Influence of HCl on Thermal Decomposition of PCDDs/ PCDFs in Fly Ash from MSW Incinerator.

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Introduction

In Japan, "New Waste Management and Public Cleaning Law" [1] became effective in 1992. This law classifies fly ash from a municipal solid waste incinerator as strictly controlled waste which is required to prevent heavy metal compounds from being eluted when disposed. Although PCDDs/PCDFs in the fly ash are not subjects to this law, they are expected to be reduced to less than allowable limitation.

Some studies revealed that thermal treatment decomposes PCDDs/PCDFs in waste incinerator fly ash [2,3]. In these studies, thermal treatments at 573-773 K in oxygen deficient atmosphere were very effective on detoxification of the fly ash. These studies indicate waste incinerator fly ash would be treated with electric heaters in oxygen deficient atmosphere with nitrogen injection. But from the view point of energy saving, thermal treatment with high temperature flue gas which contains HCl has a great advantage compared to treatment with electric heaters. No study has reported thermal treatment of fly ash with flue gas.

Therefore, this paper focuses on influence of HCl on thermal decomposition of PCDDs/PCDFs in fly ash in various atmosphere.

Experimental

Fly ash for this study, 20g (wet basis) in each experiment, was from an electrostatic precipitator in a municipal solid waste incinerator which equipped a semi-dry type acid gas removal facility. Experimental gases were nitrogen, air and simulated flue gas (O_2 10 %, N_2 82 % ,CO_2 8%). And HCl vapor was mixed with these gases to make 500, 1000 ppm HCl concentration. H_2O concentration was 20 %.

Fly ash was put on aluminum boat in the center of a quartz tube (1000mm x 50 mm I.D.) of an electric tubular oven and kept at 573, 673 and 773 K for 2, 10 and 60 minutes with gas flow at 2L/min. PCDDs/PCDFs concentration in fly ash was analyzed according to the standard Japanese guideline methods by using a KRATOS CONCEPT-1S GC/MS with a SP-2331 column (60m x 0.32mm I.D.) and a DB-5 column (30m X 0.32 mm I.D.).

Results and Discussion

Fig.1 shows toxicity equivalence ratios (International-TEQ) in treated fly ash to untreated

fly ash. In a nitrogen atmosphere without HCl, the ratio decreased with temperature increase. No change of toxicity ratio was observed at 573K. On the other hands, the ratio decreased sharply at 773K and concentration of PCDDs/PCDFs in fly ash reduced to less than 0.001 ng-TEQ/g after more than 10 minutes treatment. In a nitrogen atmosphere containing 1000ppm

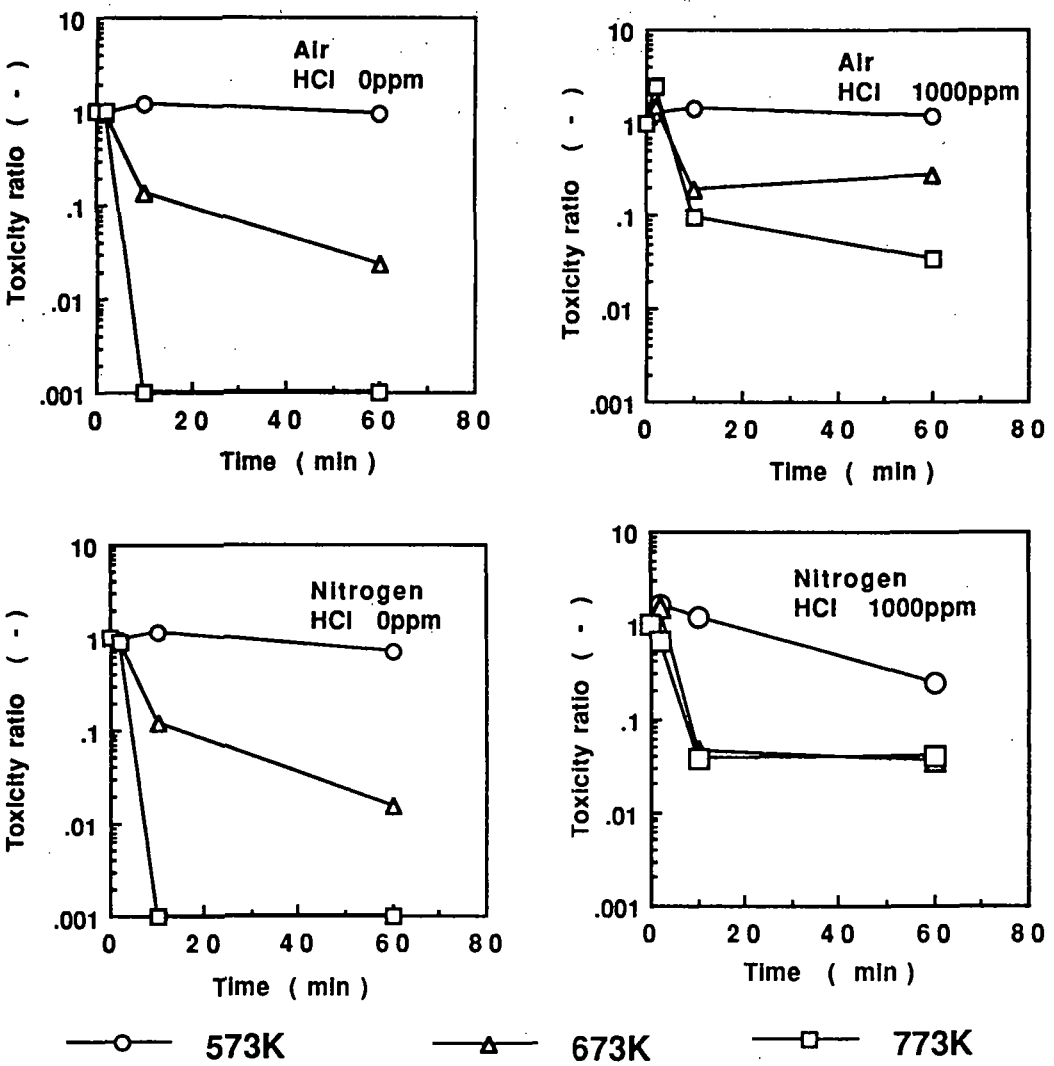

Fig.1 Change of toxicity in fly ash with time under various gas atmosphere

HCl, the ratio decreased to only 0.04 even at 773K. This result suggests that HCl inhibits complete detoxification.

In oxygen rich conditions of air atmosphere, all experiment results were very similar to those in nitrogen atmosphere. Theses results showed that thermal decomposition of PCDDs/PCDFs in fly ash would sufficiently occur in the oxygen rich condition at over 673 K regardless of HCl presence.

Fig. 2 shows the results in 10% oxygen atmosphere condition with 1000 ppm HCl. This condition represented actual combustion gas in a MSW incinerator. The results in this condition brought slight difference compared to others. At 573 K, toxicity ratios remarkably increased to 4.6 in 10 minutes treatment and then decreased to 1.9. No toxicity change was observed at 673 K. On the other hand, the ratio decreased after some retention time at 773 K to less than 0.001 in 60 minutes treatment. Concentration of PCDDs/PCDFs in the treated fly ash became 0.001 ng-TEQ/g.

Fig 3 shows the influence of HCl on fly ash toxicity change. The degree of thermal decomposition of PCDDs/PCDFs decreased with HCl concentration increase in gas.

Fig. 4 shows congener patterns of PCDDs/PCDFs in fly ash in the treatment at 773 K in simulated flue gas containing 1000 ppm HCl. Concentration of octa- and hepta-chlorides of PCDDs/PCDFs remarkably decreased with time. On the other hand, T_4CDD/F were increasing in the first 2 minutes and then decreasing. It was presumed that dechlorination reaction occurred in the heat treatment of fly ash under simulated flue gas , which was consistent with reaction mechanism obtained from studies on thermal treatment in air or nitrogen.

From all these results, combustion flue gas from a MSW incinerator seems to be useful for the thermal treatment of fly ash. In order to confirm this, we carried out thermal treatment experiment in a commercial MSW incinerator. Fly ash was fed to a boiler ash feeder installed at the bottom of boiler section. Fig. 5 showed the results. Concentration of PCDDs/PCDFs in the fly ash reduced to 0.01 ng-TEQ/g in over 30 minutes treatment.

Conclusions

The results showed difference in thermal decomposition behavior of PCDDs/PCDFs in fly ash from a MSWI in various atmosphere. In nitrogen or air without HCl, concentration of PCDDs/PCDFs decreased to less than 0.001ng-TEQ/g at 773 K in more than 10 minutes treatment. Even in simulated flue gas with 1000 ppm HCl, concentration of PCDDs/PCDFs in fly ash reduced to 0.001 ng-TEQ/g at 773 K in 60 minutes treatment. In a commercial MSWI, it was demonstrated that concentration of PCDDs/PCDFs in fly ash reduced to less than 0.01ng-TEQ/g at the bottom of boiler section under flue gas by utilizing its heat.

References

1. Kaburagi, Y., Waste under Special Control, Waste Management Research, VOL. 3, NO.3, pp 192-201, 1992 (in Japanese).
2. Hagenmaire, et. al., Copper-Catalyzed Dechlorination/Hydrogenation of Polychlorinated Dibenzo-p-Dioxins, Polychlorinated Dibenzofurans, and Other Chlorinated Aromatic Compounds, Environ. Sci. Technol., Vol. 21, pp 1085-1088, 1987.
3. Shida, et. al., Decomposition Apparatus of Dioxin in Fly Ash From Municipal Refuse Incinerator, Dioxin '92 Organohalogen Compounds, Vol 8, pp 281-284, 1992.

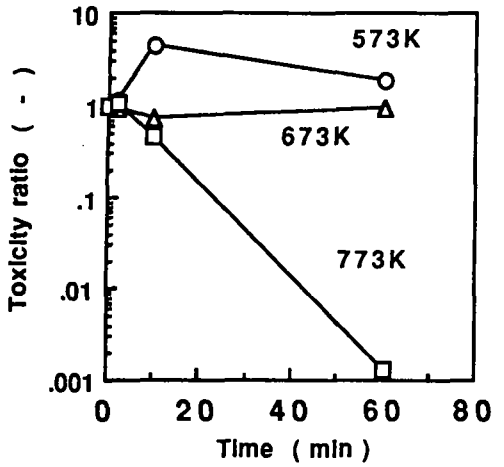

Fig.2 Change of fly ash toxicity (Oxygen;10vol% ,HCl;1000ppm)

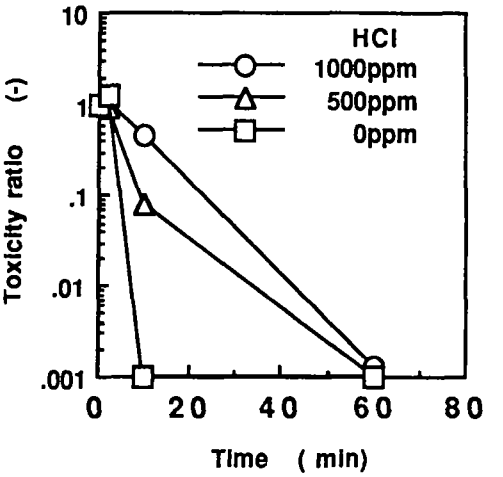

Fig.3 Influence of HCl on change of fly ash toxicity (773K, oxygen 10vol%)

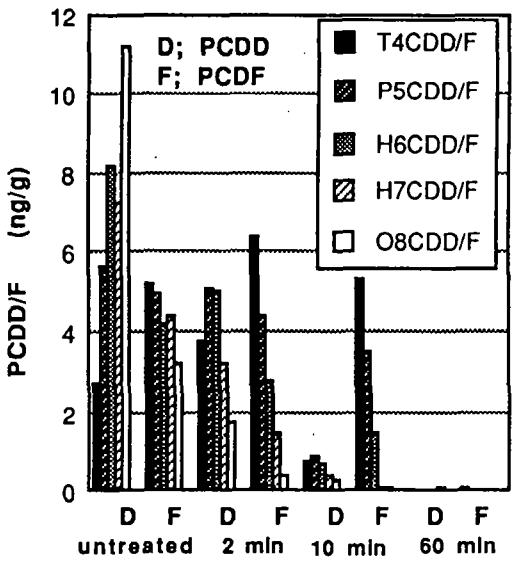

Fig.4 Change of congener patterns for heat treatment (773K, Oxygen 10vol%, HCl 1000ppm)

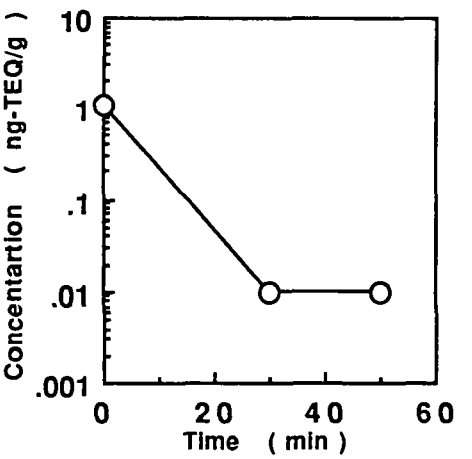

Fig.5 Change of dioxins concentration in fly ash for heat treatment at the bottom of boiler section in MSWI