

## Adsorption Characteristics of Dioxins and Hg in MSWI Flue Gas on Activated Coke

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### 1. Introduction

In Japan, a guideline for the emission of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) was issued on the incineration of municipal solid waste<sup>1</sup>). Under the guideline, PCDDs/PCDFs in Municipal Solid Waste Incinerator (MSWI) flue gas is expected to be reduced to less than 0.5 ng-TEQ/Nm<sup>3</sup>.

To reduce PCDDs/PCDFs in MSWI flue gas, combustion control of incinerator, low temperature operation of a bag house with/without activated carbon injection, catalytic destruction, and activated coke/carbon bed adsorption etc., have been demonstrated<sup>2,3</sup>). Particularly, activated coke/carbon bed techniques are of much concern due to not only removal efficiency of dioxins but also adsorption capability of HCl, SO<sub>2</sub>, and heavy metals such as Hg<sup>4</sup>).

Since 1991, NKK has tested a moving bed adsorber (MBA) with activated coke in a pilot scale plant and verified its high efficiency of PCDDs/PCDFs and Hg removal<sup>5</sup>). With activated coke, it was confirmed that PCDDs/PCDFs concentration in MSWI flue gas could be easily reduced to less than 0.1 ng-TEQ/Nm<sup>3</sup> even at gas space velocity of 1000 h<sup>-1</sup>. In contrast to many studies on removal of PCDDs/PCDFs in MSWI flue gas with activated coke/carbon, only few studies reported change of adsorbent properties<sup>6</sup>).

Thus, we discussed adsorption characteristics of dioxins and Hg from change of coke properties in MBA for about one month.

### 2. Experimental

Flue gas at outlet of an electrostatic precipitator in a MSW incinerator was used as tested feed gas. As can be seen in Fig.1, MBA equipped an upper hopper on a coke bed, a gas distributor, a coke withdrawal equipment and a bottom hopper under the coke bed. The coke bed's cross sectional area was 3.2 m<sup>2</sup> and its height was 0.5/1.5 m. Fresh coke was charged in the upper hopper and descended gravitationally. Contaminated coke with pollutants was discharged to the bottom hopper through the coke withdrawal equipment. Flue gas was cooled to 403/423 K in a gas cooler and fed to the gas distributor. The gas contacted with the coke in counter current flow. Activated coke with a specific surface area about 150 m<sup>2</sup>/g was used as an adsorbent and the coke bed was moved downward 5 mm at one time in a day. Properties of the coke were listed in Table 1.

In this MBA operation, we controlled operating conditions, such as gas feed rate, feed gas temperature, and bed height, as shown in Table 2. After the operation, activated cokes left in MBA were sampled to be analyzed.

According to the standard Japanese guideline methods, PCDDs/PCDFs concentration in coke was determined by using a KRATOS CONCEPT-1S GC/MS with SP 2331 column (length : 60 m, I.D. : 0.32 mm) and DB-5 column (length : 60 m, I.D. : 0.25 mm). To evaluate Hg concentration in coke, coke was pulverized and extracted with acid. Then, the extract was analyzed in the method of JIS K 0222. Volatile matter in coke was analyzed according to JIS M 8812. Specific surface area and pore size distribution of coke were measured with Yuasa Ionics's Autosorb 1 in the BET method.

**Table 1** Properties of form-activated coke

diameter (mm)	PCDDs/PCDFs (ng/g)	Hg (mg/g)	VM* (%)	S** (m <sup>2</sup> /g)
5 (cylindrical)	0.00	Tr	5.8	152

\* volatile matter \*\* specific surface area

**Table 2** Operating conditions and concentration of PCDDs/PCDFs and Hg in feed gas and treated gas

Run No.	1	2	3	4	5	6	7
feed gas temp. (K)	423	423	423	423	423	403	423
feed gas flowrate (Nm <sup>3</sup> /h)	1500	1500	2000	2500	3000	2500	2500
bed height (m)	0.5	1.5	1.5	1.5	1.5	1.5	1.5
<hr/>							
<b>feed gas</b>							
PCDDs/PCDFs (ng/Nm <sup>3</sup> )	*	55	100	67	54	74	*
Hg (mg/Nm <sup>3</sup> )	*	0.059	0.055	0.036	0.033	0.018	*
<b>treated gas</b>							
PCDDs/PCDFs (ng/Nm <sup>3</sup> )	*	9.0	1.2	2.9	3.1	0.65	*
Hg (mg/Nm <sup>3</sup> )	*	0.015	0.026	0.010	0.010	0.003	*

Total operation time = 809 hours

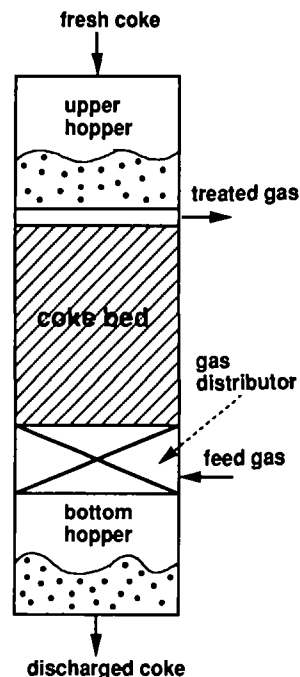
### 3. Results and Discussion

#### (a) Removal of pollutants in MSW flue gas with MBA

Table 2 provides gas compositions at inlet and outlet of MBA. In this table, average concentrations of PCDDs/PCDFs and Hg in feed gas were 70 ng/Nm<sup>3</sup> and 0.040 mg/Nm<sup>3</sup> respectively in Run 2 through 6. On the other hand, average concentrations of PCDDs/PCDFs and Hg in treated gas were 3.4 ng/Nm<sup>3</sup> (0.06 ng-TEQ/Nm<sup>3</sup>) and 0.01 mg/Nm<sup>3</sup>. Removal efficiencies on average were 95 % for PCDDs/PCDFs, 71 % for Hg, 63 % for HCl. The concentration of SOx in treated flue gas was less than the detectable level.

#### (b) Properties of the activated coke in MBA

Fig. 2 shows concentrations of PCDDs/PCDFs, Hg, specific surface area and volatile matter in activated coke. Fig. 3 provides pore size distribution of the activated



**Fig.1** Moving bed adsorber (MBA)

coke. Fig.4 presents PCDDs/PCDFs congener pattern in the feed gas and the discharged activated coke.

Although concentrations of PCDDs/PCDFs and Hg in the discharged coke were very high (198 ng/g, 0.48 mg/g respectively), those in the coke at the height of 30 cm from the bottom of the coke bed were low (10 ng/g, 0.026 mg/g respectively). This indicated PCDDs/PCDFs and Hg were mostly removed in the gas distributor and the lower part of the coke bed. As coke moved downward, small pores in coke under 20 Å disappeared gradually and specific surface area of coke decreased to 14 m<sup>2</sup>/g, which is about ten times smaller than that of fresh coke, as shown in Figs. 2 & 4. It was suggested specific surface area could be used as indicator for deactivation of activated coke as to dioxins removal.

Despite large differences of concentrations between PCDDs/PCDFs and Hg in the feed gas, the change of PCDDs/PCDFs concentrations in the coke showed same profile as that of Hg concentration, which was consistent with results of Eicken et al.<sup>6)</sup>. Eicken used lignite coke with specific surface area of 300 m<sup>2</sup>/g as an adsorbent. The specific surface area was twice of that in our study.

Boiling point increased roughly from 700 K to 780 K for PCDDs and from 710 K to 810 K for PCDFs with the increase of the number of substituted Cl atoms from 4 to 8<sup>7)</sup>. Fig. 3 shows same PCDDs/PCDFs congener patterns between in the feed gas and the discharged coke. This was mainly due to large difference between adsorption temperature and boiling points of PCDDs/PCDFs.

Concentrations of volatile matter in coke inside the bed were one to two times higher than those in the fresh coke. This was due to the adsorption of Hg, HCl, SO<sub>x</sub>, chlorobenzen and chlorophenol, etc., contained in the feed gas.

#### 4. Conclusion

Within the experimental conditions, following conclusions were obtained.

- 1) PCDDs/PCDFs and Hg in MSWI flue gas were mostly removed in the gas distributor and the lower part of the activated coke bed.
- 2) Coke properties, such as concentrations of PCDDs/PCDFs and Hg, volatile matter, specific surface area, and pore size distribution, greatly changed in the moving bed adsorber.
- 3) It was demonstrated that specific surface area could be used as indicator for deactivation of coke as to dioxins removal.

#### 5. References

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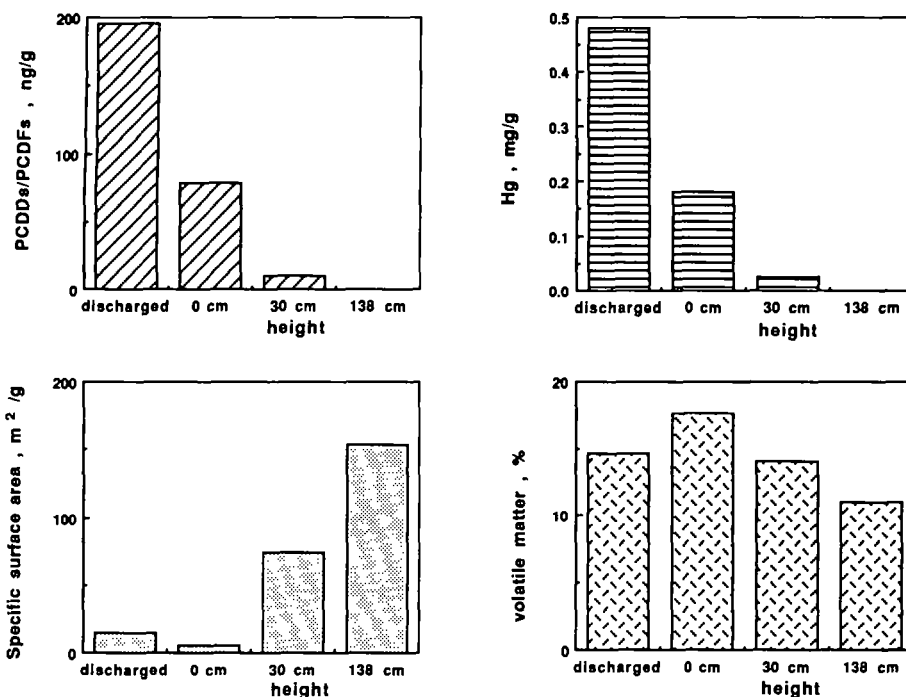


Fig.2 Change of dioxins, Hg, Specific surface area and volatile matter in activated coke

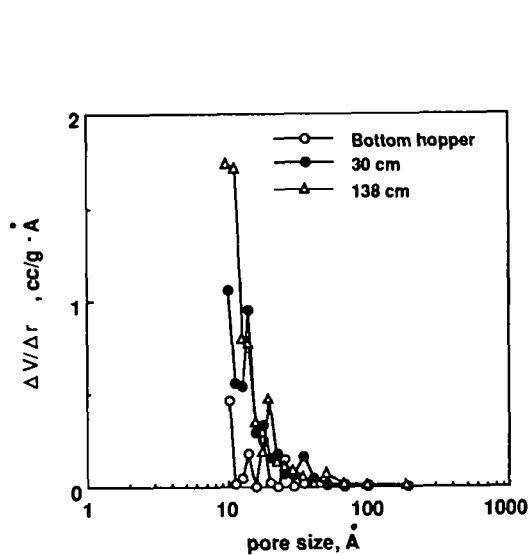


Fig.3 Change of pore size distribution of activated coke in coke bed

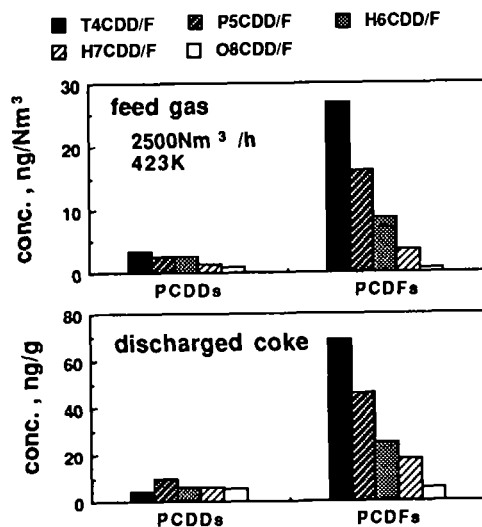


Fig.4 PCDDs/PCDFs congener pattern in feed gas and discharged coke