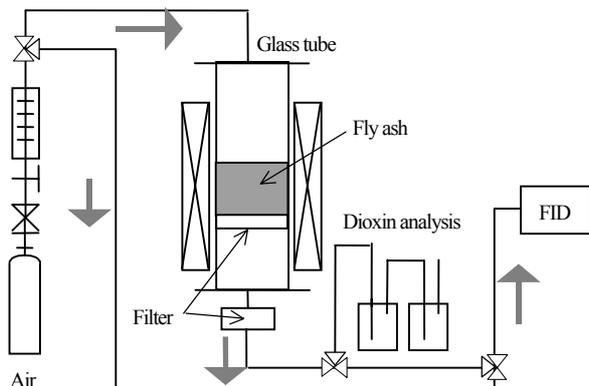


Fig.2 Experimental set-up for analysis of dioxin and organic compounds volatilized from fly ash

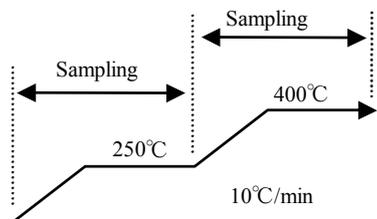


Fig.3 Heating step for dioxin analysis

3.2 Pilot plant test

A schematic diagram of the pilot plant is shown in Fig.4, and the conditions of the test are listed in Table 1. The pilot plant did not have cooling system for the fly ash after heat treatment. Measurements of dioxin and heavy metals were done at the sampling points (1)-(6) indicated in Fig.4. Co-PCB was quantified in addition to PCDDs/PCDFs, and the TEQ value was included in the Co-PCB.

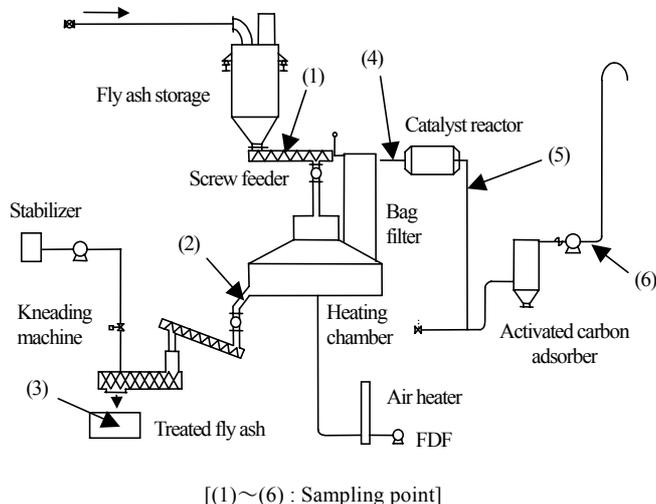


Fig.4 Schematic diagram of pilot plant

Table 1 Operating conditions

Fly ash feed rate	kg/h	50
Air flow rate	m ³ N/h	50
Heating chamber temperature	°C	420
Catalyst temperature	°C	350
Activated carbon adsorber temperature	°C	110

4. Results and discussion

4.1 Volatilization behavior of organic compounds and dioxin from fly ash

Fig.5 shows the volatilization profile of organic compounds from fly ash at elevated temperatures. Two peaks were observed, at 250°C and 400°C. The lower temperature peak started at approx.200°C, and the FID intensity returned to the zero base after 30 minutes at 400°C. This result implied that volatile organic compounds in the fly ash can be removed by heating at 400°C for a certain period.

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

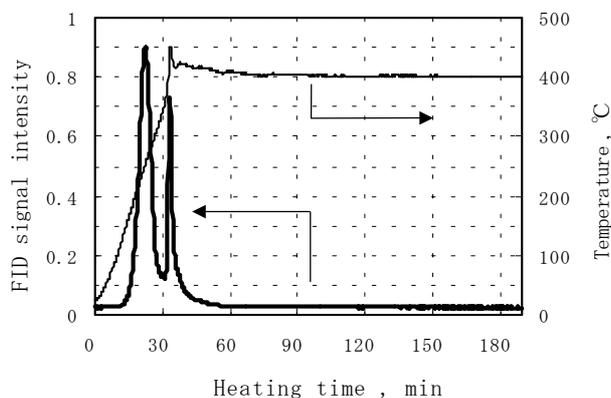


Fig.5 Volatilization profile of organic compounds from fly ash

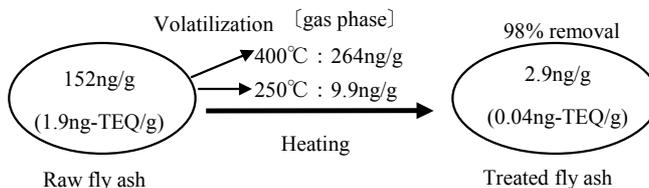


Fig.6 Volatilization behavior of dioxin from fly ash

4.2 Pilot plant test

The results of measurements of dioxin and heavy metals in the fly ash are shown in **Table 2**. The TEQ value at the heating chamber outlet (2) was sufficiently low at 0.0044ng-TEQ/g. The TEQ value observed at the kneading machine outlet (3) was slightly higher than that at (2). This was mainly caused by fluctuations in operation. The value of 0.015ng-TEQ/g at (3) was also considerably below 0.1ng-TEQ/g. The removal efficiency of dioxin in the fly ash was 97.5%. These results showed significant suppression of dioxin reformation by de-novo synthesis in the treated fly ash, even without a cooling process. Leaching test results of the fly ash at (3) in **Table 3** indicated that heavy metals were completely stabilized by kneading with a liquid polymer chelating agent (NKK-A200). In addition, the lead concentration in the leachate from fly ash at (2) was considerably less than that of untreated fly ash (1). This indicated that the amount of chelating agent needed to stabilize heavy metals could be reduced.

Table 2 Dioxin and heavy metal concentrations in fly ash

Sampling point in Fig.6	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

Table 3 Leaching test results of fly ash

Sampling point in Fig.6	Cr ⁶⁺	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
Landfill standard	1.5	0.3	0.3	0.005	0.3	0.3

Table 4 shows concentrations of dioxin and heavy metals in the gas phase. Dioxin volatilized from fly ash was decomposed by catalyst to 0.032ng-TEQ/m³N, and the concentration of dioxin was further decreased to 0.018ng-TEQ/m³N (<0.1ng-TEQ/m³N) at the activated carbon adsorber outlet (6). Concentrations of heavy metals were decreased to a very low level at (6).

Table 4 Dioxin and heavy metal concentrations in flue gas

Sampling point in Fig.6	Dioxin	Heavy metal					
		Cr	Cd	Pb	Hg	As	Se
	ng-TEQ/m ³ N	mg/m ³ 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

5. Conclusion

Dioxin in fly ash was volatilized and removed by heating in an air flow. Most of the dioxin shifted to the gas phase by heating at 400°C. The pilot plant test revealed that the volatilization and decomposition process could provide 97.5% removal efficiency and low concentrations of dioxin of 0.015ng-TEQ/g in the fly ash and 0.018ng-TEQ/m³N in the gas phase. These are considerably below their respective limits of 0.1ng-TEQ/g and 0.1ng-TEQ/m³N. This process provides significant suppression of dioxin reformation by de-novo synthesis in the treated fly ash without a cooling process for the fly ash after heat treatment.

This work was performed as a co-research project of Kawasaki city and NKK.

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