VOLATILIZATION AND DECOMPOSITION PROCESS FOR REMOVAL OF DIOXIN FROM FLY ASH WITH AGITATING FLUIDIZED BED

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Abstract

A dioxin volatilization and decomposition process has been developed to reduce dioxin from fly ash in municipal solid waste (MSW) 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 >773K caused by chloride content, and yet heating up to 673K 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.

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 0.1 ng-TEQ/g to achieve emissions below 5 μ g-TEQ/ton MSW [1)].

We have developed a dioxin volatilization and decomposition process to reduce dioxin from fly ash, and have confirmed that the process showed good performance[2,3)]. 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 >773K, and yet heating up to 673K 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. The performance of this process had been confirmed by pilot plant test, and the commercial plants have been operated smoothly[4)]. This paper describes the performance of the heating chamber and shows test results for a pilot plant.

Materials and Methods

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 473K. Recently, fly ash in the flue gas is filtered out by dust collectors such as bag filters and electrostatic precipitators operated at below 473K 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 is shown in Figure 1. Dioxin adsorbed

in fly ash is effectively desorbed and/or volatilized to the gas phase by heating and airflow. Rordorf reported that dioxin has a boiling temperature ranging from 588K to 810K and a vapor pressure ranging from 5.1E-4Pa to 3.2E+2Pa at 398K [5]. Altwicker showed that 94% of the dioxin was detected in the gas phase when fly ash was heated in a gas flow with 10% oxygen at 623K[6]. These reports imply that the dioxin can be effectively 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. An activated carbon adsorber treats the outlet gas from the catalyst reactor to remove heavy metals evaporated in the heating chamber.

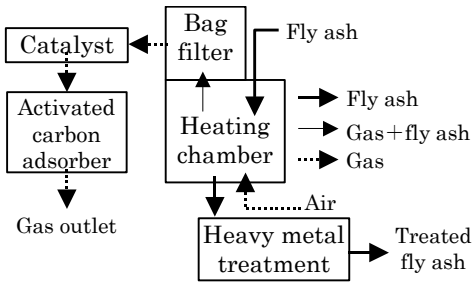

Fig. 1 Flow chart of volatilization and decomposition process of dioxin from fly ash.

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 characteristic of powders and gas velocity, fly ash in MSW incinerators having mean particle size of 20 to 30 μm is very difficult to fluidize. In order to fluidize fly ash, an additional device is required in addition to the gas flow at the optimum gas velocity through the distributor.

We attempted to adopt the agitating device to form a homogeneous fluidized bed of the fly ash. In the cold model (acrylic, ID = 120 mm) 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 fluidized bed was formed.

A pilot plant with agitating fluidized bed heating chamber (ID = 450 mm) 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 100 kg/h. Figure 2 shows the structure of the agitating fluidized bed heating chamber. The outside wall of the cylindrical

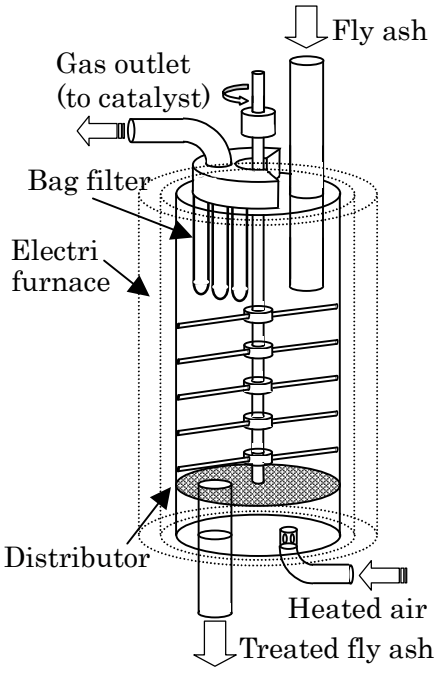

Fig. 2 Agitating fluidized bed heating chamber.

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 air 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.

Results and Discussion

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 was 60 kg/h and the temperature of the electrically heated chamber wall was 698K, the temperature of the fly ash fluidized bed was maintained at 673K. The temperatures measured at six different points in the fluidized bed were within the deviation of 5K. The heat transfer coefficient from the chamber wall to fly ash was calculated to be 150 W/m^2·K. 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.

Table1 Operation results of agitating fluidized bed heatingchamber.

Fly ash feed rate [kg/h]	60
Air flow rate [m^{3}N/h]	18
Heating chamber wall temperature [K]	698
Fluideized bed average temperature [K]	673
Heat transfer coefficient [W/(m^2·K)]	150

Dioxin removal efficiency

A schematic diagram of the pilot plant is shown in Figure 3. 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. 3. 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.

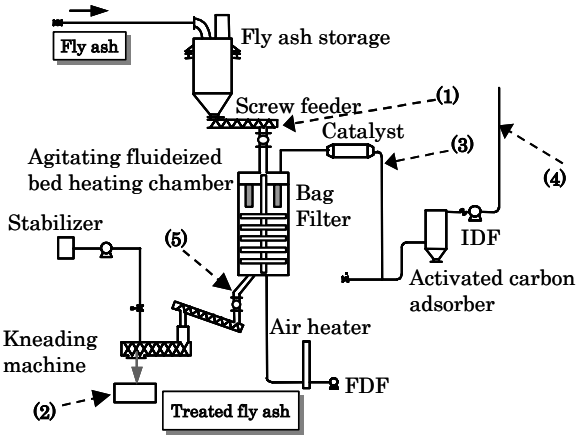

Fig. 3 Schematic diagram of pilot plant.

The conditions of the test are listed in Table 2. The temperature of the electrically heated chamber wall was 733K, and the temperature of the fly ash fluidized bed was maintained at 713K. Air was introduced via the distributor after being heated at the flow rate of 18 m^{3}N/h. The catalyst and activated carbon adsorber temperatures were controlled to 603-643K and 383K, respectively.

Table 2 Operating conditions of pilot plant.

Fly ash feed rate [kg/h]	48
Air flow rate [m^{3}N/h]	18
Heating chamber wall temperature [K]	733
Catalyst temperature [K]	603～643
Activated carbon adsorber temperature [K]	383

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 0.0085 ng-TEQ/g, and was considerably below 0.1 ng-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. 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/m^3N (<0.1 ng-TEQ/m^3N), and the concentration of dioxin was further decreased to 0.0016 ng-TEQ/m^3N at the activated carbon adsorber outlet (4). Concentrations of heavy metals were less than the detectable limit except Hg at bag filter outlet (3). Hg was also decreased to a very low level at activated carbon adsorber outlet (4).

Table 3 Dioxin concentrations in fly ash.

Sampling point in Fig.3	Dioxin [ng-TEQ/g]
(1)	2.0
(2)	0.0085

Table 4 Dioxin concentrations in flue gas.

Sampling point in Fig.3	Dioxin [ng-TEQ/m^3N]
(3)	0.060
(4)	0.0016

Table 5 Heavy metal concentrations in flue gas.

Sampling point in Fig. 3	Heavy metal [mg/m^3N]					
	Cr	Cd	Pb	Hg	As	Se
(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

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 698K. Pb, Hg and Se concentrations in the leachate from treated fly ash (5) were considerably lower than those of untreated fly ash (1). Except for Hg 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 in Fig. 3	Heavy metal [mg/L]					
	Cr6+	Cd	Pb	Hg	As	Se
(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

Commercial Plant Operation

The volatilization and decomposition process has commercialized, and several commercial plants have been operated smoothly. This process is contributing to suppress the total dioxin released from MSW incinerators.

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