Decomposition of Dioxins and Related Compounds in MSW Ash Melting Process

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Abstract
In Japan, the ash-melting technology is studied most actively to detoxify and reduce the amount of residue which is generated in municipal solid waste (MSW) incinerators. When this melting technology is used, the total amount of dioxins can be cut down to approximately 0.5 μg per one ton of waste incinerated, which means that the total amount of dioxins released into the environment is reduced to 1/100 or less the amount from conventional incinerators.
Mixing plastic wastes with the ash did not cause the increase of dioxin emission. It is also advantageous in saving fossil fuel required for the melting process.

Introduction
In January, 1997, " Japan's Guidelines for Controlling Dioxins and Dibenzofurans in Municipal Waste Treatment" was revised. It was originally enacted in December, 1990 to cope with the dioxin problems arising from MSW incineration.
The new guideline has given its top priority to the reduction of dioxins in flue gas and their load on the environment and also has outlined a program which consists of four phases aiming at an almost 100% reduction within 20 years. Above all, the guideline has remarkably indicated that all emissions of dioxins including those in ash and flue gas are to be measured and using appropriate technologies, the total emission from MSW incinerator is expected to be reduced to below 5 μg per ton of waste incinerated, which would be equivalent to 1/10 of the present level of the total emission. This measure was derived from the fact that dioxins in bottom and fly ash amount to 80 to 90% of total emission of dioxins from MSW incinerator and also from the estimation that the ratio will continue to rise through thoroughgoing execution of flue gas treatment.
The new guideline has illustrated some technologies for decomposition of dioxins. Among them, the melting technology is considered to be most effective if both decomposition of dioxins and reduction/utilization of the incineration residue are aimed at.

Experimental methods

(1) Test Facility

The configuration of test facility and flow diagram are shown in Fig. 1 and 2. The capacity of the test facility is 20 ash·t/day and fuel gas of 11000 kcal/m^{3}N was used as a heat source. The ash is melted in a high temperature atmosphere of 1200°C or more. The ash after melting is discharged into water to be cooled ; then it becomes chemically stable glass-like slag with 5mm particle diameter.

In this surface melting furnace with a rotation device, the melting materials are continuously fed from a rotating circumference so that the angle of repose of the melting surface formed in the furnace can be maintained automatically. This furnace is allowable to water content of the melting materials so that in most cases no drying process is required. In addition, it has no limitation of the combustibles content of the melting materials.

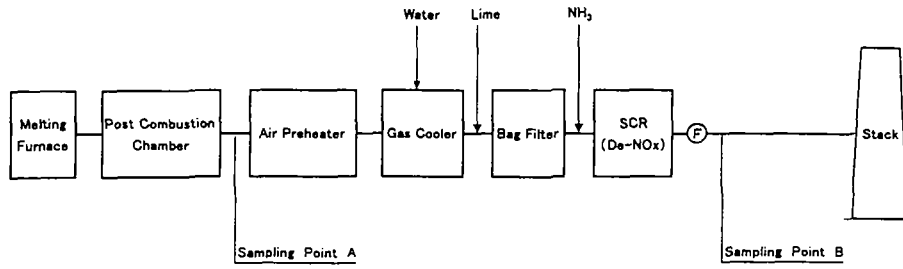

Fig. 1 Flow Diagram and Flue Gas Sampling Points

(2) Properties of Samples

Table 1 shows the properties of the samples used in the test. The bottom ash and fly ash were sampled from the residue generated in the combustible wastes incineration plant of Tokyo Metropolis. Samples of plastic wastes were obtained from sorted wastes collected by Tokyo Metropolis after being crushed and magnetically separated.

Table 1 Properties of Samples

Items		Bottom Ash	Fly Ash	Plastic Wastes
Moisture Content	(%)	32.2	0.3	6.31
Ash Content	(%)	-	-	24.8
Calorific Value	(kcal/kg)	-	-	3,750 ~ 6,150
SiO_2	(%)	31.0	24.6	3.37
Al_2O_3	(%)	14.8	15.2	0.93
CaO	(%)	19.7	20.0	1.84
Na_2O	(%)	3.57	5.44	0.785
K_2O	(%)	1.04	4.18	0.087
ZnO	(mg/kg)	4,480	10,090	1,140
PbO	(mg/kg)	499	1,050	240
T-S	(%)	0.62	2.13	0.13
T-Cl	(%)	0.61	7.03	2.0
Combustibles				
Paper and Woods	(%)	-	-	ca. 30
Plastics	(%)	-	-	ca. 50
Rubber and Leathe	(%)	-	-	ca. 3
Others	(%)	-	-	ca. 17

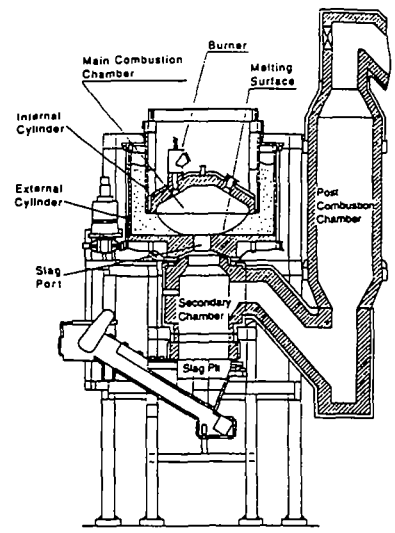

Fig. 2 Sectional View of Surface Melting Furnace

(3) Sampling Points and Analytical Methods

Flue gas sampling points are shown in Fig. 1. The analytical methods of dioxins were referred to the guideline [1]. The sampling and analysis of homologues with low chlorine numbers which have been excluded from TEQ evaluation were referred to the previous report [2].

Results and Discussion

(1) Test Results

Table 2 shows the outlines of the test results. The melting treatment targets the stabilization of heavy metals and decomposition of dioxins contained in the incineration residue. In order to realize these two targets simultaneously, the experiment was executed in such two atmospheres in the furnace that an oxidizing condition was $CO \fallingdotseq 0$ under a few % or more O_2, and a reducing condition was $CO \fallingdotseq$ a few % or more under $O_2 \fallingdotseq 0$.

In respect of dioxins in the slag both under these conditions, only small amount of dioxins with high chlorine numbers of Hepta and Octa were detected, but TEQ was below 0.005ng/g [3]. The result also indicates that the melting treatment under reducing condition is more preferable for restraining the concentrations of lead and zinc in the slag. This observation is consistent with a result of thermodynamics simulation [4]. At this time, the concentrations of HCℓ, SOx, and NOx in the flue gas are reduced to 1/2 or less compared to those under oxidizing condition.

Fig.3 shows the relation between gas temperature and residence time for RUN1 in the course of gas flow from the furnace to the post combustion chamber.

Table 2 Test Conditions and Results

	RUN No.		RUN1		RUN2			RUN3		RUN4	
	Melting Materials		Bottom Ash		Bottom Ash+Fly Ash			Bottom Ash+Plastic Wastes		Bottom Ash+Plastic Wastes	
Operation Results	Capacity(wet-base)	kg/h	776		641+301			431+158		368+332	
	Fuel Gas Consumption	m³/h	192~193		196~197			120~130		50~54	
	Temperatures										
	Main Combustion Chamber	℃	1310~1320		1320~1340			1315~1345		1345~1380	
	Outlet of Post Combustion	℃	900~920		980~995			940~1010		900~930	
	Bag Filter Inlet	℃	170~180		145~150			151~154		148~152	
	Outlet of SCR(De-NOx)	℃	240~255		235~240			220~235		180~190	
	Properties of Flue Gas		Outlet of Post Combustion	Outlet of SCR (De-NOx)	Outlet of Post Combustion		Outlet of SCR (De-NOx)	Outlet of Post Combustion	Outlet of SCR (De-NOx)	Outlet of Post Combustion	Outlet of SCR (De-NOx)
	O_2	%	4.0	10.9	2.7		10.1	3.0	11.0	3.8	10.3
	CO *1	ppm	3	4	35		2	4	3	2	3
	NOx *1	ppm	96	46	84		26	41	19	48	17
	SOx *1	ppm	74	< 1	72		27	35	2 *2	46	3 *2
	HCl *1	ppm	323	10	2060		18	630	< 2 *2	630	15 *2
	Dust	g/m³N	1.02	< 0.001	10.00		0.002	-	<0.001 *2	-	0.001 *2
	Dioxins(ngTEQ/m³N) *1		0.07	0.036	0.019		0.022	0.044	0.046	0.011	0.090
Dioxins and Related Compounds			Bottom Ash	Flue Gas at Outlet of Post Combustion	Bottom Ash	Fly Ash	Flue Gas at Outlet of Post Combustion	Bottom Ash	Flue Gas at Outlet of Post Combustion	Bottom Ash	Flue Gas at Outlet of Post Combustion
			ng/g	ng/m³N	ng/g	ng/g	ng/m³N	ng/g	ng/m³N	ng/g	ng/m³N
	$PCDD_4$		31	1.7	45	70	1.2	45	1.5	45	0.55
	$PCDF_4$		37	4.4	59	270	2.2	59	4.5	59	0.58
	Total		68	6.1	100	340	3.4	100	6.0	100	1.1
	TEQ		0.77	0.070	1.1	4.1	0.019	1.1	0.044	1.1	0.011
	CB_4		480	1900	1000	2700	3900	1000	3700	1000	2800
	CP_4		150	210	380	1100	280	380	150	360	140
	Total		630	2100	1400	3800	4200	1400	3900	1400	2900

Note 1) : The values marked *1 are values converted based on 12% O_2.
2) : The values marked *2 are measured at Bag Filter outlet.
3) : The concentrations of dioxins and related compounds in the flue gas are values converted based on 12% O_2.

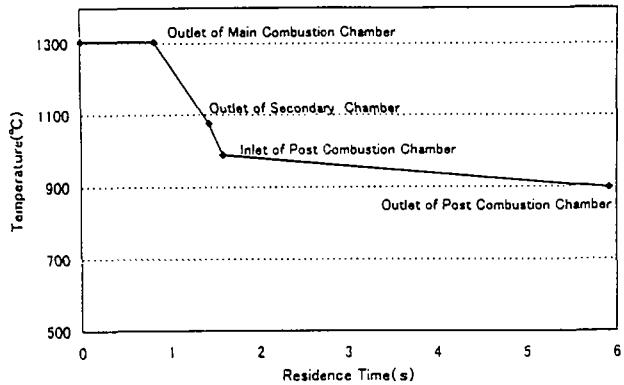

Fig. 3 Flue gas Residence Time and Gas Temperature (RUN 1)

(2) Decomposition of Dioxins and PCBs

Table 3 shows PCBs concentrations for Run 1. Decomposition efficiencies for each homologue of dioxins and related compounds are illustrated in Fig. 4 through 9. As shown in these figures, decomposition efficiencies for homologues with lower numbers of chlorines which are not counted in TEQ were comparatively low. However, high efficiencies were obtained both for PCDDs and PCDFs with high chlorine numbers of greater than Tetra. A shift to homologues with low chlorine numbers by dechlorination was not observed, indicating an effective destruction of the structures of dioxins and furans.

Decomposition efficiencies for PCBs and Co-PCBs also were high as shown in Fig. 6 and 7 and TEQ concentration including Co-PCB contribution (described as TEQ (PCDDs+PCDFs)+TEQ(Co-PCBs)) was below 0.1ng/m^{3}N in the flue gas at the outlet of post combustion chamber.

It is proved that the decomposition of dioxins is 99.9% or more in the melting process and consequently, the total emission per one ton of MSW incinerated from the facility comprising an incinerator and a melting furnace proves to be about 0.5μg which is approximately 1/100 of the amount from conventional incinerators and also is 1/10 of 5μg , the target value of the new guideline.

Table 3 Concentration of PCBs and Co-PCB(RUN 1)

	Items	Bottom Ash ng/g	Outlet Gas of Post Combustion Chamber ng/m^{3}N
PCBs	Mono-PCBs	0.0042	N.D.
	Di-PCBs	0.21	0.41
	Tri-PCBs	0.42	1.8
	Tetra-PCBs	0.74	0.87
	Penta-PCBs	0.51	1.2
	Hexa-PCBs	0.45	0.79
	Hepta-PCBs	0.27	0.28
	Octa-PCBs	0.39	0.16
	Nona-PCBs	0.27	0.062
	Deca-PCBs	0.43	0.090
	PCBs	3.7	5.6
Coplanar-PCBs	3,3',4,4'-Tetra-PCB	0.14	0.075
	2',3,4,4',5-Penta-PCB	0.011	0.005
	2,3',4,4',5-Penta-PCB	0.068	0.29
	2,3,4,4',5-Penta-PCB	0.012	0.015
	2,3,3',4,4'-Penta-PCB	0.072	0.17
	3,3',4,4',5-Penta-PCB	0.14	0.038
	2,3',4,4',5,5'-Hexa-PCB	0.027	0.022
	2,3,3',4,4',5-Hexa-PCB	0.10	0.078
	2,3,3',4,4',5-Hexa-PCB	0.035	0.0089
	3,3',4,4',5,5'-Hexa-PCB	0.074	0.01
	2,2',3,4,4',5,5'-Hepta-PCB	0.026	0.03
	2,2',3,3',4,4',5-Hepta-PCB	0.032	0.079
	2,3,3',4,4',5,5'-Hepta-PCB	0.10	0.076
	Coplanar-PCBs	0.84	0.90
	TEQ	0.015	0.0041

Note 1) : The concentrations of PCBs and Co-PCBs in the flue gas are converted values based on 12% O_2

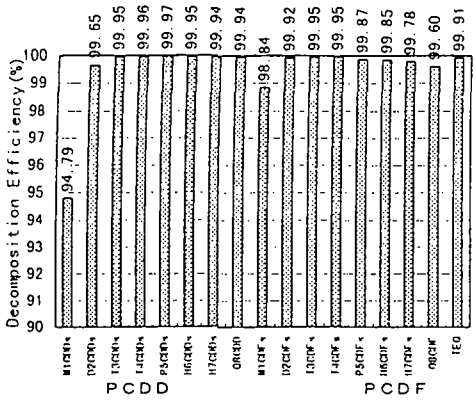

Fig. 4 Decomposition Efficiency of Dioxins (RUN1)

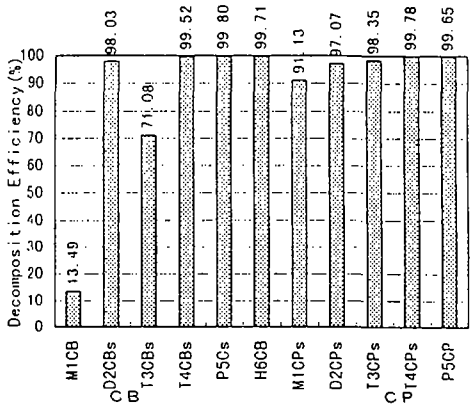

Fig. 5 Decomposition Efficiency of Dioxins Precursors (RUN1)

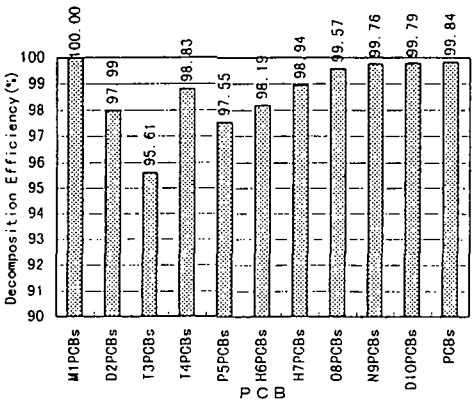

Fig. 6 Decomposition Efficiency of PCBs (RUN1)

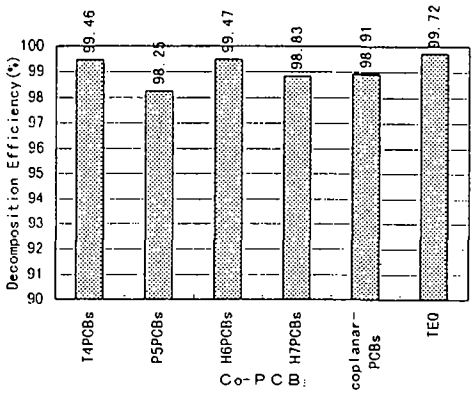

Fig. 7 Decomposition Efficiency of Co-PCBs (RUN1)

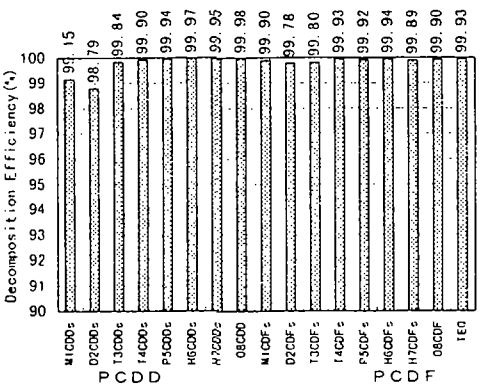

Fig. 8 Decomposition Efficiency of Dioxins (RUN3)

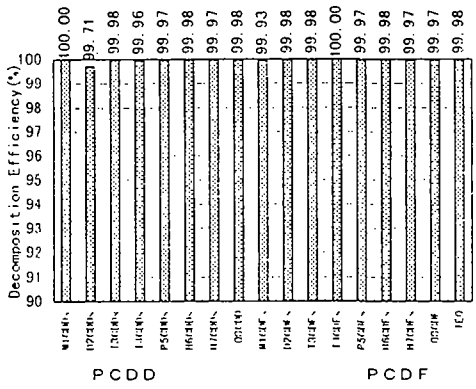

Fig. 9 Decomposition Efficiency of Dioxins (RUN4)

(3) Effect of Plastic Wastes

Plastic wastes contained approximately 50% of plastics. However, notwithstanding the fact that the mixing ratio of the plastic wastes to the ash increased, dioxin and related compounds measured at the outlet of melting furnace did not increase from the case in which only bottom ash was melted and as a result the decomposition efficiency of the same level was obtained.

Table 4 Flue Gas Constituents at Outlet of Melting Furnace

Constituents	Units	Concentrations
H_2	%	12.4
CO	%	7.2
CO_2	%	13.3
T-HC	ppm as C	5.9

In a range where the water vapor partial pressure is high with a temperature of higher than 1000℃, a carbonaceous material forms water gas which consists mainly of H_2 and CO. In this study as well, the water vapor partial pressure was as high as P_{H_2O}=0.2 and the furnace temperature was approximately 1300℃. This brought about a gas composition, measured at the outlet of the furnace, of H_2 12.4%, CO 7.2%, CO_2 13.3%, and THC 5.9ppm as C as shown in Table 4. The concentration of total hydrocarbons(THC) was fairly low even under the reducing condition, which possibly supports a presumption mentioned above. All this leads to a conclusion that even plastic wastes can be treated without increasing emissions of dioxins and related compounds through this system, to say nothing of carbonaceous combustible materials. The results shown in Table 2 are consistent with this conclusion. Table 2 further indicates that the consumption of fuel gas used as a subsidiary fuel decreases in inverse proportion to the increase of the mixing ratio of the plastic wastes.

Conclusions

Melting tests of ash from a MSW incinerator were implemented employing a 20 ash·t/day test facility. Conclusions are summarized as follows.

(1) Ash melting technology achieves both detoxification and reduction of the amount of incineration residue (bottom ash and fly ash). Dioxins in the ash were decomposed at a efficiency of greater than 99% by a melting process.

(2)More than 99% of PCBs and Co-PCBs was decomposed in the same way as dioxins.

(3)Mixing plastic wastes into the bottom ash did not cause the increase of the emission of dioxins and related compounds, and the decomposition efficiency was almost at the same level with the melting of ash only.

(4)Owing to decomposition of dioxins in the ash by a melting process, total emission of dioxins to the environment is expected to be reduced to 0.5 μg per ton of MSW incinerated; approximately 1/100 of the amount from conventional incinerators.

Literature Cited

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