Catalytic Decomposition of Dioxins from MSW Incinerator Flue Gas

Ide, Y., Kashiwabara, K., Okada, S., Mori, T. & Hara, M.

Kawasaki Heavy Industries, Ltd. 1-1-3, Higashikawasaki-cho, Chuo-ku, Kobe, Japan

1. Introduction

Hitherto, in the cases where electrostatic precipitators were used as the dust collectors, the catalytic denitration units had often been operated at relatively high temperature regions around 300°C on account of such restrictions as the operational conditions of the electrostatic precipitators and the temperature dependence of the catalytic activity. To solve the problem of resynthesis of dioxins when the electrostatic precipitators are operated at such high temperatures, in the recent trend flue gas temperature is lowered to allow the use of bag filters instead. As a result, improvement in the activity of denitrifying catalyst at the low-temperature regions and development of the multi-functional catalyst are now in demand.

Aiming at providing the dioxins removal performance of the denitrifying catalyst, a field test was conducted in our research using flue gas from the Municipal Solid Waste (MSW) Incinerator, with the temperatures, dioxins concentrations and the amounts of the catalyst added being used as the parameters.

As the test results, dioxins decomposition performance of the low-temperature denitrifying catalyst has been confirmed. Also, data on the catalytic decomposition of chlorobenzenes, chlorophenols which are regarded as the precursors for dioxins, and coplanar-PCBs. From these test results, the basic data have been obtained on the catalytic reactor taking its de-dioxins performance into consideration.

2. Test Apparatus and Analytical Method

The authors have proved on a bench-scale type test apparatus of such indicator gas decomposition performance as monochlorobenzenes, orthochlorophenols, etc. with catalyst.¹⁰ As the next step, a field test was conducted with the test apparatus installed on the MSW incineration plant at work to determine the dioxins decomposition performance of the catalyst when applied to flue gas from the incinerator.

1) Test apparatus

Flow sheet of the field test apparatus used is shown in Fig. 1. The test apparatus is composed of the catalytic reactor, electric heater, induced draft fan and the

FMCO

flow/temperature controllers. The catalytic reactor is packed in series with four layers of the catalyst including of titanium-vanadium-tungsten (Ti-V-W) oxides, manufactured for use at low temperature regions.

Flue gas is sucked up with the induced draft fan to be returned to the existing denitration unit. Temperature of gas in the catalytic reactor is controlled at the constant level with the electric heater.

Analytical method

Measurement of dioxins is done first by collecting dust in a cylindrically formed filter paper and then letting flue gas absorbed at the downstream side with water, resin and the solvent. In the normal analysis, all the dioxins are extracted in a batch and then concentrated for measurement on GC/MS. In our test, separate samples of dioxins were taken, the one sampled before they have reached the cylindrically formed filter paper at the dust-collecting part, and the other collected in the piping at the downstream and in the dust-collecting part. In this paper, the former is called the particulate dioxins and the latter is called the gaseous, which were analyzed separately.



Fig.1 Flow Sheet of the Field Test Apparatus

3. Test Results

Catalytic decomposition of dioxins

The results of analysis on the dioxins decomposition are shown in Fig. 2, in which the data are arranged about the AV (Area Velocity) of the catalyst. From these test results, the following can be concluded;

- (1) The higher the AV, the lower the dioxin decomposition conversion resulted.
- (2) The higher dioxins decomposition conversion can be achieved with the catalyst temperature of 260°C than that obtained at 210°C. (The higher the catalyst temperature, the higher the dioxins decomposition conversion resulted.)

Fig. 3 shows the results of analysis made on the particulate sample and on the gaseous sample. As seen in the data shown here, the ratios of the particulate dioxins to the gaseous ones measured at the different measuring points became greater as it went to the subsequent layers of the catalyst. This shows the higher dioxins decomposition conversion achieved with the gaseous dioxins than that obtained with the particulate ones.

Figs. 4 and 5 show the concentrations of individual compositions (converted as 12 % O₂ base) determined with the total dioxin contents, as well as those measured with the particular and the gaseous dioxins contents, respectively. From Fig. 4, it is known that the particulate components contain much octa- or hepta chrorinated dioxins and furans of the



Fig.2 Test Result of Dioxin Conversion in the Catalyst



Fig.3 Dioxins Concentration at Each Catalyst Layers

higher molecular weights. In the gaseous components, on the other hand, much tetraor penta chrorinated dioxins and furans of the relatively low molecular weights existed, together with the octa- and/or hepta chrorinated dioxins and furans existed in nearly the same amounts as those observed with the particulate components. (Fig. 5)

Since the gas temperature in the test (at 210°C) was nearly equal to the melting point of the tetra chlorinated dioxins, it is so assumed that those components of lower molecular weights than those of the tetra chlorinated dioxins exist in the liquid state on the catalyst layers, while they are present in the flue gas in the mist state or adhering on other dusts. In the cylindrically formed filter paper at the dust-collecting part, where temperature is kept at about 110°C, dioxins are normally exist as solids. Since the particle sizes of the tetra chlorinated dioxins are smaller than those of the octa chlorinated dioxins, it is so assumed that the former can pass through the filter paper without being captured with it. The relatively lower boiling- and melting points of such tetra chlorinated dioxins may be also considered to contribute to it.



Fig.4 Concentration of Each Component (Particulate)



Fig.5 Concentration of Each Component (Gaseous)

2) Catalytic decomposition of chlorobenzenes and chlorophenols

Table 1 shows the concentrations of chlorobenzenes and chlorophenols and their decomposition conversions. While 90% or higher decomposition conversions were achieved with all runs with chlorophenols, what was achieved with chlorobenzenes was only the poor decomposition, which were no better than $3 \sim 30\%$.

3) Catalytic decomposition of coplanar-PCBs

Concentration of coplanar-PCBs at the catalyst inlet measured 0.02ng/Nm3, which was

equivalent to about 3% of that of dioxins measured 0.64ng/Nm³. The analysis data on coplanar-PCBs at the different catalyst layers are shown in Fig. 6. As in the case of dioxins, they were decomposed at each of those catalyst layers, with the higher decomposition conversions observed with the gaseous components.



Fig.7 Decomposition Characteristic of Dioxins.

4. Discussion

1) Dependence on dioxins decomposition

Fig. 7 shows the relation of the inverse of the area velocities (AVs, which represent the reaction times) to the corresponding dioxins decomposition conversions (the reaction rates). As it appeared in a linear relation, decomposition of dioxins with the catalyst can be explained as a first-order reaction. The results here correspond to those obtained on the bench test conducted using the indicator gases. These facts suggest that the decomposition conversions of dioxins with the catalyst are not dependent on the concentrations at the inlet.



Run No.	Temperature °C	NH3/ NOx [-]	AV [Nm³/m²/hr]	Chlorobenzenes concentration [ng/Nm ³]		Chlorophenols concentration [ng/Nm³]		Decomposition conversion [%]	
				inlet	Outlet	Inlet	Outlet	CBs	CPs
A	210	0.8	5.41	9100	8300	2500	91	8.8	96
В	260	0.4	10.8	27000	19000	11000	1100	3.4	86
С	210	0.8	5.41	12000	9200	14000	290	23.3	98
D	210	0.4	10.8	8600	8300	2200	300	29.6	90

Table 1 Decomposition conversion of chlorobenzenes and chlorophenols

2) Decomposition of dioxins contained in the dust

Assuming that the concentration of dioxins contained in the flue-gas borne dust will be equal to the dioxins concentration in the incineration ash, concentration of the particulate dioxins in the flue gas was calculated. The resultant theoretical particulate dioxins concentrations obtained from the dust concentration were nearly equal to the measurements. If it is so assumed that the dust-borne dioxins cannot be decomposed with the catalyst, then the concentration of dioxins measured at the outlet of the catalyst layers is supposed not to become lower than the concentration of the dust-borne dioxins. This makes us assume that the dust-borne dioxins could not be decomposed with the catalyst. From this, it can be said that to improve the efficiency of dioxins decomposition with the catalyst, removing the dust before it enters the catalyst layers will work effectively.

5. Conclusion

A field test was conducted by feeding flue gas from the MSW incinerator to the catalytic reactor in the field test apparatus to confirm on the following:

- It has been known that the dioxins decomposition reaction can be explained as a first-order reaction; i.e. the decomposition conversions are not dependent on the concentrations of dioxins measured at the inlet to the catalyst layers.
- The decomposition conversions of gaseous dioxins is higher than that of the particulate type dioxins.
- Dioxins contained in the dust is assumed that they have not been decomposed with the catalyst.
- While chlorophenols showed the catalytic decomposition conversion of 90% or higher, that of chlorobenzenes was considerably low measuring only 3 ~ 30%.
- As was the case of dioxins, coplanar-PCBs has been decomposed with the catalyst, with the higher decomposition conversion having been obtained with the gaseous components.

Reference

1) Okada, S., Kashiwabara, K., Mori, T. and Hara, M.: Catalytic decomposition of dioxins and NOx from MSW incinerator flue gas, JSME 4th symposium on environmental technology.