Volatilization and Decomposition of Dioxin from Fly Ash with Agitating Fluidized Bed Heating Chamber

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A dioxin volatilization and decomposition process has been developed to reduce dioxin from fly ash in MSW (Municipal Solid Waste) incinerators. The design of the heating chamber is very important for achieving a stable, efficient process because of the difficulty of heating fly ash stably and effectively due to its poor heat conductivity and agglomeration at >500 $^{\circ}$ C caused by chloride content, and yet heating up to 400 $^{\circ}$ C is essential to remove dioxin adsorbed on the surface of the fly ash. The authors have developed and adopted an agitating fluidized bed heating chamber having very high heating efficiency for the volatilization and decomposition process. This paper describes the performance of the heating chamber and shows test results for a pilot plant using the heating chamber.

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 to suppress the total dioxin released from MSW incinerators. Reductions of dioxin in the fly ash will greatly lower the total amount released because the dioxin quantity in fly ash is higher than in any other stream from an MSW incinerator. The concentration of dioxin in fly ash should be less than 0.1ng-TEQ/g to achieve emissions below 5 μ g-TEQ/ton MSW¹).

We have been developing a dioxin volatilization and decomposition process to reduce dioxin from fly ash, and have confirmed that the process shows good performance²⁾⁻⁵⁾. In the development, the design of the heating chamber is very important for achieving a stable, efficient process because of the difficulty of heating fly ash stably and effectively due to its thermal characteristics. Fly ash is mainly composed of oxides and has poor heat conductivity, making it very difficult to raise the temperature in the fly ash layer homogeneously. Furthermore, fly ash contains chlorides which lead to agglomeration of the fly ash at >500°C, and yet heating up to 400°C is essential to reduce dioxin adsorbed on the surface of the fly ash. A heating method that is appropriately designed for fly ash is required for the best performance of the process.

The authors have developed and adopted an agitating fluidized bed heating chamber having very high heating efficiency for the volatilization and decomposition process. This paper describes the performance of the heating chamber and shows test results for a pilot plant concerning dioxin reduction efficiency and suppression effect for heavy metal leaching from the treated fly ash.

2. Volatilization and decomposition process

Most of the dioxin in the flue gas of MSW incinerators is adsorbed on the surface of the fly ash because of the low vapor pressure of dioxin below 200°C. Recently, fly ash in the flue gas is filtered out by dust collectors such as bag filters and electrostatic precipitators operated at below 200°C to obtain high removal efficiency of dioxin as well as fly ash particles themselves. Although this decreases the emission of dioxin from the stack, it increases the concentration of dioxin in the fly ash.

A flow chart of the volatilization and decomposition process of dioxin from fly ash is shown in **Fig.1**. Dioxin adsorbed in fly ash is effectively desorbed and/or volatilized to the gas phase by heating and airflow. 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° C⁶. When fly ash was heated in a gas flow with 10% oxygen at 350° C, 94% of the dioxin was detected in the gas phase⁷. These reports imply that the dioxin can be ef-

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fectively volatilized to the gas phase. In this process other organic compounds can be removed simultaneously with dioxin, thus eliminating sources for dioxin reformation in treated fly ash. Significant suppression of the reformation of dioxin by de-novo synthesis in treated fly ash is expected without a cooling process after the heating chamber. Dioxin in the gas phase is decomposed by the 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 process of dioxin from fly ash

3. Agitating fluidized bed heating chamber

In an ideal fluidized bed, powders and gas form a homogeneous mixing zone and powders circulate intensively in the fluidized bed. These phenomena provide very high contact efficiency of the powders and gas as well as high exchange frequency of the powders against the heating chamber wall. If a fluidized bed is used as a heating chamber for powders, effective heating can be achieved by using either heated gas flow through a distributor or electric heating of the chamber wall.

The use of a fluidized bed heating chamber to heat the fly ash offers several advantages:

(1) Homogeneous temperature in the fly ash in the chamber,

(2) Excess heating of the wall to heat the fly ash to a sufficient temperature for dioxin removal is not needed, and so agglomeration of the fly ash caused by chlorides in the fly ash can be avoided, and

(3) Dioxin volatilization is promoted by good contact efficiency of the fly ash and air.

The fluidization phenomenon strongly depends on the powders and gas velocity, and so it is necessary to opti-

mize the fluidization conditions for the fly ash to obtain the advantages listed above. Fig.2 shows the classification of powders for fluidization by air⁸⁾. The behavior of powders in a gas falls into four distinct groups, characterized by density difference (ρ_{p} - ρ_{g}) and mean particle size (d_{p}). Group A powders exhibit dense phase expansion after the minimum fluidization velocity and prior to the beginning of bubbling. When the gas supply is suddenly cut off, the bed collapses slowly. In contrast with group A powders, in group B powders naturally-occurring bubbles start to form at the minimum fluidization velocity. Bed expansion is small and the bed collapses very rapidly when the gas supply is stopped. Group C powders are extremely difficult to fluidize, because the inter-particle forces are greater than those which the fluid can exert on the particle, generally resulting from very small particle size, strong electrostatic charges, etc. In group D powders, large bubbles rise more slowly than the interstitial fluidizing gas; these powders can form a stable spouted bed if gas is admitted only through a central hole.

Fly ash in MSW incinerators having mean particle size of 20 to $30 \,\mu$ m is classified into group C, which is very difficult to fluidize. In order to fluidize group C fly ash, an additional device is required in addition to the gas flow at the optimum gas velocity through the distributor.



Fig.2 Classification of powders by Geldart Case of fluidization by air at room conditions

We attempted to adopt the agitating device to form a homogeneous fluidizing bed of the fly ash. In the cold model (acrylic, ID=120mm) test without supplemental agitating device, channels were formed in the fly ash layer and gas passed up through the channels. On the other hand, with the agitating device, a homogeneous fluidizing bed without bubbles was formed. A pilot plant with agitating fluidized bed heating chamber (ID=450mm) was built to evaluate the heating efficiency and the performance concerning dioxin and heavy metals. The maximum fly ash treatment capacity of the pilot plant is 100kg/h.

Fig.3 shows the structure of the agitating fluidized bed heating chamber. The outside wall of the cylindrical chamber is heated by an electrical heater. Fly ash is fed from the upper part of the chamber and treated fly ash is extracted from the bottom of the chamber. Preheated gas is introduced via the distributor at the bottom of the chamber, and the outlet gas passes through a bag filter to trap accompanying fly ash.



Fig.3 Agitating fluidized bed heating chamber

4. Results and discussion

4.1 Heating efficiency of agitating fluidized bed heating chamber

Table 1 shows the operation results of the agitating fluidized bed heating chamber. When the fly ash feed rate is 60kg/h and the temperature of the electrically heated chamber wall is 425°C, the temperature of the fly ash fluidized bed is maintained at 400°C. The temperatures measured at six different points in the fluidized bed are within 5°C of each other. The heat transfer coefficient from the chamber wall to fly ash is calculated to be 129kcal/m²·h·°C. These results revealed that a homogeneous fluidized zone of fly ash could be formed by including an agitating device in addition to airflow, and that fly ash could be heated effectively because of the very high heat transfer coefficient. No agglomeration was observed in the heating chamber after the tests. The agitating fluidized bed heating chamber having such a high heat transfer coefficient provides advantages including no need to heat the wall to an excessively high temperature, and small heating chamber in comparison with the conventional heating methods for fly ash.

Fly ash feed rate	kg/h	60
Air flow rate	m ³ N/h	18
Heating chamber wall temperature	°C	425
Fluidizing bed temperature	°C	400
Heat transfer coefficient	kcal/m ² h °C	129

 Table 1
 Operation results of agitating fluidized bed heating chamber

4.2 Dioxin removal efficiency

A schematic diagram of the pilot plant is shown in Fig.4. The pilot plant did not have a system for cooling the fly ash after heat treatment. Measurement of dioxin and heavy metals was done at sampling points (1) to (4) indicated in Fig.4. The sampling and analysis of PCDDs, PCDFs and Co-PCBs were based on JIS K 0311. The TEQ value discussed in this paper included PCDDs, PCDFs and Co-PCBs.



Fig.4 Schematic diagram of pilot plant

The conditions of the test are listed in **Table 2**. The temperature of the electrically heated chamber wall is 460°C, and the temperature of the fly ash fluidized bed is maintained at 440°C. Air is introduced via the distributor after being heated at the flow rate of $18m^3N/h$. The catalyst and activated carbon adsorber temperatures are controlled to $330-370^{\circ}$ C and 110° C, respectively.

Fly ash feed rate	kg/h	48
Air flow rate	m ³ N/h	18
Heating chamber wall temperature	°C	460
Catalyst temperature	°C	330~370
Activated carbon adsorber temperature	°C	110

 Table 2
 Operating conditions of pilot plant

The results of measurements of dioxin in the fly ash are shown in **Table 3**. The TEQ value at the kneading machine outlet (2) was sufficiently low at 0.0085ng-TEQ/g, and was considerably below 0.1ng-TEQ/g. This result showed that the dioxin volatilization and decomposition process with the agitating fluidized bed heating chamber provided high dioxin reduction efficiency. Significant suppression of dioxin reformation by de-novo synthesis in treated fly ash was also confirmed because this performance was obtained without a cooling process.

 Table 3
 Dioxin concentrations in fly ash

Sompling point in Fig.4	Dioxin	
Sampling point in Fig.4	ng-TEQ/g	
(1)	2.0	
(2)	0.0085	

Tables 4 and 5 show concentrations of dioxin and heavy metals in the gas phase. Dioxin volatilized from fly ash was decomposed by catalyst to 0.060 ng-TEQ/m³N (<0.1 ng-TEQ/m³N), and the concentration of dioxin was further decreased to 0.0016 ng-TEQ/m³N at the activated carbon adsorber outlet (4). Concentrations of heavy metals are less than the detectable limit except mercury at bag filter outlet (3). Mercury was also decreased to a very low level at activated carbon adsorber outlet (4).

Compliance a sint in Fig. 4	Dioxin		
Sampling point in Fig.4	ng-TEQ/m ³ N		
(3)	0.060		
(4)	0.0016		

Table 5 Heavy metal concentrations in flue gas

	Heavy metal					
Sampling point in Fig.4	Cr	Cd	Pb	Hg	As	Se
Ū	mg/m ³ N					
(3)	<0.1	< 0.01	< 0.01	1.1	< 0.01	< 0.02
(4)	< 0.1	< 0.01	< 0.01	< 0.003	< 0.01	< 0.02

4.3 Suppression of heavy metal leaching from fly ash

The results of leaching tests of the fly ash are shown in **Table 6**. Untreated fly ash (1) and treated fly ash sampled at (5) were evaluated. The fly ash used in this evaluation was treated by a volatilization and decomposition process at 425° C. Lead, mercury and selenium concentrations in the leachate from treated fly ash (5) were considerably lower than those of untreated fly ash (1). Except for mercury which was found to move to the gas phase, the oxidation conditions of the heavy metals were considered to have been changed by the heat treatment in the oxidizing atmosphere. Consequently, the leaching of heavy metals from the fly ash was suppressed after heat treatment.

Table 6 Leaching test results of fly ash

Sampling point	Cr ⁶⁺	Cd	Pb	Hg	As	Se
in Fig.4		mg/L				
(1)	< 0.02	< 0.02	15.1	0.0014	< 0.01	0.006
(5)	< 0.02	< 0.02	6.67	< 0.0005	< 0.01	0.0016

Table 7 shows the relationship between heavy metal concentration in leachate and the amount of chelating agent NKK-A200. Generally, the optimum amount of chelating agent to be added is approximately 1g for 100g of fly ash when the concentration of lead in the fly ash is 1000mg/kg⁹⁾. The lead concentration of the fly ash evaluated in this study was 3500mg/kg, so 3.5g of chelating agent is considered to be sufficient for stabilizing 100 g of fly ash. However, the results in **Table 7** indicate that 2g of chelating agent is enough to stabilize the heavy metals and suppress leaching from fly ash to within the regulations for landfill. It is also confirmed that there is no difference of lead concentration in the fly ash between before and after heat treatment.

These results show that the amount of chelating agent needed to stabilize the heavy metals could be reduced because of the change of the oxidation condition of heavy metals by heat treatment in the oxidizing atmosphere.

Table 7Relationship between heavy metal concentration in
leachate and amount of chelating agent NKK-A200

A200-wt/ fly ash-wt.	Cr ⁶⁺	Cd	Pb	Hg	As	Se	
	mg/L						
0.01	< 0.04	< 0.01	8.8	< 0.0005	< 0.01	0.04	
0.02	< 0.04	< 0.01	0.06	< 0.0005	< 0.01	0.04	
0.03	< 0.04	< 0.01	< 0.01	< 0.0005	< 0.01	0.02	
Landfill regulation	1.5	0.3	0.3	0.005	0.3	0.3	

5. Conclusions

The heating efficiency of the heating chamber, dioxin removal efficiency and suppression of heavy metal leaching for a dioxin volatilization and decomposition process with agitating fluidized bed heating chamber were analyzed, with the following results:

(1) The agitating fluidized bed heating chamber showed a very high heat transfer coefficient of $129 \text{kcal/m}^2 \cdot \mathbf{h} \cdot \mathbf{\hat{C}}$. This heating chamber provides advantages such as high heating efficiency without having to heat the wall to an excessively high temperature, thus enabling the dimensions of the heating chamber to be made smaller than the conventional one.

(2) The TEQ value of treated fly ash was sufficiently low at 0.0085ng-TEQ/g, and was considerably below 0.1ng-TEQ/g. This result shows that the process enables the total release of dioxin from MSW incinerators to be decreased below 5μ g-TEQ/ton MSW. Dioxin reformation by de-novo synthesis in treated fly ash was suppressed effectively even without a cooling process.

(3) Dioxin volatilized from fly ash to the gas phase was decomposed by catalyst to 0.06ng-TEQ/m³N (<0.1 ng-TEQ/m³N). Heavy metal concentrations were decreased to the less than the detectable limits at the activated carbon adsorber outlet.

(4) The amount of chelating agent needed to stabilize heavy metals could be reduced for the fly ash treated by this process because of the change of the oxidation condition of heavy metals by heat treatment in the oxidizing atmosphere.

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