Thermal Decomposition of PCDDs/PCDFs in MSW Incineration Fly Ash

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1. Introduction

The thermal behavior of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in electrostatic precipitator ash from a Municipal Solid Waste (MSW) incineration plant has been reported since 1986,[1)2)] and the results have been applied in several decomposition (or de-chlorination) devices.[3)4)5)] The essence of these techniques is, in short, how to heat ash effectively to the decomposition temperature, and how to cool the ash quickly to room temperature so as not to re-generate PCDDs/PCDFs from remaining compounds.

A thermal decomposition device of the rotary kiln type was selected for our experiments, because its heating efficiency is better than that of a mixing moving bed type. Heating capacity, retention time, oxygen concentration in the kiln, and relationship of decomposition efficiency between Chlorinated Benzens (ClBzs) and PCDDs/PCDFs were investigated.

2. Experiment

2.1 Fly Ash Sample

Bag filter ash from an actual MSW incineration plant (fluidized bed incinerator + water spray quencher + dry $Ca(OH)_2$ injection + bag filter, capacity 40ton/16hour) was used for the experiment. Characteristics and main components of the ash are shown in Table 1.

Table 1 Fly Ash Sample

Characteristics	unit		
average grain size	μm	25	weight 50%
specific heat	kJ / kg K	0.97	25-400 ℃ average
heat conductivity			
loosely packed	W / m K	0.088	r = 500 kg / m³
closely packed	W / m K	0.10	r = 700 kg / m³
Main Components			
moisture	wt%	0.33	
ignition loss (600℃)	wt%	4.94	dry matter base
SiO_2	wt%	20.60	d.m.base
Al_2O_3	wt%	20.00	d.m.base
CaO	wt%	24.60	d.m.base
Fe_2O_3	wt%	4.94	d.m.base
MgO	wt%	2.81	d.m.base
Na_2O	wt%	4.97	d.m.base
K_2O	wt%	2.76	d.m.base
Cl	wt%	8.29	d.m.base
SO_3	wt%	2.48	d.m.base
Zn	wt ppm	3500	d.m.base
Cu	wt ppm	1500	d.m.base
Pb	wt ppm	800	d.m.base
Cd	wt ppm	13	d.m.base
Cr	wt ppm	150	d.m.base
Hg	wt ppm	5	d.m.base

2.2 Experimental Device

Fig. 1 is a schematic flow diagram of an experimental device. Fly ash was fed into a rotary kiln at a fixed rate by a feeder. Inside the rotary kiln, ash is agitated and moves downstream where it is heated by

heat exchange with wall surface and internal gas.
Decomposition (or dechlorination) of PCDDs/PCDFs starts when the ash reaches the reaction temperature. Air or nitrogen gas was injected into the kiln from a feeding port, and internal gas was discharged by a vacuum pump to keep a little negative pressure. Oxygen concentration was measured at an outlet. Maximum ash temperature, which cannot be directly measured, was represented from the gas temperature at the middle of the rotary kiln. An electric heater was controlled by inputting the temperature. The retention time of ash was controlled by the inclination of the rotary kiln, and the number of revolutions was fixed.

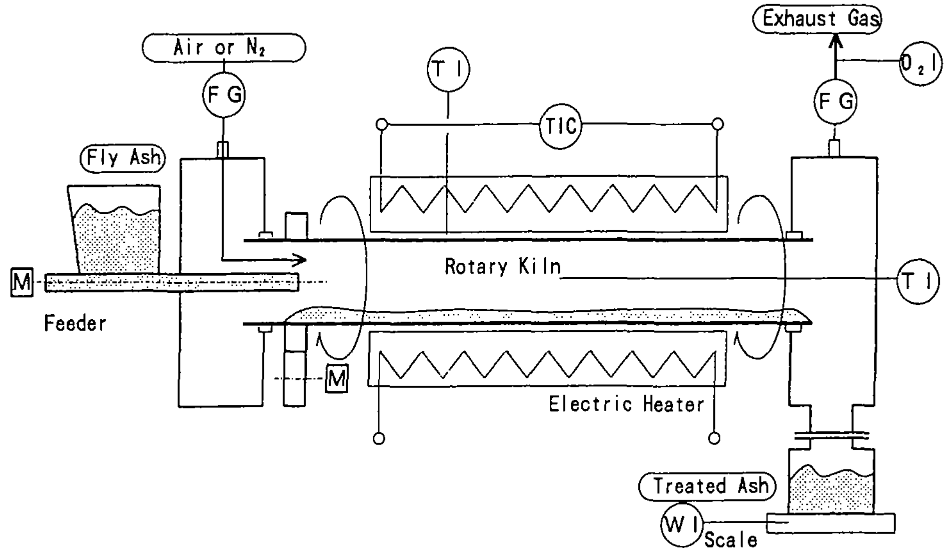

Fig. 1 Schematic Flow Diagram of Experimental Device

2.3 Operating Conditions

Operating conditions are shown in Table 2.
Oxygen concentration was 7 to 8% when air was injected, and 3 to 3.5% when nitrogen was injected, because of the combustion of remaining materials in ash and air leaking in.

2.4 Sampling and Analysis

Treated ash samples were cooled to a room temperature within a few minutes after sampling. In addition, some samples were stored in an insulated container on kept at over 300 ℃ for 2 hours, so that re-generation should be investigated. PCDDs, PCDFs and ClBzs were extracted into toluene and analyzed by GC/MS SIM method.

Table 2 Operating Conditions

Item	unit	
Ash Sample		Bag Filter Ash
Treatment Capacity	kg/h	18
Retention time	min	4.5 or 9.0
Gas Injected		Air or Nitrogen
Gas Flow Rate	Nm^3/h	0.6
Oxygen Concentration	vol %	7 - 8 (Air) 3 - 3.5 (N_2)
Ash Temperature	℃	450,500,550,600,700

3. Results and Discussion

3.1 Decomposition and Re-generation

One example is given in Fig.2.
Fly ash was treated at 500℃, for nine minutes from inlet to discharge, while nitrogen gas was being injected. Over 95% PCDDs/PCDFs was decomposed in treated ash. Re-generation was confirmed in a sample which had been kept at over 300℃ for two hours. PCDFs tended to re-generate more than PCDDs.

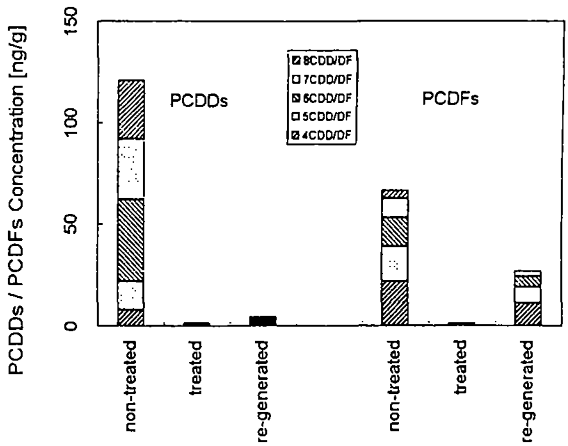

Fig. 2 Example of Decomposition and Re-generation

3.2 Decomposition Efficiency

Decomposition efficiency is illustrated in Fig. 3, where the vertical axis shows the remaining ratio of PCDDs+PCDFs concentration to non-treated ash.
PCDDs+PCDFs were 95 to 99.5% decomposed. One result of a Toxic Equivalent (TEQ) analysis is shown in Table 3.
Higher ash temperatures did not necessarily improve the decomposition efficiencies. The reason is assumed to be that the efficiencies relate to retention time at around 300 ℃ in which re-generation occurs.
Both 4.5 and 9 minute-treatments could achieve the same performance without showing marked differences. This result suggests that decomposition itself should be completed in a short time, though it takes more time to heat ash to reach a reaction temperature.
Even when air was injected, oxygen concentrations were 7 to 8%, about 4% more than nitrogen injection tests, because of organic material's combustion in ash. It is not required to use nitrogen or other inert gas in an actual device, when the air flow rate should be controlled to keep a low oxygen concentration in the kiln.

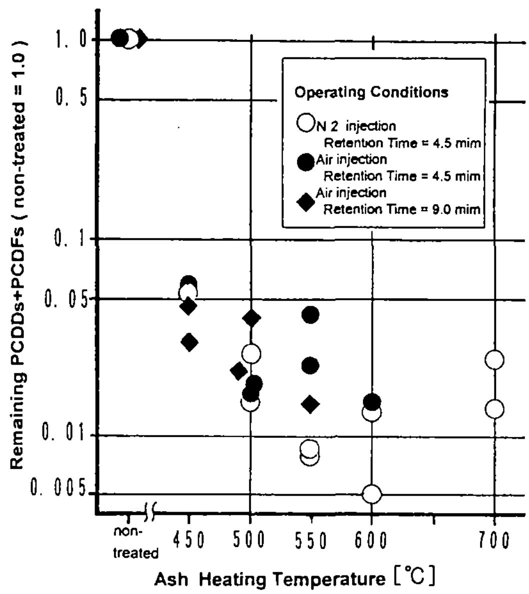

Fig. 3 Decomposition Efficiency

3.3 ClBzs vs. PCDDs/PCDFs

The relationship between ClBzs' and PCDDs+PCDFs' reduction rate is shown in Fig.4, where reduction rate η =(concentration in treated ash)/(concentration in non-treated ash).

Table 3 TEQ Analysis unit ng/g

Item	non-treated		treated ash	
PCDDs				
4CDD (2378-)	12	(0.02)	1.2	(0.02)
5CDD (2378-)	20	(0.20)	0.85	(0.03)
6CDD (2378-)	41	(2.7)	0.65	(0.06)
7CDD (2378-)	24	(12.)	0.22	(0.10)
8CDD (2378-)	23	(23.)	0.16	(0.16)
PCDD Total	120		3.1	
PCDFs				
4CDF (2378-)	13	(0.21)	1.5	(0.03)
5CDF (12378)	21	(1.5)	1.2	(0.07)
(23478)		(1.3)		(0.05)
6CDF (2378-)	15	(5.4)	0.42	(0.12)
7CDF (2378-)	9.1	(5.7)	0.10	(0.06)
8CDF (2378-)	0.6	(0.6)	0.04	(0.04)
PCDF Total	59		3.3	
PCDDs+PCDFs	180		6.4	
TEQ*		**1.9**		**0.09**
Decomposition rate (%)			96.4	(**95.3**)

500 ℃ , 4.5 minutes, Air injected , *TEQ International

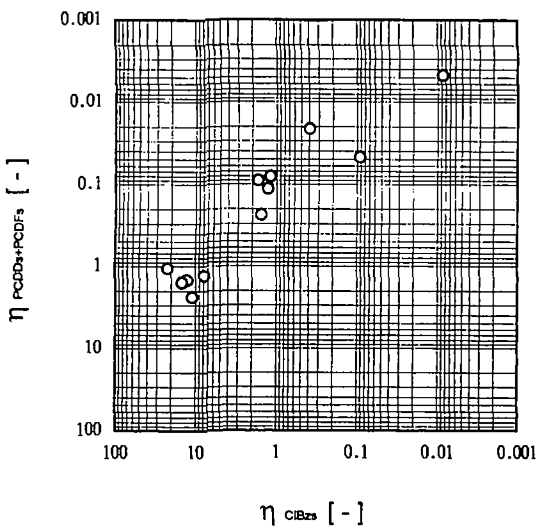

Fig. 4 ClBzs' and PCDDs+PCDFs' Reduction Rate

The reduction rates η varied according to the cooling conditions as described in 2.4, though concentrations of PCDDs +PCDFs in non-treated ash were about 200 ng/g for all samples. ClBzs were thermally more stable than PCDDs/ PCDFs. It is recognized from the figure that ClBzs' monitoring can be used for estimating the PCDDs' decomposition performance, for example, when a 95% reduction of PCDDs+PCDFs is required, ClBzs should be reduced by about 90%.

4. Conclusion

1) Using the rotary kiln device, PCDDs/PCDFs concentration in bag filter ash from MSW incineration plant can be reduced to 0.1 ng/g TEQ level.
2) Oxygen concentration in the kiln is low enough to maintain decomposition conditions, because of organic material's combustion in ash. Inert gas injection like N_2 is not necessary for our device.
3) ClBzs' monitoring can be used for estimating the PCDDs' decomposition performance.

A commercial plant equipped with our thermal decomposition device (capacity 120kg/h x 2 trains) will start operation from October 1994.

6. References

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