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Full-scale Plant Study on Low Temperature Thermal Dechlorination of PCDDs/PCDFs in Fly Ash

Michio ISHIDA, Ryozo SHIJI, Peng NIE and Noriyuki NAKAMURA
Hitachi Zosen Corp. Environmental System Headquarters,
3-40, Sakurajima 1-chome, Konohana-ku, Osaka 554, Japan
Shin-ichi SAKAI
Kyoto University, Environment Preservation Center
Yoshida-honmachi, Sakyo-ku, Kyoto-city, Kyoto 606-01, Japan

1. Introduction

It is generally known that fly ash collected in municipal solid waste incinerators(MSWI) contains PCDDs/PCDFs. It was originally developed by Hagenmaier that PCDDs/PCDFs in fly ash would be dechlorinated under the condition of[1, 2] (1) Oxygen deficiency condition; (2) Heating temperature 250-400° C; (3) Retention time about 1 hour and (4) Discharge temperature of treated ash <60° C . Using this principle, we developed and designed a low temperature thermal dechlorination process of PCDDs/PCDFs in fly ash. A pilot test equipment was constructed at the Hitachi Zosen's works in 1993, and the following test results were confirmed in processing fly ash from MSWI[3] .
(1) PCDDs/PCDFs decomposition ratio increases with the increase of retention time(1-3hours) and apparent ash temperature(350-400° C).
(2) In a condition of apparent ash temperature 400° C and retention time 1 hour, 99% or more PCDDs/PCDFs decomposition ratio can be obtained.
(3) PCDDs/PCDFs in the vent gas and the condensed water are slightly detected.
Based on these results and experience, we designed and constructed an actual dechlorination process for Matsudo MSWI in Japan. It was completed and delivered in October 1995 and now it is running well.
The purpose of this study is to disduss the treatment efficiency of PCDDs/PCDFs in both flue gas and fly ash in Matsudo MSWI.

2. Flue gas cleaning and fly ash treatment in Matsudo MSWI

The outline of Matsudo MSWI is given in Table 1, the treatment flow of flue gas and fly ash is shown in Figure 1 and the outline of the fabric filter and the DeNOx reactor is given in Table 2. Flue gas from the economizer(incinerator+WHB+economizer) is fed to gas cooling chamber, mixed with sprayed water and cooled down to an appropriate temperature(170° C) and then flue gas is injected with a powdered hydrated lime. Fly ash, consisting of dust, reaction products of HCl and SOx surplus, hydrated lime and other toxic substance (such as PCDDs/PCDFs, heavy metals), is collected effectively by fabric filter. Flue gas from fabric filter is fed to wet scrubber for further removal of HCl and SOx. Then flue gas is heated to the temperature of 200° C and is fed to

DeNOx reactor in which NOx is removed by reacting with the injected ammonia in presence of the catalyst. Fly ash from fabric filter and gas cooling chamber is fed into a fly ash treatment process, that is; firstly for thermal dechlorination of PCDDs/PCDFs and sencondly for stabilizing heavy metals by cement solidification process.

Table 1 Outline of Matsudo MSWI

Site area	Approx.24,600 m^2
Capacity	300t/24h (100t/24h × 3furnaces)
Furnace type	Continuous combustion incinerator (stoker furnace)
Gas cooling facility	Waste Heat Boiler (WHB)
Flue gas treatment	Fabric filter + Wet Scrubber + DeNOx reactor

Table 2(a) Outline of fabric filter

Type	Pulse type
Element size, No's.	0.16m(ϕ) × 5.0m(L), 400 (Double fold glass fiber cloth)
Gas flow	33,000 Nm^3/h
Gas Temp.	170°C

Table 2(b) Outline of DeNOx Reator

Type	SCR
Volume	6.2m^3 (V_2O_5/TiO_2, Cell pitch 5.0mm)
Gas flow	34,000 Nm^3/h
Gas Temp.	200°C

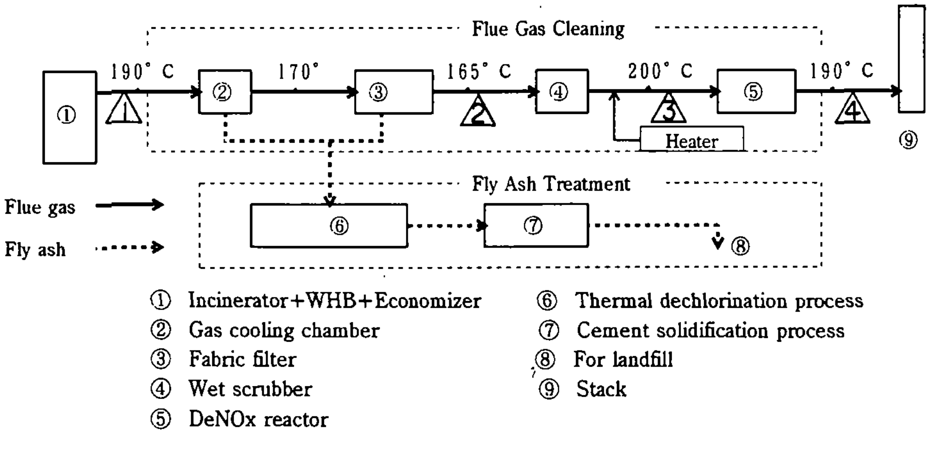


Figure 1 Flow of flue gas cleaning and fly ash treatment in Matsudo MSWI

The process specifications are given in Table 3 and the flow diagram is shown in Figure 2. Dechlorination process consists of a reactor and a cooler as main equipments. Fly ash stored in a silo is charged into the reactor through the inlet rotary valve, heated up by an electric heater arranged around the reactor with agitating paddles, cooled down in the cooler by water cooling and discharged through the outlet rotary valve. Gas treatment system is also installed to condense the vapor from fly ash during heating up. N_2 gas is used to maintain oxygen deficiency condition.

3. PCDDs/PCDFs samping and analysis

Samping and analysis of PCDDs/PCDFs in both flue gas and fly ash were carried out according to "Measuring Manual of Dioxins for Waste Treatment" by Japan Waste Research Foundation(JWRF).

In order to evaluate the thermal dechlorination of PCDDs/PCDFs, decomposition ratio was calculated by the following formula.

$$A = (B-C)/B \times 100\ \%$$

where, *A: PCDDs/PCDFs decomposition ratio (%)*
B: PCDDs/PCDFs concentration in the untreated ash (ng/g)
C: PCDDs/PCDFs concentration in the treated ash (ng/g)

Table 3 Process specifications of dechlorination

Capacity		500 kg/h
Inlet temp. of fly ash		60° C
Discharge temp. of fly ash		60° C or below
Reaction temp.		300～400° C
Reactor	Type	Electrical Heated Cylindrical
	Size	1.2 m(ϕ) × 5.0 m(L)
Cooler	Type	Water Cooling Jacket Cylindrical
	Size	0.41 m(ϕ) × 3.44 m(L)
Dimensions		7m(H) × 12m(L) × 7m(W)

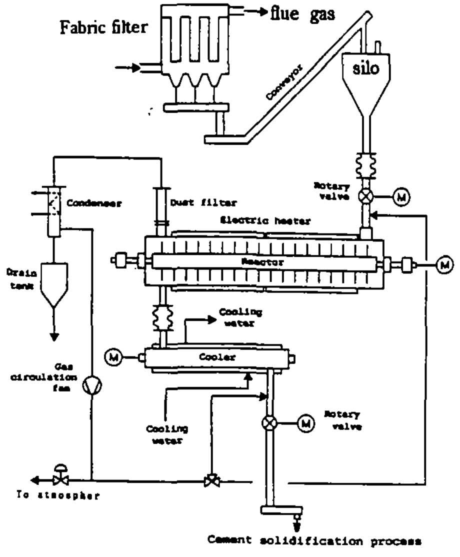


Figure 2 Flow diagram of the process

4. Results and Discussion

4.1 PCDDs/PCDFs concentration in flue gas

PCDDs/PCDFs in the flue gas were sampled at 4 points shown in Figure 1. PCDDs/PCDFs concentrations in the flue gas are shown in Table 4. It is shown that PCDDs/PCDFs in the flue gas would be removed by both fabric filter and DeNOx(SCR) reactor. Finally, PCDDs/PCDFs in the stack are less than 0.1 I−TEQ ng/Nm^3.

Table 4 Results of PCDDs/PCDFs in flue gas (I−TEQ ng/Nm^3 @O_2 12%)

Point	1 WHB outlet	2 fabric filter outlet	3 DeNOx reactor inlet	4 Stack inlet
Sample 1	4.4	0.31	0.38	0.08
Sample 2	4.4	0.29	0.34	0.05
Sample 3	4.3	0.22	0.26	0.06

4.2 Thermal dechlorination of PCDDs/PCDFs in fly ash

Temperature and retention time of fly ash in Reactor:

Electric heaters are arranged around the reactor and temperature of the reactor shell metal is maintained at a preset operating temperature by use of an automatical control. In order to know temperature distribution of fly ash in the reactor, a set of thermocouples are inserted into the reactor at 6 different longitudinal sensing places in short pause of paddle rotation. One of results is shown in Figure 3. It is understood that the area between sensor I, II and III is a heating up zone and the remainder is a temperature stable zone. So apparent thermal dechlorination temperature is defined as an average among temperatures at sensor IV, V and VI. Also the retention time is defined as the ash residence time after the sensor IV.

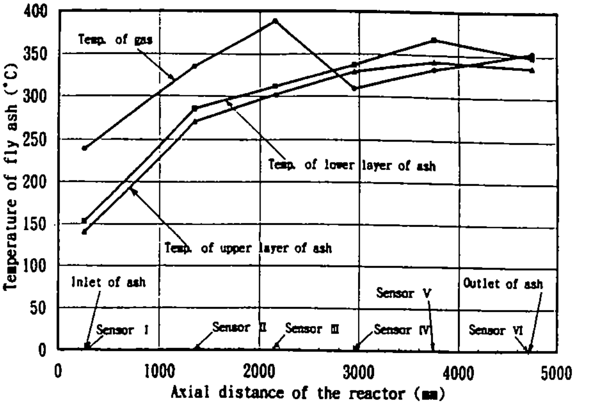


Figure 3 Temperature distribution of fly ash in the reactor

PCDDs/PCDFs decomposition ratio:

Test conditions of dechlorination process are shown in Table 6 and decomposition ratios are shown in Figure 4. It is shown that PCDDs/PCDFs decomposition ratio appears to increase with the increase of apparent ash temperature and retention time, while the range of oxygen concentration is up to 0.01%. Approximately 99.7% of PCDDs/PCDFs decomposition ratio that PCDDs/PCDFs was decreased from 0.6 I-TEQ ng/g in untreated ash to 0.002 I-TEQ ng/g in treated ash, was obtained in condition of 350° C of apparent temperature and 1.0 hour of retention time.

Table 6 Test conditions of dechlorination process

Run No.	R 1	R 2	R 3	R 4	R 5	R 6	R 7	R 8	R 9
Temp. of ash (°C)	306	309	316	320	324	324	325	344	350
Retention time (h)	1.3	1.3	1.4	1.4	2.0	2.0	1.5	1.1	1.0
O2 concentration (%)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

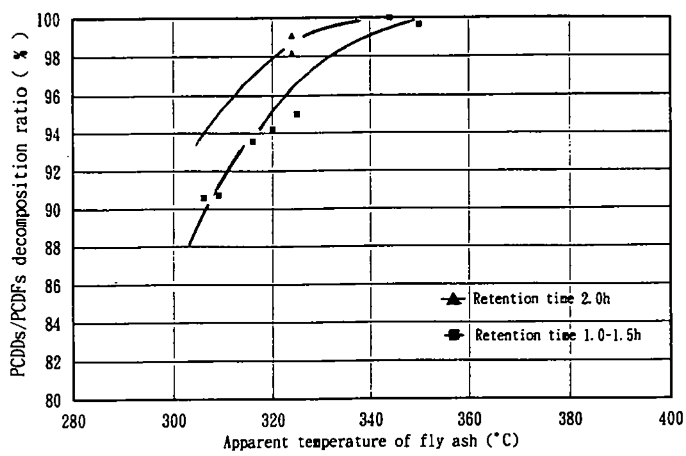
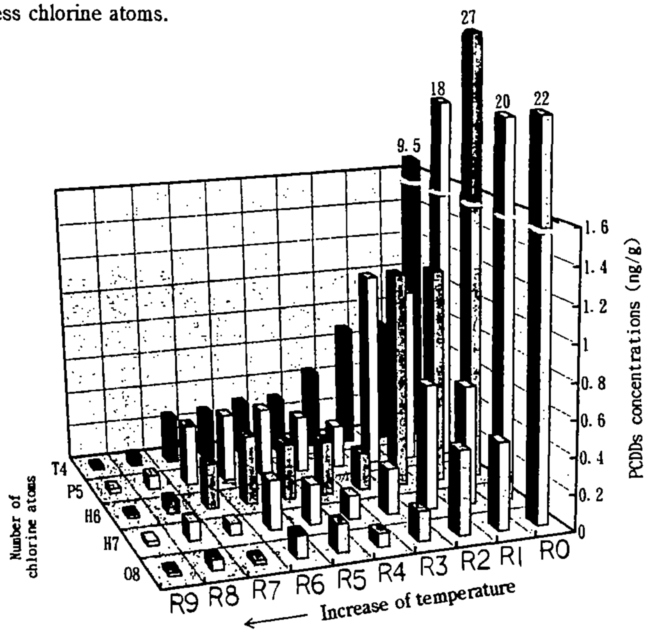


Figure 4 Relationship between apparent ash temp. and PCDDs/PCDFs decomp. ratio

PCDDs/PCDFs concentration in both untreated ash and treated ash:

Congener patterns of T4 ~ O8 PCDDs/PCDFs in untreated ash and treated ash are given in Figure 5. Comparing untreated ash(R0), it is shown that T4 ~ O8 of both PCDDs and PCDFs in treated ash decreased largely in concentrations of two figures, by the low temperature thermal dechlorinaton process. And it is also shown that the congener concentration(T4 ~ O8) of both PCDDs and PCDFs decreased gradually with the increase of ash temperature (R1 → R9).

In the case of PCDDs, concentration of H7 and O8 in treated fly ash became lower than that of T4, P5 and H6, though H7 and O8 were higher than T4 and P5 in untreated fly ash. It means that low temperature thermal dechlorination moved on from PCDDs having more chlorine atoms to those of less chlorine atoms.



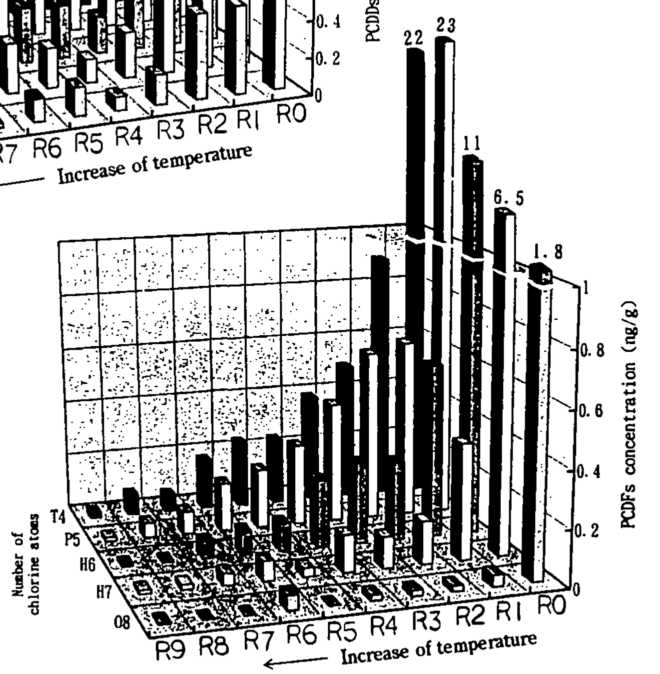


Figure 5 PCDDs/PCDFs concentration in untreated fly ash and treated fly ash (R0: Untreated fly ash)

To check the results above, thermal dechlorination laboratory test was carried out, by using the same fly ash from Mastudo MSWI. Test conditions and M1 ~ O8 of PCDDs/PCDFs in untreated ash and treated ash are shown in Figure 6. It is understood that PCDDs/PCDFs having more chlorine atoms are decreased, on the other hand M1 ~ T3 of PCDDs and M1 of PCDFs are increased.

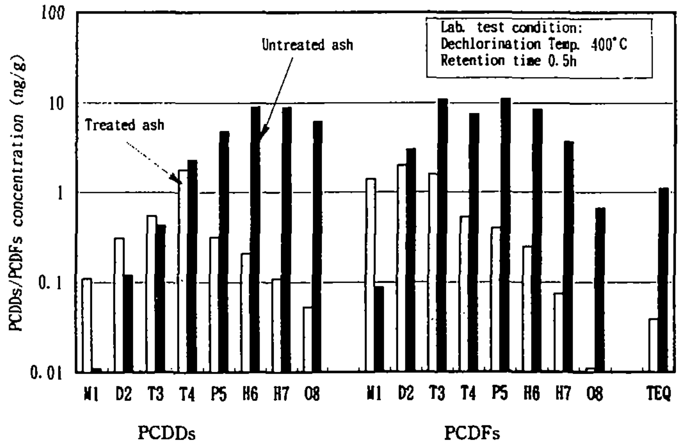


Figure 6 PCDDs/PCDFs concentration in untreated fly ash and treated fly ash in lab. test

5. *Conclusion*

Reduction of PCDDs/PCDFs in both flue gas and fly ash was studied in Matsudo MSWI. The conclusions are as follows:

(1) PCDDs/PCDFs in flue gas would be removed by both fabric filter and DeNOx reactor(SCR) to be less than 0.1 I-TEQ ng/Nm^3.

(2) PCDDs/PCDFs decomposition ratio increases with the increase of apparent ash temperature and retention time. In a condition of apparent ash temperature of 350° C and retention time of 1 hour, more than 99% of PCDDs/PCDFs decomposition ratio would be obtained.

(3) Congener concentration(T4 ~ O8) decreased gradually with the increase of ash temperature . And thermal dechlorination moved on from PCDDs/PCDFs having more chlorine atoms to those of less chlorine atoms.

Finally, we would like to express our appreciation to the people concerned in Matsudo city for the detailed information provided for purposes to this study.

6. References

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3) M.Ishida, R.Shiji, P.Nie and N.Nakamura: Low Temperature Thermal Cracking of PCDDs/PCDFs in Fly Ash, 14th International Symposium on Chlorinated Dioxins, PCB and Related Compounds, Vol.19, p.485(1994).