A Study on the Behavior of PCDDs/DFs in a Municipal Refuse Fly-ash Melting Experiment

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1. Introduction

The volume of municipal refuse has been steadily increasing. To cope with this situation, municipal refuse in Japan has been incinerated to reduce its volume as well as to stabilize it. However, problems have arisen over the disposal of incinerated refuse, due to difficulties in securing disposal sites. Accordingly, melting treatment is attracting the interest of experts in this field, because it permits the further reduction of refuse volume and the usage of molten slag.
In addition, the revised Waste Treatment Law, which went into effect in July 1992, stipulates that fly-ash (ash from electrostatic precipitators and bag filters) be designated General Wastes subject to special control, as a result, it has become obligatory to treat fly-ash via melting, cementitious solidification, chemical fluid application, or other suitable methods. This report discusses the results of a study on the behavior of PCDDs/DFs during the treatment of municipal refuse fly-ash via melting, using a coke-bed melting furnace.

2. Melting Experiment

In the coke-bed type melting method, a high-temperature bed of burning coke, functioning as a grate, is formed in the lower part of the melting furnace. Municipal refuse fly-ash is then melted in the coke-bed at a temperature of more than 1,300℃, and discharged from the furnace continuously as slag[1).
An experiment was conducted using a small furnace to determine the characteristics of exhaust, clarify mass balance of heavy metals, and study the behavior of PCDDs/DFs. The duration of the experiment was set at three hours, to allow sufficient time for the measurement of variables related to PCDDs/DFs. A flow chart showing the operation of

the experimental equipment is shown in Fig.1. The small furnace used for the experiment has a capacity of approx. 30 kg/hr. Fly-ash, coke and gravel were supplied to the furnace in batches. The air for coke combustion was preheated to approx. 500 ℃ by a gas heating furnace and then an electric heater. The air for secondary combustion, used to reduce the carbon monoxide concentration, was sent at normal temperature to the upper part of the melting furnace. Exhaust was discharged into the air through a cyclone, a bag filter and a stack.

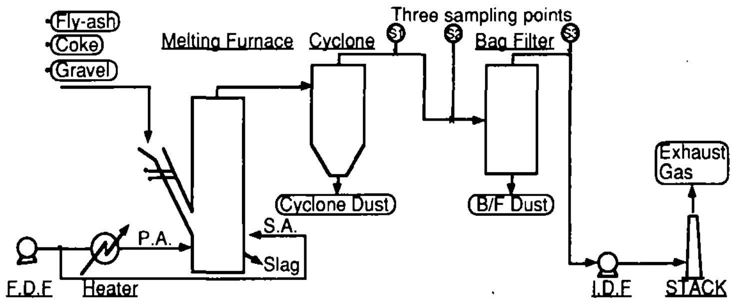

Fig.1 Schematic flow diagram of the experimental equipment.

3. Experimental Results and Discussion

3.1 Fly-ash Characteristics

Electrostatic precipitator dust collected at a municipal incinerator in continuous operation was used as sample fly-ash. The properties of the fly-ash are shown on the third column of Table 1.

Table 1 Properties of Fly-ash, Slag, and Dusts

Item		Unit	Fly-ash	Slag	Cyclone Dust	Bag filter Dust
Heating Value		MJ/kg-DS	0.71	–	–	–
Ignition Loss		wt%-DS	9.8	0	10.1	21.8
Ash		wt%-DS	90.2	100	89.9	78.2
Heavy Metals (D.S Base)	T-Hg	mg/kg	7.5	<0.2	7.4	69
	As	mg/kg	12	<1.0	47	32
	Cd	mg/kg	120	5.7	1,200	830
	Pb	mg/kg	1900	160	9,300	10,000
	Cu	mg/kg	670	93	5,900	420
	Zn	mg/kg	9900	84	36,000	48,000
	T-Cr	mg/kg	110	310	330	220
Ash Components (Ash Base)	SiO_2	wt%	18.9	32.9	11.0	3.5
	Al_2O_3	wt%	12.3	19.8	2.6	1.1
	Fe_2O_3	wt%	2.3	1.4	5.0	3.2
	CaO	wt%	27.1	33.8	4.9	4.5
	MgO	wt%	4.3	4.9	0.8	0.7
	TiO_2	wt%	2.1	2.6	0.2	<0.1
	P_2O_5	wt%	2.0	1.6	1.3	0.3
	MnO	wt%	0.3	<0.1	0.2	0.2
	Na_2O	wt%	5.0	<0.1	15.7	18.5
	K_2O	wt%	5.4	0.1	16.4	19.3
	Cl	wt%	21.8	2.0	24.2	47.3
	C	wt%	–	<0.1	0.2	<0.1
	S	wt%	2.4	4.0	7.6	3.1
Melting Properties	Softening Point	℃	990	–	–	–
	Melting Point	℃	1190	–	–	–
	Pouring Point	℃	1380	–	–	–

Water was added to the sample fly-ash, which was then submitted to extrusion; this process was necessary because the fly-ash contained a large volume of calcium. As a result of the extrusion, the fly-ash was formed into lumps 10 mm in diameter and 30 mm long. For the experiment, gravel was added to these lumps to decrease the basicity to 1.2 and lower the melting temperature to 1,300℃.

3.2 Experimental Results

The fly-ash was melted in the coke-bed type melting furnace on a stable basis, resulting in the smooth discharge of slag. Table 2 shows the experimental conditions for data collection. At that time, the average concentration of carbon monoxide in the exhaust was 140 ppm or less; for calculation purposes, the proportion of oxygen in the air at the cyclone outlet was assumed to be 12%.

Table 2 Experimental Conditions

Items			Bench-scale Experiment
Fly-ash Feed Rate		[kg/h]	29.0
Moisture		[%]	12.0
Coke Feed Rate		[kg/h]	12.8
Gravel Feed Rate		[kg/h]	0.7
Primary Air Volume		[Nm³/h]	91
Primary Air Temp.		[℃]	518
Secondary Air Volume		[Nm³/h]	31
Secondary Air Temp.		[℃]	33
Exhaust Gas Temp.	Middle of Furnace	[℃]	884
	Outlet of Furnace	[℃]	774
	Outlet of Cyclone	[℃]	228
	Inlet of Bag Filter	[℃]	92
Exhaust Gas Components at Outlet of Cyclone.	O_2	[vol%]	8.9
	CO_2	[vol%]	13.4
	CO	[ppm]	140*
	NOx	[ppm]	115*
	HCl	[mg/Nm³]	4,388*

* Converted with 12% O_2

(1) Mass balance

The mass balance is shown in Fig. 2. Approx. 80% of the fly-ash and coke ash turned into slag.

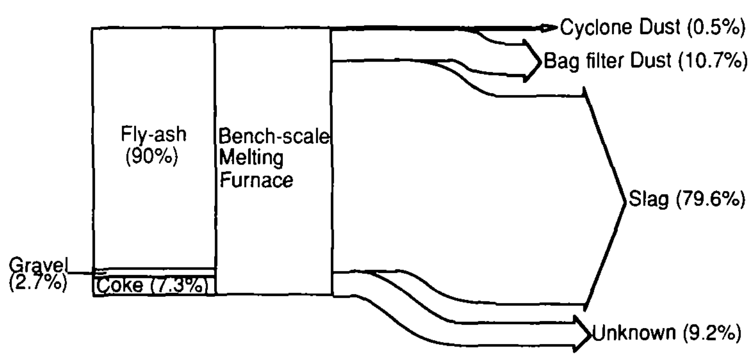

Fig.2 Mass Balance of Ash

After discharge from the furnace, approx. 0.5% of the ash was collected at the cyclone, and approx. 11% at the bag filter. The remainder (approx. 9%) is assumed to consist of substances with low boiling points, which therefore turned into exhaust.

(2) Behavior of PCDDs/DFs.

Table 3 shows the concentrations of PCDDs/DFs in solids and exhaust. The fly-ash contained these substances at the concentration of 550 ng/g (7.3 ng-TEQ/g); as a result of decomposition due to melting, the concentration decreased to 0.24 ng/g (0.001ng-TEQ/g). Cyclone dust contained 750 ng/g (4.3ng-TEQ/g) of these substances, while the bag filter held 220 ng/g (2.0 ng-TEQ/g), and the exhaust 120 ng/m^3N (0.38 ng-TEQ/m^3N; for calculation purposes, the proportion of oxygen in the exhaust was assumed to be 12%). Fig. 3 shows the mass balance of PCDDs/DFs. According to this figure, approx. 5% of the original amount of these substances remained in the cyclone dust and bag filter dust, while the amount remaining in the slag and the exhaust was negligible (approx. 0.1%). Accordingly, approx. 95% of the total amount of PCDDs/DFs was decomposed.

Table 3 PCDDs/DFs Concentrations

Items		Fly-ash	Solid (ng/g)			Exhaust Gas (ng/m^3N, O_2=12%)		
			Slag	Cyclone Dust	Bag filter Dust	Outlet of cyclone	Inlet of Bag filter	Outlet of Bag filter
Dioxins	T_4CDDs	25	N.D.	0.7	0.12	N.D.	0.14	0.11
	P_5CDDs	49	0.012	3.0	0.70	N.D.	1.5	0.05
	H_6CDDs	100	0.092	15	3.3	4.2	12	0.38
	H_7CDDs	76	N.D.	53	6.4	68	82	3.7
	O_8CDD	71	0.049	360	34	400	380	25
	T-PCDDs	320	0.15	430	44	470	470	29
Dibenzofurans	T_4CDFs	65	0.014	6.7	3.9	14	36	1.6
	P_5CDFs	55	0.022	18	11	64	120	0.96
	H_6CDFs	51	0.025	48	28	280	340	2.2
	H_7CDFs	40	0.006	88	56	680	740	27
	O_8CDF	20	0.022	160	85	1100	1000	58
	T-PCDFs	230	0.090	320	180	2100	2200	90
T-PCDDs+T-PCDFs		550	0.24	750	220	2600	2700	120
TEQ		7.3	0.001	4.3	2.0	19	23	0.38

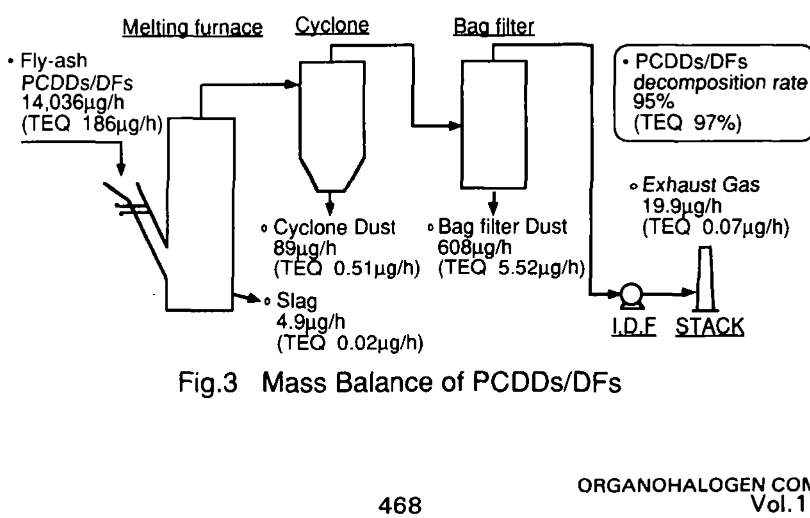

Fig.3 Mass Balance of PCDDs/DFs

Fig. 4 shows the congeners profile of PCDDs/DFs in fly-ash, as well as in the cyclone dust and bag filter dust. The total amount of PCDDs contained in the fly-ash was larger than that of PCDFs; the largest being H_8CDD. Similarly, the total amount of PCDDs in the cyclone dust was larger than that of PCDFs; higher chlorides accounted for a greater proportion of the total PCDDs. On the other hand, the total amount of PCDFs was larger than that of PCDDs; higher chlorides accounted for a greater proportion of the remaining PCDFs. Fig. 5 shows the congeners profile of the PCDDs/DFs in the exhaust at the bag filter outlet. As shown in this figure, the amount of PCDFs in the exhaust was larger than that of PCDDs; O_8CDD/DF accounted for a greater proportion of the PCDFs. These results were similar to the results of an experiment conducted in an oxygen atmosphere permitting satisfactory combustion[2] .

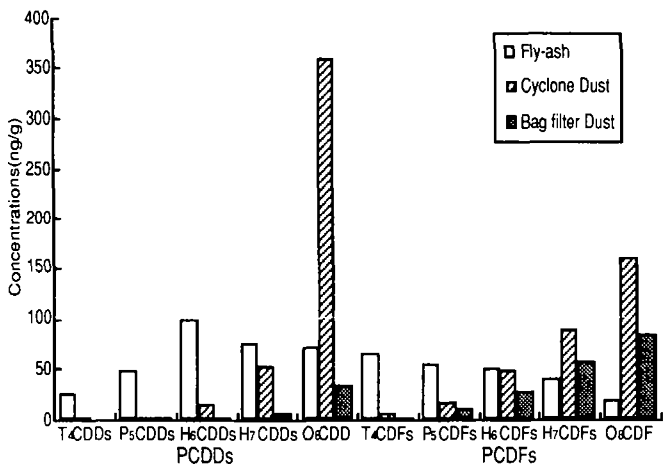

Fig.4 Congeners Profile of PCDDs/DFs in Fly-ash, Cyclone Dust, Bag Filter Dust

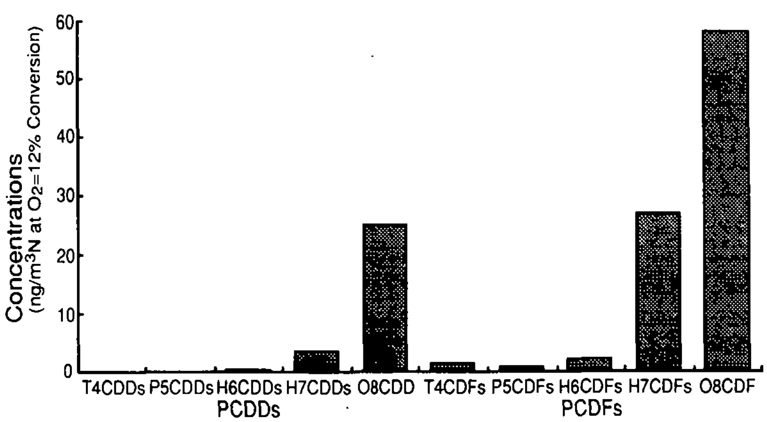

Fig.5 Congeners Profile of PCDDs/DFs in Exhaust Gas

4. Conclusion

The results of the experiment involving bench-scale melting of municipal refuse fly-ash revealed the following :
(1) The experimental results confirmed the feasibility of municipal refuse fly-ash melting using a coke-bed type furnace.
(2) 80% of the original volume of fly-ash turned into slag.
(3) Slag contained PCDDs/DFs at a concentration of 0.001 ng-TEQ/g.
Presumably, these substances could not be decomposed perfectly because slag residence time in the experimental equipment (approx. 8 minutes) was shorter than that in the actual equipment (approx. 20 minutes).
(4) 95% (97% in the TEQ standard) of the amount of PCDDs/DFs was decomposed.

5. References

(1) Takeda, N., Hiraoka, M., Sakai, S., Tsunemi, T., Sewage Sludge Melting Process by Coke-bed Furnace: System Development and Application, Wat. Sci. Tech, 21, 925-935 (1989)
(2) Hiraoka, M., Formation and Control of Dioxins in Municipal Solid Waste Treatment (in Japanese), Waste Management Research, Vol.1 No,1 pp.20-37 (1990)