

## EFFECT OF DE NOVO DIOXIN SYNTHESIS FROM BOILER DUST ON DIOXINS EMISSION FROM IRREGULAR OPERATION OF MSW INCINERATOR

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### Abstract

The mechanism of dioxins formation at startup of a continuously operated MSW incinerator has been explored. The findings suggest that the dioxins increase between outlets of the furnace and the boiler is caused by the de novo synthesis at the dust adhered to the boiler water tubes, and is shifted to gaseous phase. We have also discovered that although dioxins concentration of the superheater dust is much lower than that of the economizer dust before startup, most of the syntheses take place at the superheater dust due to the high operating temperature of the latter. It has been observed that the synthesis rate rises rapidly between 250°C and 300°C, while no change occurs between 300°C and 350°C. For preventing dioxins formation at startup, it appears to be effective to remove dust adhered to the boiler water tubes beforehand.

### Introduction

The dioxins emission during startup and shutdown has been an issue with incinerators of batch operation or semi-continuous operation.<sup>1</sup>

With continuously operated incinerators, various reduction measures have reduced the dioxins emission under steady operations to a very low level, but they still can not avoid several yearly startups and shutdowns for maintenance works etc. The length of such irregular operations is very small compared with the total hours of steady operation, but it has been reported that dioxins emissions higher than those of steady operation do occur much as they do with the intermittent-operation furnaces.<sup>2,3</sup> It is known that the final dioxins concentration in the exhaust gas can be controlled to remain as low as that of the steady operation by achieving optimum operating conditions of the burners and the exhaust gas treatment facilities. However, dioxin formation under irregular operations, particularly at startup, has not been studied closely.

With this background, we focused on the de novo synthesis from the boiler dust, and recreated the startup conditions on the laboratory level to see if it can explain the phenomena observed at the working facilities.

### Boiler dust reheating test

By studying a working furnace where large amount of dioxins are formed at startups, we have presumed that syntheses and evaporation of the dioxins occur from the dust adhered to the furnace walls and boiler water tubes. Boiler dust reheating tests have been conducted to define the mechanism as described below.

#### 1. Test samples

Dust adhered to the superheater and the economizer has been collected before startup to use as the sample for the reheating tests.

The principal ingredients of the sample are listed in Table 1.

The copper concentrations are roughly the same, whereas unburned carbon, chlorine and dioxins are higher with the dust from the economizer.

Table 1 unburned carbon, Cl, Cu and dioxins concentrations in the samples

|                         | superheater<br>dust | economizer<br>dust |
|-------------------------|---------------------|--------------------|
| unburned carbon (mg/kg) | 220                 | 1030               |
| Cl (mg/kg)              | 12700               | 97900              |
| Cu (mg/kg)              | 1020                | 1030               |
| dioxins (ng-TEQ/g)      | 0.15                | 3.8                |

## 2. Test methods

The heating temperatures were determined to match those of the time period when the dioxins formation occurs during the actual startup. The superheater dust was heated to three stages, 250°C, 300°C and 350°C, while the economizer dust was subjected to 150 °C, 200°C and 250°C, with the same samples heated successively in rising order. The carrier-gas conditions copied those of the operating data of the working furnace. The O<sub>2</sub> concentration was 15%, and the flow rates during heating for the superheater dust was 0.7m/s, while that for the economizer dust was 1.5m/s.

The outline of the test equipment and the gas-collection unit is shown in Figure 1 while Table 2 and Table 3 list the test conditions. Due to the large gas flow of the test, two electric furnaces were connected in tandem, with the first furnace heating the gas to its capacity and feed the heated gas to the second unit to attain the required heating temperature.

A sample bed, approximately 5.0cm long, made with alumina and loaded with the sample, was inserted in a quartz tube of 1.5cm I.D. that was placed in the second furnace. After all the connections were made, the carrier gas (O<sub>2</sub> 15%–N<sub>2</sub> balance) was supplied, and the leak tests were conducted before the furnaces and other heat-shielding devices were turned on.

As the gas volume in this test was too large to capture the entire flow, we tapped just 4.0 L/min from the second furnace, and used it as the captured sample. The toluene traps caught gas at each temperature stage, and the gas supply was interrupted while the traps were retrieved manually, and the dioxins concentrations were measured. The residue was taken out from the quartz tube roughly 30 minutes of natural cooling after the series of heating were completed, and used as the residue sample. Trapping fluid and the residue samples were pretreated and analyzed according to JIS K 0311 ruling.

Table 2 Heating conditions

| sample           | heating temperature        | heating time                            |
|------------------|----------------------------|---|
| superheater dust | 250 (ambient temp. ~ 250 ) | 145min(heating up 25min+120min at 250 ) |
|                  | 300 (250 ~ 300 )           | 125min(heating up 5min+120min at 300 )  |
|                  | 350 (250 ~ 300 )           | 125min(heating up 5min+120min at 350 )  |
| residue          | ambient temp. ~ 350        | 395min                                  |
| economizer dust  | 150 (ambient temp. ~ 150 ) | 135min(heating up 15min+120min at 150 ) |
|                  | 200 (150 ~ 200 )           | 125min(heating up 5min+120min at 200 )  |
|                  | 250 (200 ~ 250 )           | 125min(heating up 5min+120min at 250 )  |
| residue          | ambient temp. ~ 250        | 385min                                  |

Table 3 Other conditions

| sample           | sample quantity | flow rate             | heating up rate | O <sub>2</sub> concentration |
|------------------|-----------------|-----------------------|-----------------|------------------------------|
| superheater dust | 2.0g            | 8.0L/min<br>(0.7m/s)  | 10 /min         | 15%                          |
| economizer dust  | 1.5g            | 16.0L/min<br>(1.5m/s) |                 |                              |

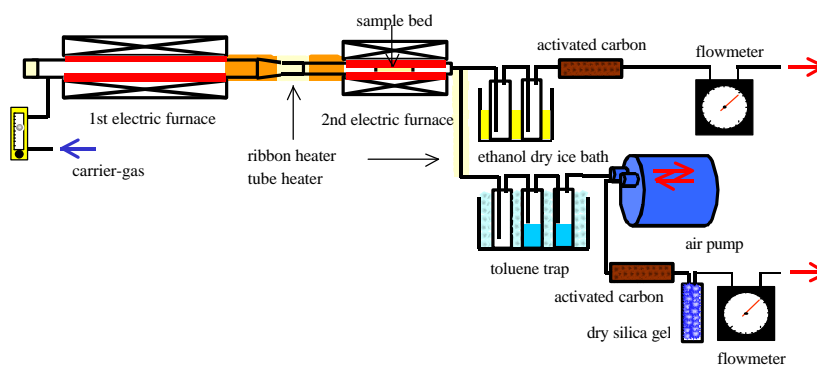


Figure 1 Outline of the test equipment

**Results and Discussion**

The measured dioxins formations by heating the superheater dust and the economizer dust at the laboratory level are shown in Figure 2 and Figure 3, respectively. Here, “untreated dust” means dust before reheating, “exhaust gas xxx°C” stands for the amount moved to gas phase per 1g of dust when heated to xxx°C, “exhaust gas total” represents the total amount that moved to gas phase per 1g of dust after going through the three stages of the heating temperatures, and “residue” means the ash remnant of the sample after the reheating tests are completed. Figure 2 shows that the superheater dust generated little dioxins when heated to 250°C, but nearly 3-times as much dioxins as that of the untreated dust shifted to the exhaust gas each time the temperature reached 300°C and 350°C. After the three heating stages, the dioxins concentration grew to almost 8 times as high as that of the untreated dust, and roughly 80% of this shifted to the exhaust gas. With the economizer dust, the dioxins concentration did not increase due to its lower heating temperatures. Only several percentage points moved to the gas. Also we observed some decrease in the dioxins concentration before and after the reheating, suggesting that some dioxin disintegration took place during the process.

From the above results, we have concluded that between 150°C~350°C, the higher the temperature, the more dioxins are formed and moved to the exhaust gas, most prominently in the 250°C~300° range. Since there is no discernible change between 300°C and 350°C, it is presumed that the maximum synthesis takes place in this temperature range. As mentioned earlier, superheater dust generates more dioxins than the economizer dust, even though the former has lower concentrations of unburned carbon, chlorine and dioxins in its untreated form than the latter. Figure 4 illustrates the congener distribution of dioxins that were formed and evaporated during the dust reheating test, together with that of the gaseous dioxins formed between the furnace and the boiler outlets at startup of a continuously operated furnace. Congener distributions of dioxins synthesized at a working furnace and those of the dioxins from heating dusts from the superheater and the economizer are quite similar in many areas even though differences can be seen with some congeners. This leads us to assume that dioxins formation at the boiler is caused by its synthesis at the dust adhered to the boiler water tubes and subsequent shift to gaseous

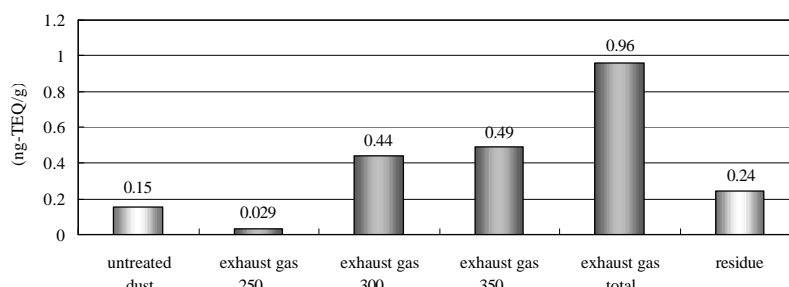


Figure 2 Dioxins formations by heating the superheater dust

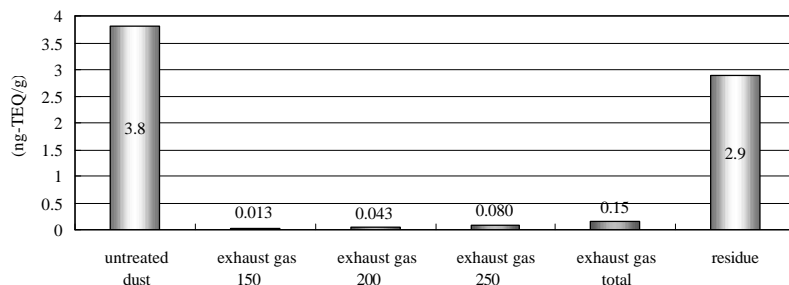


Figure 3 Dioxins formations by heating the economizer dust

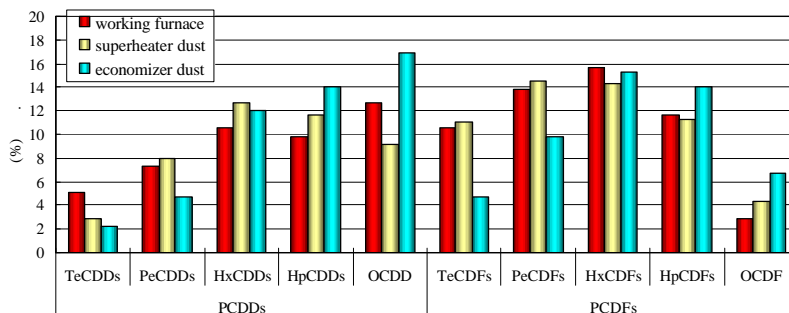


Figure 4 Congener distribution of dioxins

phase.

Table 4 and 5 show the comparison between the dioxins increase in the exhaust gas from a working furnace and the estimated increase based on the reheating test results. Here, calculations were made assuming the thickness of the dust adhered to the superheater and economizer tubes to be 3mm and the specific gravity of the dust as  $0.3\text{t/m}^3$ . The results coincide; again suggesting that the dioxins increase in the boiler is caused by its synthesis from the dust adhered to the boiler water tubes, and its shift to the gaseous phase.

Table 4 Dioxins increase in the exhaust gas at a working furnace

|                  | time (min) | dioxins ( $\mu\text{g-TEQ}$ ) |
|------------------|------------|-------------------------------|
| furnace outlet   | 412        | 1900                          |
| boiler outlet    |            | 3200                          |
| dioxins increase | -          | 1300                          |

Table 5 Estimated dioxins increase based on the test results

|                  | dioxins formations ( $\text{ng-TEQ/g}$ ) | dust quantity (ton) | estimated dioxins increase ( $\mu\text{g-TEQ}$ ) |
|------------------|--|---------------------|--|
| superheater dust | 0.96                                     | 1.25                | 1200   |
| economizer dust  | 0.15                                     | 0.765               | 110  |
| total            | -  | -                   | 1300   |

### Conclusions

Our recent research was intended to discern the mechanism of the dioxins formation at startup. The test result has indicated that the dioxins increase between the furnace and the boiler outlets is caused by the de novo synthesis at the dust adhered to the boiler tubes that shifts to gaseous phase. We have also discovered that most of the syntheses take place at the superheater dust due to higher temperatures even though its dioxins concentration is much lower than that of the economizer dust before startup. We have also found out that the amount of synthesis grows rapidly between  $250^\circ\text{C}$  and  $300^\circ\text{C}$ , while there is little difference between  $300^\circ\text{C}$  and  $350^\circ\text{C}$ . This strongly suggests that removing dust from the boiler tubes is very effective in reducing dioxins formation at startup.

### References

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