

Destruction of Dioxins in MSW Fly Ash by Melting Process

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1. Introduction

The treatment and disposal of fly ash from municipal solid waste (MSW) incineration has become a matter of great concern. In Japan, the Amendment of the Waste Disposal and Public Cleansing Law of 1991 has strictly regulated the treatment and disposal of fly ash as a hazardous waste called "Waste under Special Control". This is because fly ash contains not only dioxins in high concentrations but also heavy metals with low boiling points such as lead and zinc. When considering fly ash treatment, it is essential to accomplish both decomposition of dioxins and removal of heavy metals. The authors originated a two-step treatment method for fly ash satisfying the both requirements. In the first step, fly ash from MSW incineration is treated by the KUBOTA melting treatment process, where dioxins in the fly ash are decomposed at temperatures of more than 1300 °C in the melting furnace, and heavy metals are concentrated in ash from the electrostatic precipitator of the melting process (ESP ash). In the second step, heavy metals in the ESP ash is separated and re-concentrated by water-cleansing. In this paper the test results of the each step are described, and applicability of the method is considered.

2. Fly ash melting test

2.1 Outline of the melting plant

Figure 1 shows the flow diagram of a full-scale melting process used for the fly ash melting test. The process includes the melting furnace having a double cylindrical structure. Materials are fed from the top of the furnace and melted into slag in the furnace, where a high temperature of 1300 °C is kept by oil (kerosene) burning and combustion air supply. Slag is discharged by the slag conveyor placed under the furnace, and the flue gas flows through the waste heat recovery, scrubber and dust removal systems. This plant melts both bottom and fly ashes (mixed ash) from the MSW incinerator at

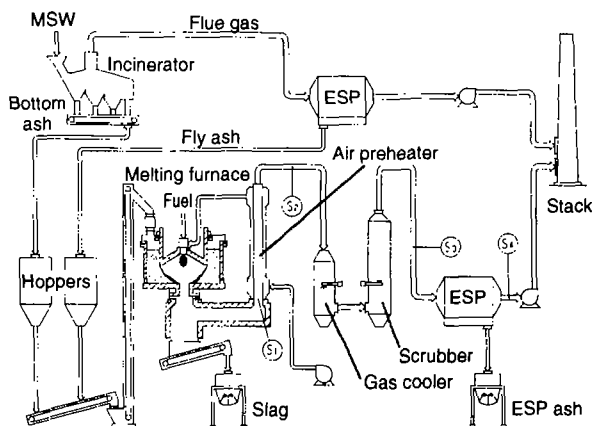


Fig. 1 Flow diagram of the melting process

a rate of 18.5 t/24 h. During the test, the bottom ash line was stopped and only fly ash from the MSW incinerator was fed into the furnace to execute a 48 hour continuous operation. The measurement points are indicated as S1-S4 in Figure 1.

2.2 Stability of the melting treatment

Table 1 shows the composition of solid materials sampled during the test : supplied fly ash from the MSW incinerator, discharged slag and ESP ash from the melting process. The operating conditions of the process are shown in Table 2. When the in-furnace temperature reached 1300 °C in six hours after the main burner was ignited, melting treatment started. The temperature was in the range of 1330 ± 10 °C, indicating a greatly stabilized operation. Fly ash was steadily converted into environmentally safe and reusable slag. The treatment capacity at this test was 15.7 t/day which was 15 percent reduction compared to the mixed ash melting. The reasons are as follows:

- The melting-fluidity point of fly ash is 50 to 100°C higher than that of mixed ash.
- Since the angle of repose of fly ash is smaller than that of mixed ash, it is necessary to operate

Table 2 Operating conditions

Item	Operation data
Throughput, kg/h	600 - 670
Kerosene consumption rate, L/h	165 - 172
Combustion air flow rate, Nm ³ /h	2000 - 2200
Combustion air temperature, °C	250 - 270
In-furnace temperature, °C	1320 - 1340
Slag production rate, kg/h	480 - 520
Flue gas flow rate, Nm ³ /h	3300 - 3600
Flue gas temperature, °C	920 - 940

Table 1 Composition of solid materials

Item*	Fly ash	Slag	ESP ash from M.F.
Moisture, %	0.56		
Heating value, kcal/kg	580		
Ash, %	89.3		
Combustibles, %	10.7		
C, %	5.9	<0.1	1.80
H, %	0.28	<0.1	<0.1
N, %	<0.01	<0.01	<0.01
Volatile-S, %	<0.1		
Volatile-Cl, %	<0.05		
O, %	4.5		
Total-S, %	0.56	0.33	1.8
Total-Cl, %	10.3	0.32	40.5
Si, %	11.3	14.2	<0.01
Ca, %	13.7	19.2	0.20
Al, %	5.4	7.5	<0.01
Na, %	2.1	0.7	17.8
K, %	2.1	0.3	13.8
Mg, %	1.5	2.1	0.01
Fe, %	1.5	2.1	0.38
P, %	0.67	0.96	<0.01
TiO ₂ , %	1.3	1.7	<0.01
Mn, %	0.06	0.09	0.02
Cd, mg/kg	46	3.0	420
Pb, mg/kg	1600	110	15000
Zn, mg/kg	4900	1200	25000
Cu, mg/kg	440	1300	2500
As, mg/kg	13	5.0	64
Total-Cr, mg/kg	400	1000	42
Total-Hg, mg/kg	2.7	0.13	1.6

* All data are on dry-solid basis except for moisture.

Table 3 Concentration of PCDD/PCDF and TEQ in solid and flue gas samples

Items	Solids, ng/g			Flue gases, ng/Nm ³ @ O ₂ =12%			
	Fly ash	Slag	ESP ash from M.F.	Inlet of air preheater (S1)	Inlet of gas cooler (S2)	Inlet of ESP (S3)	Outlet of ESP (S4)
T ₄ CDD _s	1600	<0.004	0.032	0.45	0.45	1.2	0.23
P ₅ CDD _s	910	0.010	0.010	0.63	0.41	1.3	0.31
H ₆ CDD _s	640	0.008	0.013	1.7	0.91	3.8	0.97
H ₇ CDD _s	110	0.004	0.021	1.7	0.52	9.6	1.8
O ₈ CDD	88	0.020	0.25	3.5	7.0	15	3.5
PCDD _s	3300	0.042	0.33	8.0	9.3	31	6.8
T ₄ CDF _s	34	<0.004	<0.004	3.5	1.8	8.2	1.3
P ₅ CDF _s	43	<0.004	0.007	5.1	1.9	7.0	2.0
H ₆ CDF _s	49	<0.004	0.022	4.7	2.5	8.5	3.3
H ₇ CDF _s	16	0.004	0.050	3.3	0.91	10	3.4
O ₈ CDF	7.4	0.017	0.33	5.5	4.1	14	5.9
PCDF _s	150	0.021	0.41	22	11	48	16
PCDD _s + PCDF _s	3500	0.063	0.74	30	20	79	23
TEQ	10	0.00	0.00	0.40	0.13	0.54	0.25

with the furnace ceiling lowered, resulting in the treatment capacity reduction of the furnace.

The utility consumptions per ton of fly ash were 260 L kerosene, 235 Kwh and 2 m³ water. Since these figures depend on the treatment capacity, further reductions are possible for a larger furnace.

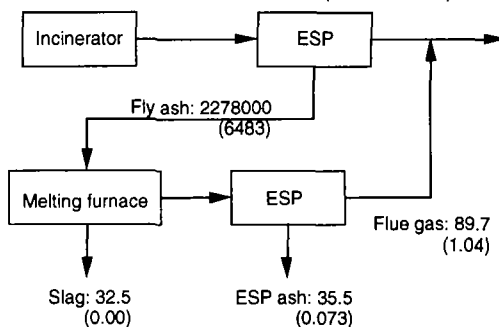
2.3 Concentrations and mass balance of dioxins

PCDD/PCDF concentrations and toxicity equivalents (TEQ) of all solid and flue gas samples are summarized in Table 3. By the melting treatment, dioxin concentration in the input fly ash as high as 3500 ng/g PCDD/PCDF (10 ng TEQ/g) was converted to 0.063 ng/g (0.00 ng TEQ/g) in slag and 0.74 ng/g (0.00 ng TEQ/g) in ESP ash. Fig. 2 represents the mass balance of dioxins around the melting process. Dioxin decomposition efficiency is calculated to be 99.993 % for PCDD/PCDF concentration and 99.983 % for TEQ. This calculation was performed on the assumption that the total outflow of dioxins from the process was equal to the summation of the dioxin amounts in slag, ESP ash and flue gas.

Fig. 3 indicates the distribution of PCDD/PCDF homologues in the input fly ash. PCDDs take 97 % of total dioxins, and especially T₄CDDs have the highest concentration. The feature of the distribution is that the larger the number of chlorines in the compounds, the lower the concentration becomes. The dioxin level of fly ash is much higher and the distribution pattern of dioxins is different compared to the reported ones¹⁾.

Fig. 4 shows the distribution of PCDD/PCDF congeners in the flue gas samples at different points of the melting process. From this distribution, it is found out that the more chlorines the chemical compounds have, the higher the concentrations, and this tendency of PCDDs is greater than that of PCDFs. Besides, entirely the PCDF concentrations are higher than the PCDD ones. Since the distribution in Fig. 4 differs from that of supplied fly ash shown in Fig. 3, it is recognized that the dioxins in the fly ash almost entirely decomposed in the

Decomposition efficiency of PCDD/PCDF: 99.933%
(99.983 TEQ%)



Note: 1. Figures indicate PCDD/PCDF (μg/h).
2. Figures in () indicate TEQ (μg/h).
3. Decomposition efficiency of PCDD/PCDF =
$$\left(1 - \frac{\text{Slag} + \text{ESP ash} + \text{Flue gas}}{\text{Fly ash}}\right) \times 100$$

Fig. 2 Mass balance of PCDD/PCDF of the melting process

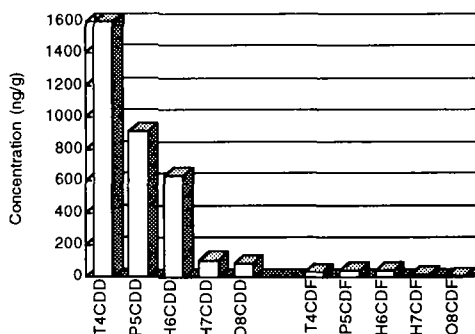


Fig. 3 PCDD/PCDF homologue distribution in the input fly ash

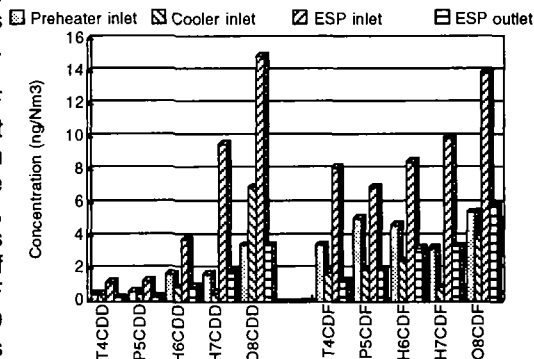


Fig. 4 PCDD/PCDF homologue distribution in flue gas samples at the different points

melting furnace. Fig. 4 indicates, after flowing through the furnace, a small amount of dioxins is generated/decomposed along the flue gas treatment systems. Since the amount is, however, as small as 20 - 30 ng/Nm³, the level of discharged dioxins to the atmosphere can be made low enough by operating the dust collecting system properly.

3. Heavy metals recovery test from ESP ash

3.1 Composition of ESP ash

As shown in Table 1, the main constituents of ESP ash discharged from the melting process are water soluble salts such as Na⁺, K⁺, Cl⁻ and SO₄²⁻, which take approximately 80 % of the total ash weight. Moreover, the melting treatment volatilizes heavy metals with low boiling points such as Cd, Pb and Zn under the high temperature atmosphere, and concentrates them into ESP ash. Percentages of the heavy metals are more than 4 wt-% in ESP ash, which is about the same value as the lower limits of mineral content for metal mining ("cutoff grade"). In contrast, high boiling point materials such as Si, Al, Ca and Fe are only 1 wt-% in total. From these features, heavy metals such as Pb and Zn are expected to be easily extracted in a condensed state by separating water soluble salts from ESP ash. A lab-scale test was conducted to examine the possibility of heavy metals recovery from ESP ash, and the following results are obtained.

3.2. Method of separating heavy metals

The flow diagram of the heavy metals separation method, the "water-cleansing method", is shown in Fig. 5. 100 g ESP ash was mixed with water in the weight ratio of 1 : 9, and stirred for 30 minutes while adjusting the pH value of the mixture to 10.5 with NaOH, and then filtered into filtrate (Filtrate No. 1) and residue (hydroxide sludge). Further, adding some sodium hydrogen sulfur (NaHS) to the filtrate to remove trace heavy metals, Filtrate No. 2 was separated from sulfide sludge. NaHS was added in three weight cases of 0.015 g, 0.03 g and 0.06 g to 100 g ESP ash; Zn, Pb, Cu and Cd contents of the separated filtrates were measured in each case.

3.3 Possibility of heavy metals recovery

The compositions of Filtrate No. 1 and the hydroxide sludge are given in Table 4 and Table 5. Table 6 shows the composition of Filtrate No. 2 and the percentage of NaHS added. Also, Table 7 gives the calculated composition of the mixture of the both sludges. From these results, it is found out that heavy metals are recovered in the sludge concentrated approximately 7 times as much as those in ESP ash. 9 m³ cleansing water and 0.3 kg NaHS are needed to treat a ton of ESP ash. The concentrations of Zn, Pb and Cu are approximately 30 %, which is high enough to be purified into mono-metals by the existing techniques of

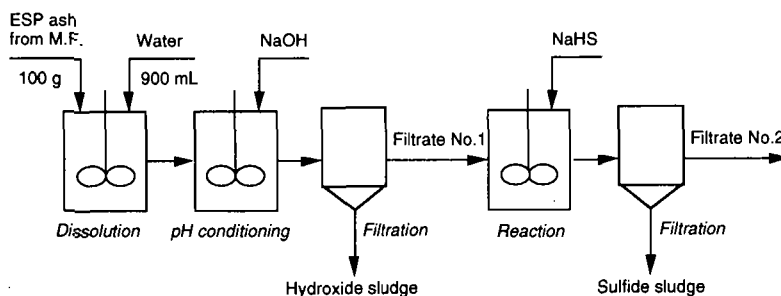


Fig. 5 Flow diagram of heavy metals separation from ESP ash (Water-cleansing method)

Table 4 Composition of Filtrate No.1

Item	Measured value
Amount of filtrate, mL	863
Total dry solid, mg/L	97600
Na, mg/L	21200
K, mg/L	20400
Cl, mg/L	44800
SO ₄ , mg/L	5090
Zn, mg/L	2.92
Pb, mg/L	77.2
Cu, mg/L	2.90
Cd, mg/L	2.35

Table 5 Composition of the hydroxide sludge

Item	Measured value
Sludge production, g	49.3
Sludge moisture, %	70.0
Dried sludge, g	15.3
Soluble salts, %*	50.5
Zn, %*	16.3
Pb, %*	9.34
Cu, %*	1.62
Cd, %*	0.26

* Dry solid basis

Table 6 Composition of Filtrate No.2

Item	Percentage of NaHS addition*, %		
	0.015	0.03	0.06
Zn, mg/L	<0.1	<0.1	<0.1
Pb, mg/L	5.19	<0.1	<0.1
Cu, mg/L	<0.1	<0.1	<0.1
Cd, mg/L	<0.01	<0.01	<0.01

* Weight % of added NaHS to EPS ash

Table 7 Composition of the sulfide sludge
(Calculated value)

Item	Calculated value
Sludge production, g	49.4
Sludge moisture, %	70.1
Dried sludge, g	15.4
Soluble salts, %*	50.5
Zn, %*	16.4
Pb, %*	9.8
Cu, %*	1.64
Cd, %*	0.27

* Dry solid basis

non-ferrous extractive metallurgy. It is also possible to concentrate the separated salt water and obtain solid salts.

4. Conclusions

A two-step treatment method for fly ash from MSW incineration and the test results for each step have been discussed. Conclusions are summarized as follows:

- (1) Fly ash from MSW incineration can be stably melted alone and turned into environmentally safe and reusable slag using the melting treatment process.
- (2) Dioxins in the fly ash are decomposed at a DRE of 99.99 % by the melting treatment.
- (3) Heavy metals with low boiling points are volatilized under the high temperature atmosphere and concentrated in ESP ash from the melting process.
- (4) Sludge with approximately 30 % Zn, Pb and Cu is obtained by washing the ESP ash with water, which is easily recycled to the non-ferrous metal works.

5. References

- 1) M. Hiraoka: Formation and Control of Dioxins in Municipal Solid Waste Treatment, Waste Management Research, The Japan Society of Waste Management Experts, Vol. 1, No. 1, pp. 20-37 (1990)