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## Dioxins/Furans Formation and Removal Characteristics in MSW Incinerator Dust Collection Processes

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## Introduction

Since research results showed that fly ash has some catalytic effect to generate dioxins, there have been several papers to try to reveal the relations between catalytic components in fly ash and dioxins levels. There are, however, some limitations by testing artificial exhaust gas or by changing the components level artificially, which made it difficult to generalize the effects and in turn, to get insights to how it works at actual systems<sup>1,2)</sup>.

There are also several reports that show higher dioxins levels per unit mass for smaller dust size in bottom ash and fly ash<sup>3</sup>. In incineration process, particulate size is determined through complex coagulation and condensation. Wey et al.<sup>4</sup>) showed that carbon content decreases as particle size decreases. On the other hand, heavy metals and PAHs contents show different trends. Forestier and Libourel<sup>5</sup> investigated particle size, heavy metal content, chemical compositions of electrostatic precipitator ashes, wet filter cake in scrubbers, semi-dry absorber(SDA) residues in MSW incinerators. Active temperature zone for dioxins formation exists in the dust collection process, but these are not consistent in terms of temperature and residence time for different incineration processes. Residence time generally means that of gas flow, however, residence time of collected dust is generally neglected.

In this study, fly ashes from an electrostatic precipitator(EP) and a bag filter(BF) of incineration process were sampled to investigate composition characteristics to affect dioxins formation for different particle size in actually operating process. The effects of residence time of dust in ducts and differential bag pressure were also analyzed to observe dioxin level variations for this operating parameter in SDA/BF process of 2,000Nm<sup>3</sup>/hr gas volume branched from an actual plant.

### **Experimental Procedure**

### 1. Analysis of Dust Compositions and Dioxins

Fly ash from EP and BF was meshed and analyzed for components with positive potential to affect dioxin formation and isomers of dioxins. The average temperature of EP inlet was 200°C and that of BF was 140°C. Samples were taken from these dust removal equipment of real plants. The samples were dried up in an oven of 110°C for 1 day and classified by a shaker for 40 minutes.

XRF(ARL940) and ICP (ICPS-1000) were utilized to analyze the Catalytic Components following EPA3505 method and dioxins were analyzed Korean Air Pollution Standard Test Method using high resolution GC/MS(resolution > 10,000).

#### 2. Dust Residence Time Change Tests

Experimental apparatus is shown in Figure 1 to test the effects of residence time of dust material in exhaust duct and it is some modified form of dioxins sampling systemand dust emission test equipment. Isokinetic sampling was performed and dust residence time was varied. The average duct temperature was 256°C and oxygen concentration was 12.6%.

### 3. Differential Bag Pressure Change Test

Pilot plant tested is composed of a several units to treat 2,000m<sup>3</sup>/hr gas out of 40,000m<sup>3</sup>/hr

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exhaust gas from an incinerator of capacity of 200 tons/day. All the fly ash was cleaned from the bag and hopper was also cleaned, then samples were taken at end of BF after bag pressure became set point. After sampling, the hopper door was opened and fly ash was taken. The average inlet temperature of the SDA was 250°C, the inlet of BF, 180°C and outlet of BF, 120°C. Oxygen concentration was 12.9% and the average activated carbon injection rate was 100mg/Nm<sup>3</sup>.



Figure 1. System Layout for Dioxins Formation Experiments

### **Results and discussion**

1. Composition of Catalytic Components and Their Relations with Dioxins Emissions

Results of compositions of catalytic components and dioxins analysis for different fly ash sizes are summarized in Table 1 for the samples of bag filter processes. As the diameter of fly ash deceases, the contents of SO<sub>3</sub>, Cl, ZnO, Zn increase and those of Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub> decrease, while the content levels of NiO, CuO, Al, Fe, Cu, Zn show scattered patterns. The content levels of dioxins show increasing trends to particulates both smaller and larger than 62-45 $\mu$ m.

When standard deviations are compared for relative concentrations of each particle size range, that of dioxins shows 7.88, which is relatively high value, indicating that content level differences are larger than those of other metal contents.

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	355 Up	355-250	250-150	150-90	90-62	62-45	45-26	26 Down	Mean	SD*
Al <sub>2</sub> O <sub>2</sub>	2.39	2.49	2.20	2.04	1.36	1.31	1.14	0.92	1.73	4.44
SÕ <sub>3</sub>	4.48	5.70	5.53	5.25	6.29	6.09	6.68	7.05	5.88	1.75
CI	17.64	21.03	21.12	21.66	24.63	24.76	26.30	26.99	23.02	1.72
Fe <sub>2</sub> O <sub>3</sub>	1.23	1.12	1.28	1.17	0.95	0.79	0.67	0.65	0.98	3.23
NiO	0.008	0.005	0.009	0.010	0.0073	0.008	0.006	0.009	0.008	2.68
CuO	0.078	0.091	0.088	0.071	0.100	0.092	0.110	0.120	0.094	2.14
ZnO	0.36	0.43	0.40	0.35	0.44	0.41	0.47	0.51	0.42	1.59
Al	19.58	19.36	22.00	19.56	12.01	8.75	6.69	9.88	14.73	5.10
Cu	0.24	0.38	0.33	0.30	0.30	0.37	0.46	0.53	0.36	3.25
Fe	6.78	4.77	5.52	5.27	4.18	3.30	2.97	4.98	4.72	3.27
Zn	0.80	1.09	1.14	1.03	0.99	1.16	1.29	1.51	1.13	2.32
PCDD/Fs	13.46	11.81	10.63	4.81	3.46	1.77	14.16	20.60	10.09	7.88

Table 1 Relative Ratio of Chemical Composition of BF Fly Ash (Unit : Al. Cu. Fe. Zn = mg/g. PCDD/Fs = ng/g others = %)

\* SD : Standard Deviation for Relative Ratio of Each Component

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When the results of contents of metals and dioxins in electrostatic precipitator (EP) are analyzed in terms of dust size, the content levels show similar trend with the case of BF. Dioxins contents show increasing trends to particulates both smaller and larger than 90- $62\mu$ m. Standard deviation of dioxins levels shows highest value like the case of BF fly ash.

Experimental results for fly ash show that dioxin content increases rapidly as dust size decreases like previous data for bottom ash, fly ash and stack dust<sup>4</sup>), while there is an increasing trend in relatively large particle size, indicating that there may be some formation mechanism in the large particle size range. More research is considered necessary for the possibility of different prevailing mechanism for large particles. Catalytic components distribution results show various patterns as other research results explained<sup>5,6</sup>)

The content levels of catalytic components were tried to relate with those of dioxins, however, there is no unique component showing similar distributions in actual fly ash and deviations of dioxins are The content levels of catalytic components were tried to relate with those of dioxins, however, there is no unique component showing similar distributions in actual fly ash and deviations of dioxins are relatively large. From the fact that catalytic component levels are relatively small over all the particle size range, these components may be considered to have similar effects of dioxin formation for different dust size in dust collection process.

### 2. Dioxins formation test results for dust residence time

2.1 The effects of dust residence time in the duct

The test results are summarized in table 2 for the dioxin levels in collected fly ash and gas passing through filters when their residence time changed.

Sampling Time (min)	Dust (ng/Nm <sup>3</sup> )	Gas (ng/Nm <sup>3</sup> )	Dust : Gas (% : %)						
5	32	192	14:86						
20	52	-	-						
40	293	588	33:67						

Table 2. Concentration of PCDD/Fs for different Sampling Time

Remark] - : no measurement

For the fly ash, dioxins content increased from 32 to 293ng/Nm<sup>3</sup> when sampling time increased from 5 to 40 minutes while dioxins concentration in the gas phase increased from 192 to 588ng/Nm<sup>3</sup> when the sampling time increased similarly, indicating that the increasing rate in the solid phase is almost 3 times higher than that of gas phase. Regardless of residence time, dioxins levels in the gas phase show high values when those in the solid phase show high values.

Even though most of dust is removed in the actual EP when operated with no active carbon injection at temperature zone above 200°C, the dioxin levels are usually high. In this test result, dust in the flue gas is removed by the filter paper, however, the dioxins levels show increasing trend. From these results, one can get a possibility of dioxin generation resulting from heterogeneous phase reaction with accumulated dust.

#### 2.2 The effects of bag pressure difference

Dioxins test results are shown in Figure 2 for fly ash samples and dust at bag filter hopper when bag filter differential pressure changes at the SDA/BF unit of pilot plant. In the case of fly ash, dioxins content level increases as the differential pressure increases up to 150mmH<sub>2</sub>O with slight decrease at 200mmH<sub>2</sub>O. The levels of dioxins in the gas phase

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show decreasing trend with the increase of bag pressure except  $50mmH_2O$  case where the levels of both gas and solid phases show relatively low values.



Figure 2. Concentration of PCDD/Fs with Bag Differential Pressure change

The large bag pressure means that the residence time of fly ash at the bag is long. The dioxins levels of fly ash show generally higher values for longer residence time, while those of gas tend to show lower values. The temperature range of the bag filter is around 180, which is out of dioxins regeneration temperature zone. In this process, activated carbon is injected. From these conditions, it can be said that there is mass transfer through adsorption and desorption in the SDA/BF process, and catalytic reactions partly.

In spite of no straightforward tendency, the dust residence time itself can be an important factor in the SDA/BF process because of significant dioxins level changes in both solid and gas phases.

#### Conclusions

Compositions of catalytic components and dioxins are analyzed for classified sizes of particles of incinerator fly ashes of electrostatic precipitators and bag filters to investigate emissions characteristics and their relationship. The content levels of dioxins show higher standard deviation or wider distribution than catalytic components and its patterns with particle size are different from that of catalytic components, indicating that it is hard to find some catalytic component to influence the levels of dioxins content in actual processes. On the other hand, various isomer distribution of dioxins show consistent pattern for different particle sizes.

As the influencing factors including waste characteristics, incinerator operating conditions are similar for different particle size, other factor like residence time may be a significant one because they can be different in the process of combustion incineration specially particle collection processes. As the residence time in the duct increases, dioxins levels in both gas and solid phases increase with higher rate in the dust. More intensive research and accumulated data are needed to reveal these effects by the dust behavior in the effluent stream.

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