Hydrothermal Decomposition of PCDDs/PCDFs in MSWI Fly Ash

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1. Introduction

According to Japanese guidelines on Municipal Solid Waste Incinerator (MSWI), the concentration of PCDDs/PCDFs in MSWI flue gas should be reduced to less than 0.5 ng-TEQ/Nm^3 [1]. Although MSWI fly ash is not subject to the guidelines, PCDDs/PCDFs in the fly ash should be also reduced to an allowable level. Therefore, thermal destruction method at around 670 - 770 K in nitrogen or oxygen deficient atmosphere and ash melting method have been studied to reduce PCDDs/PCDFs in fly ash [2,3].

Yamasaki found that hydrothermal reaction decomposed polychlorinated biphenyls (PCBs) almost 100 %[4]. Hydrothermal reaction occurrs in water under high pressure and temperature over 373 K. The reaction is accelerated with the increase of water ion product (Kw value), which increases with the increase of temperature and has the maximum value around 573 K. Thus, the reaction would be very active around 573 K. The reaction was also accelerated with the existence of alkaline and methanol.

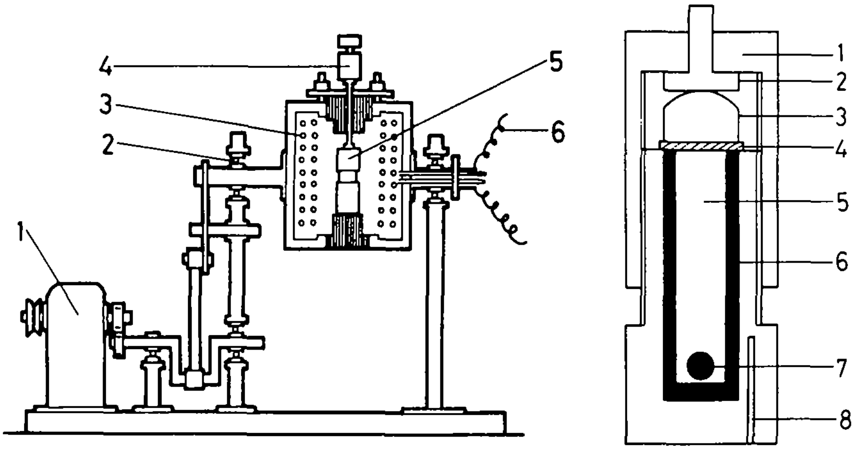
Since PCDDs/PCDFs have similar chemical structures to PCB, hydrothermal reaction was expected to be very effective on the decomposion of PCDDs/PCDFs. Few studies have reported the hydrothermal decomposition of PCDDs/PCDFs[5]. Therefore, this report discussed the influences of solvents and temperature on the hydrothermal decomposition of PCDDs/PCDFs in MSWI fly ash.

2. Experimental

A 60 ml autoclave shown in Fig. 1 was used in our study. Fly ash for this study was collected from an electrostatic precipitator in a MSWI. The fly ash contained 600 ng/g of PCDDs and 510 ng/g of PCDFs and had toxicity equivalents of 18 ng-TEQ/g, as listed in table 1. Five kinds of solvent, distilled water, three NaOH solutions (0.5, 1 and 5 N), 1 N NaOH solution containing 10 vol % methanol were used.

In each experiment, 3 g of the ash (wet basis) and 27 g of solvent were put into the autoclave. The autoclave was heated to 498, 523, 548, and 573 K with a heating rate of about 50 K/min and held at those temperatures for 5, 10 or 20 min. Fly ash slurry was stirred effectively with a hastelloy C ball during the experiment.

After cooling down the autoclave, the fly ash slurry was recovered and filtrated. PCDDs/PCDFs concentrations in the residue (on dry base) and the filtrate were analyzed according to the standard Japanese guideline methods by using a KRATOS CONCEPT-1S GC/MS with a SP-2331 column (length : 60 m, I.D. : 0.32 mm) and DB-5 column (length : 60 m, I. D. : 0.25 mm).



(a) Overview of Apparatus

1. Motor
2. Ball Bearing
3. Cut Tube Coil
4. Pressure Valve
5. Microautoclave
6. Lead Wire

(b) Detail of Microautoclave

1. Binding Nut
2. Top Weight
3. Top
4. Packing Plate
5. Chamber
6. Liner
7. Stirring Ball
8. Well for Thermocouple

Fig.1 Schematic diagram of apparatus for hydrothermal treatment

Table 1 Properties of fly ash used in our study

Metal (wt%, dry base)							Dioxins			
CaO	MgO	Al_2O_3	SiO_2	TiO_2	K_2O	Na_2O	PCDDs (ng/g)	PCDFs (ng/g)	Total (ng/g)	Total (ng-TEQ/g)
22.4	3.28	15.4	20.0	1.23	4.95	3.65	600	510	1100	18

3. Results and Discussion

PCDDs/PCDFs concentrations in the filtrate were 0.3 - 2 ng/l, which were less than 0.3 % of those in the residue. Therefore, the concentration in the residue was defined as that in treated fly ash in our study and this report discussed PCDDs/PCDFs in the fly ash.

Fig. 2 shows the effect of solvents on hydrothermal decomposition of PCDDs/PCDFs in fly ash at 573 K in 20 min. PCDDs/PCDFs concentrations in treated fly ashes with distilled water, 0.5, 1, 5 N NaOH solutions ,and 1 N NaOH solution containing 10 vol% methanol were 630, 4.6, 3.8, 0.85, and 0.45 ng/g, respectively.

PCDDs/PCDFs in fly ash decomposed only 43 % with distilled water, but more than 99 % with the other four solvents containing alkaline with/without methanol. PCDDs/PCFDs in the treated fly ashes decreased with the increase of NaOH concentration in solvents. These results indicated that alkaline with/without methanol in solvents accelerated decomposition of PCDDs/PCDFs. This tendency was consistent with that for PCBs obtained by Yamasaki et al.[4]. No difference of decomposition ratio between PCDDs and PCDFs was observed with the solvents. Toxicity equivalents of fly ash became less than 0.03 ng-TEQ/g with 1 N NaOH solution containing methanol.

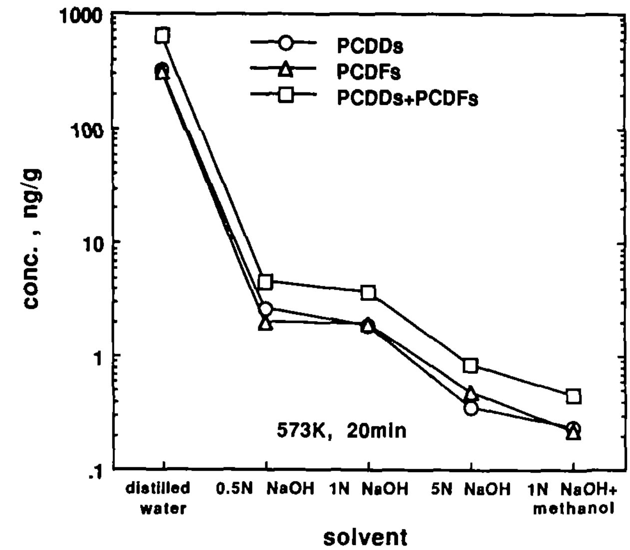


Fig.4 Effect of solvent types on hydrothermal decomposition of dioxins in fly ash A-1

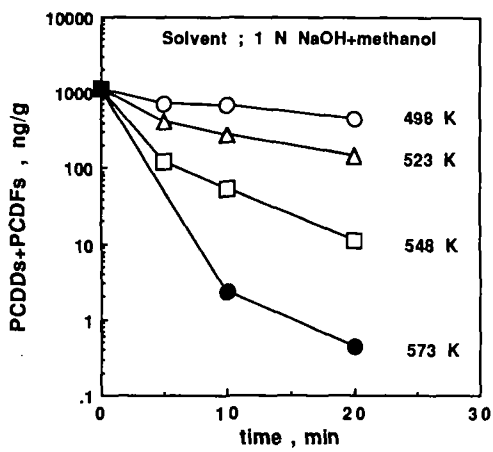


Fig.3 Effect of temperature for the reduction of dioxins concentration with time

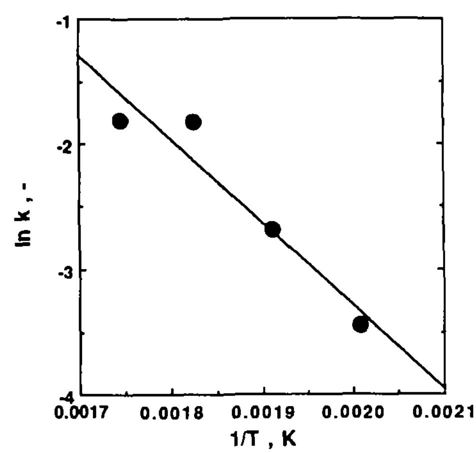


Fig.4 Change of reaction rate constant with temperature

Shida et al.[6] reported that PCDDs/PCDFs decomposed about 70 % at 573 K in 20 min under nitrogen atmosphere. Thus, hydrothermal treatment would be superior to thermal destruction as regards to PCDDs/PCDFs decomposition at this temperature.

Fig. 3 provides change of PCDDs/PCDFs concentration with temperature in fly ash with 1 N NaOH solution containing 10 vol% methanol. The concentration at 0 minute in this figure was from fly ash before the hydrothermal treatment. In this figure, PCDDs/PCDFs concentration in fly ash apparently decreased with the increase of temperature and time. Acceleration of PCDDs/PCDFs decomposition with temperature increase should be due to the increase in ion product of water, which was indicated by Yamasaki et al.[4].

Reaction rate constants of first order were calculated from the slopes of the lines in Fig. 3 and plotted against temperatures as shown in Fig. 4. In the calculation, it was assumed that tetra- through octa- chlorides of PCDDs/PCDFs decomposed into the others except for those dioxins. Calculated activation energy of the reaction was 13.2 kcal/mol and the reaction rate constant k was expressed as $k = 2.27 \times 10^4 \exp\{-13.2/(RT)\}$. The activation energy estimated in our study was similar to that (15 kcal/mol) of the thermal decomposition of PCDDs/PCDFs reported by Altwicker et al.[7].

4. Conclusions

Within the experimental conditions, following conclusions were obtained as to the hydrothermal treatment of fly ash.

1) Alkaline with/without methanol accelerated decomposition of PCDDs/PCDFs.
2) PCDDs/PCDFs in fly ash decomposed more effectively at higher temperature.
3) No difference of decomposition between PCDDs and PCDFs was observed.
4) Activation energy of the hydrothermal reaction was estimated about 13 kcal/mol.
5) Hydrothermal treatment could reduce toxicity equivalents of MSWI fly ash to very low level less than 0.03 ng-TEQ/g at 573 K.

5. References

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