Abstract: “High Clean DX” a dioxins removal technology for fly ash discharged from municipal solid waste (MSW) incinerators was developed. In the course of developing “High Clean DX,” a rapid analytical technology for the dioxins concentration in fly ash was important. A simplified analytical technology for dioxins in fly ash using flame ionization detector gas chromatography has been developed by focusing on the simple volatilization behavior of organic compounds.” This technology makes it possible to estimate the dioxins concentration of fly ash rapidly.

1. Introduction

In 1997, Japan’s Ministry of Health and Welfare issued “New Guidelines” for dioxins discharged from municipal solid waste (MSW) incinerators, which set standard values for concrete permanent countermeasures for the concentration of dioxins in incinerator exhaust gas. The “New Guidelines” also mentioned the necessity of regulating the total dioxins emissions discharged from the MSW incineration facility as a whole, and as a result, the current basis of dioxins countermeasures has shifted to “total emissions per unit of waste.” When considering countermeasures for this regulation of total emissions, effective treatment of the dioxin contained in fly ash is essential, because dioxins in fly ash account for more than 60% of the total dioxins emissions from MSW incinerators. The target value for reduction in this case is on the order of <0.1 ng-TEQ/g-fly ash.

Under the circumstances described above, JFE Engineering developed a dioxins removal technology called “High Clean DX” for dioxins contained in fly ash. Several “High Clean DX” units have been delivered as actual fly ash treatment systems and are functioning smoothly.

As the analysis method for the dioxins concentration in fly ash, a method using a high resolution gas chromatography mass spectrometer (GC-MS) is specified as the official method (Ministry of Health and Welfare Notification No. 192, 1992, Ministry of Health and Welfare Notification No. 633, revised, 2000). Although analyses by the official method achieve high accuracy, an analysis period of from several weeks to approximately 1 month is required. Therefore, various analytical techniques have been developed to shorten the analysis period. In the course of developing the “High Clean DX,” which is based on the principle of volatilization and desorption of organic compounds from fly ash, the authors established a simplified analytical technology for the concentration of dioxins by measuring the volatilization and desorption behavior of organic compounds using a flame ionization detector (FID) gas chromatograph, which is a general-purpose analytical device. This paper presents an outline of the “High Clean DX” system and describes the simplified analytical technology for dioxins which was established in the course of developing the device.

2. Outline of “High Clean DX”

2.1 Process flow

The principle and process flow chart of the “High Clean DX” are shown in Fig. 1 and Fig. 2, respectively. As shown in Fig. 1, the dioxins in fly ash is adsorbed on
In the “High Clean DX,” the dioxins in the fly ash are moved from a solid phase to a gas phase by volatilization or desorption (hereinafter, referred to simply as “volatilization”) from the fly ash by heating and air blowing, thereby detoxifying the fly ash. In this process, organic compounds other than dioxins are volatilized simultaneously, and the dioxins and these other organic compounds are separated from the fly ash in the heating stage. Accordingly, the content of residual organic compounds which might provide a source for resynthesis of dioxins is controlled in the treated fly ash, effectively preventing resynthesis of dioxins. This makes it possible to omit the rapid-cooling (quenching) process for the fly ash, which is considered necessary to prevent resynthesis.

The organic compounds, including dioxins, which have been desorbed to the gas phase are led to a catalytic reactor and are detoxified by an oxidative decomposition. A honeycomb-type catalyst, containing platinum as the active species, is adopted. An activated carbon adsorber treats the gas discharged from the catalytic reactor to remove heavy metals volatilized from the fly ash in the heating chamber.

**2.2 Structure of Agitating Fluidized Bed Heating Chamber**

For the “High Clean DX,” an agitating fluidized bed heating chamber with extremely high heating efficiency was developed. This chamber is external heated by an electric furnace. **Fig. 3** shows structure of this fluidized bed heating chamber.

In the agitating fluidized bed heating chamber, a homogeneous fluidized bed of fly ash is formed by the agitating device installed in the heating chamber and the heated air blown into the chamber through the distributor. This secures excellent gas/solid contact between the heated air and the fly ash, as well as a high exchange speed of fly ash at the heating surface, resulting in excellent heating efficiency.

Due to these distinctive features, the “High Clean DX” demonstrates the following effects: (1) Uniformity of the temperature in the fluidized bed, (2) prevention of excess heating of the wall, which would cause the agglomeration of the fly ash, and (3) accelerated volatilization of dioxins and organic compounds as result of the enhanced gas/solid contact between the heated air and fly ash. The fly ash is charged continuously from the top of the heating chamber, and treated fly ash is discharged from an outlet provided in the chamber bottom.

**3. Volatilization of Organic Compounds from Fly Ash**

**3.1 Experimental Method**

In the “High Clean DX,” fly ash is detoxified by volatilizing dioxins and organic compounds from fly ash. Therefore, when studying fly ash treatment conditions, it is important to understand the volatilization behavior of these substances. The experimental apparatus used is shown in **Fig. 4**. Fly ash is filled in a reaction tube (glass tube; inner diameter: 30 mm, length: 400 mm), then heated at a rate of 10°C/min with an electric furnace while passing air at a specified flow rate as a volatilization acceleration gas. The gas containing the organic compounds volatilized from the fly ash is led to a gas
chromatograph (Shimadzu Corp., GC-14B) equipped with a flame ionization detector (FID) with high sensitivity for organic compounds. Normally, gas chromatographs are used to analyze gas of a specified volume discontinuously with an attached column, but in order to study the volatilization behavior of organic compounds, in this work, the column was removed and the device was utilized as a continuous analyzer for organic compounds.

3.2 Volatilization Behavior of Organic Compounds from Fly Ash

An FID signal curve, which shows the volatilization behavior of fly ash A at elevated temperature, is shown in Fig. 5. Volatilization of organic compounds began at approximately 100°C, and peaks were observed at around 250°C and 400°C. Under continuous heating at 400°C, the intensity of the FID signal, which indicates volatilization of organic compounds, gradually decreased to the 0 level.

In an experiment in which fly ash A was heated to a higher temperature than 400°C, FID signal peaks were not observed in the temperature region exceeding 400°C. Therefore, it can be understood that a temperature condition of 400°C or higher is adequate for volatilization of the organic compounds contained in fly ash.

Table 1: Boiling point of dioxin(s)

<table>
<thead>
<tr>
<th>Dioxin</th>
<th>Boiling point (°C)</th>
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<tbody>
<tr>
<td>2,3,7,8-TeCDD</td>
<td>447</td>
</tr>
<tr>
<td>1,2,3,7,8-PeCDD</td>
<td>464</td>
</tr>
<tr>
<td>1,2,3,4,7,8-HxCDD</td>
<td>487</td>
</tr>
<tr>
<td>1,2,3,6,7,8-HxCDD</td>
<td>487</td>
</tr>
<tr>
<td>1,2,3,4,6,7,8-HpCDD</td>
<td>507</td>
</tr>
<tr>
<td>OCDD</td>
<td>510</td>
</tr>
<tr>
<td>2,3,7,8-TeCDF</td>
<td>438</td>
</tr>
<tr>
<td>1,2,3,7,8-PeCDF</td>
<td>465</td>
</tr>
<tr>
<td>1,2,3,4,7,8-HxCDF</td>
<td>488</td>
</tr>
<tr>
<td>1,2,3,4,7,8-HxCDF</td>
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<tr>
<td>1,2,3,4,6,7,8-HpCDF</td>
<td>507</td>
</tr>
<tr>
<td>OCDF</td>
<td>537</td>
</tr>
</tbody>
</table>

The boiling points of representative isomers of dioxins are shown in Table 1. Dioxins have boiling points in the range of 400–500°C, and the vapor pressure of the order of 10-10²Pa at 250°C(8). It can be expected that only an extremely small percentage of the dioxins will be volatilized and move to the gas phase at 250°C. This physical character indicates that volatilization of dioxins occurs at the peak observed under heating at 400°C.

4. Simplified Dioxins Analytical Technology by Volatilization Behavior Measurement

A schematic view of the “High Clean DX” pilot plant (installed at JFE Engineering’s Tsurumi Works; maximum fly ash treatment capacity: 100 kg/h) is shown in Fig. 3. In the pilot plant test, three types of MSW incineration fly ash (A, B, C) were treated at 400°C or higher, and the treated fly ash was sampled at the bottom outlet of the heating chamber.

The volatilization behavior of organic compounds from detoxified fly ash which had been treated by the pilot plant was measured in the same manner as in section 3.2.

Figure 6 shows the volatilization behavior of the organic compounds from fly ash A treated by the pilot plant. In comparison with the curve for the untreated fly ash in Fig. 5, the temperatures at which peaks were detected were substantially the same as with the untreated fly ash, but the intensity of the FID signals was far lower. This result indicates that the content of organic compounds including dioxins had been greatly reduced by the treatment.

As discussed in section 3.2, volatilization of dioxins mainly occurs in the temperature region of 400°C and higher. The authors assumed the time after achieving a temperature of 400°C in the fly ash (Fig. 6) until the FID signal intensity decreases to the 0 level as the FID
convergent time, and examined the relationship between the FID convergent time and the dioxins concentration analyzed by the official method (Fig. 7). From Fig. 7, it was shown that a correlation exists between the FID convergent time and the dioxins concentration. Based on these results, it is possible to estimate the dioxin concentration by measuring the FID convergent time of fly ash. Because the FID convergent time can be measured in several hours, a simplified evaluation of the concentration of dioxins is possible in an extremely short time.

The correlation between the FID convergent time and the dioxins concentration depends on the type of fly ash at each incinerator. Therefore, in order to estimate the dioxins concentration from the FID convergent time, it is necessary to measure the FID convergent time and the dioxins concentration by the official method for several samples in advance.

4. Conclusions

Focusing on volatilization behavior, which is the principle of dioxins removal in the “High Clean DX,” a simplified technology for analyzing the concentration of dioxins in fly ash using a general-purpose gas chromatograph was established. While there are limitations on quantitative accuracy, it is possible to shorten the dioxins analysis time, which requires from several weeks to the 1 month with the official method, to several hours with this new method.

This analytical technology is based on the simple volatilization behavior of organic compounds and therefore can also be applied to other substances such as contaminated soil and other organic compounds, including PCB, PCN, etc., by determining the relationship between the FID convergent time and the concentration of the object.

References