POLYBROMINATED SUBSTANCES IN WASTE ELECTRICAL & ELECTRONIC PLASTICS AND THEIR BEHAVIOR IN THE INCINERATION PLANTS

Shin-ichi Sakai[1], Yoshiharu Honda[2], Hiroshi Takatsuki[2], Jun Watanabe[2], Isamu Aoki[3], Kazuo Nakamura[4], and Ken Shiozaki[5]

[1]National Institute for Environmental Studies, Tsukuba 305-8506, Japan
[2]Kyoto University, Environment Preservation Center, Kyoto 606-8501,Japan
[3]Urban Infrastructure Engineering Company, Kobe Steel Ltd., Hyogo 657-0845, Japan
[4] Kyoto Municipal Government, Kyoto 604-8571,Japan
[5]Kaneka Techno Research Corporation, Kobe, Japan

Introduction

Recognized that PBDDs/DFs were formed when products contaminating organic brominated flame retardants such like PBDEs were heated, there have been concerned in recent years that those hazardous substances might have adverse impacts on the environment and human health.[1)] Particularly, it has been pointed out that organic brominated flame retardants that were added in the plastics gave rise to PBDDs/DFs by the thermal processing of shaping the plastics, and then remained PBDDs/DFs in the products. From the previous researches, it was identified that PBDDs/DFs at ppm level were contained in the flame retardants products. [2)]

In this study, we took up the total number of 15 waste TVs and waste PCs as samples of waste plastics in order to investigate the contaminated level of organic compounds, mainly PBDDs/DFs, and to consider the time trend profile by the date of manufacture. In addition, the behavior of PBDDs/DFs during the incineration process was investigated at the full-scale incineration facilities.

Materials and Methods

13 waste TVs and 2 waste PCs (made by 9 manufacturers in 1984 ~1998) were obtained as samples at the Kyoto City Clean Center. The casing parts of the samples were crushed into pieces to serve the characterization of the type of polymer resin by infrared absorption spectrometry and organic compounds like PBDDs/DFs, PCDDs/DFs and PBDEs.

And we investigated PBDDs/DFs emission in the full-scale municipal solid waste incinerators at the 3 facilities, which had stocker type incinerators in the continuous operation with different type of flue gas treatment equipment (facility A[3)], B[4)] and C[5)]). Facility A used electrostatic precipitator and facility B and C used bag filtering dust collectors. Facility A, which had an incineration capacity of 200ton/day, was set up three conditions by letting input waste qualities change. Case 1 was that domestic waste only was incinerated. Case 2 was that domestic waste mixed with shredded bulky

waste for quarter the whole amounts, and Case 3 was that crushed electrical appliances waste by half. Facility B had incinerator with a capacity of 85ton/day. At this site domestic waste mixed with both plastic waste at 6% and shredded bulky waste at 6% were burned. Facility C had incinerator with a capacity of 160ton/day and domestic waste almost without any other crushed ones were incinerated. PBDDs/DFs concentrations were measured in flue gas, incinerated bottom ashes and fly ashes at these three facilities.

Results and Discussion

Organic brominated compounds in electrical and electronic plastics and their time trend

Table 1 shows the concentration of organic compounds in the waste TVs and waste PCs casings. As the main resin materials, 2 TVs manufactured in the 1980s used polypropylene and the other 11 TVs and 2 PCs in the 1990s used polystyrene resin respectively. In terms of PBDDs/DFs, 9.8~170ng/g were detected in the 2 TVs made in 1984. On the other hand, 2,000~200,000ng/g were found in the other 11 TVs at ppm level.

Table 1 Analytical Results of Waste Electrical Appliances

	Manufacturers	Date of Manufacture	PCDDs	PCDFs	PCDDs/DFs	Co-PCBs	PBDDs	PBDFs	PBDDs/DFs	PBDEs	Resin
			ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	
TV1	N	84 first half	-	-	-	-	ND	9.8	9.8	-	Polypropylene
TV2	N	90 latter half	0.66 (0.027)	4.3 (0.050)	5.0 (0.077)	0.43 (0.000043)	0.33	21,000	21,000	290,000	Polystyrene resin (HIPS)
TV3	N	97 latter half	ND (0)	ND (0)	ND (0)	0.69 (0.000069)	1,300	670	2,000	ND	Polystyrene resin (HIPS)
TV4	S	92 latter half	ND (0)	ND (0)	ND (0)	0.32 (0.000032)	55	200,000	200,000	7,100,000	Polystyrene resin (HIPS)
TV5	M	84 first half	-	-	-	-	0.73	170	170	-	Polypropylene
TV6	M	91 latter half	-	-	-	-	34	43,000	43,000	5,400,000	Polystyrene resin (HIPS)
TV7	M	96 latter half	-	-	-	-	2.6	11,000	11,000	120,000	Polystyrene resin (HIPS)
TV8	M	97 first half	-	-	-	-	3.6	14,000	14,000	260,000	Polystyrene resin (HIPS)
TV9	T	91 latter half	-	-	-	-	0.30	41,000	41,000	87,000	Polystyrene resin (HIPS)
TV10	V	91 latter half	-	-	-	-	0.92	37,000	37,000	110,000	Polystyrene resin (HIPS)
TV11	F	94 first half	-	-	-	-	3.5	22,000	22,000	440,000	Polystyrene resin (HIPS)
TV12	F	98 first half	-	-	-	-	9.1	14,000	14,000	1,200,000	Polystyrene resin (HIPS)
TV13	H	91 first half	-	-	-	-	ND	24,000	24,000	770,000	Polystyrene resin (HIPS)
PC1	A	98 August	-	-	-	-	0.30	580	580	300,000	Polystyrene resin+ Titanium oxide
PC2	N'	unidentified	-	-	-	-	0.72	390	390	1,100,000	Polystyrene resin+ Titanium oxide

TEQ values are parenthesized. [ngTEQ/g]

From the standpoint of manufacturing year, values of 7 TVs made in early 1990s(1990~1994) showed 21,000~200,000ng/g and values of 4 TVs in late 1990s were 2,000~14,000ng/g. PBDEs was contained at the range of 87~7,100μg/g in all samples except TV 3 made in 1997,by N company. Comparing TV 3 with other waste TVs made in the 1990s, TV 3 indicated the lowest level of PBDEs. Because the 2 TVs contained PBDEs, which made by the same company and were older than TV 3 (made in 1990), it is presumed that a kind of flame retardants had changed during 1990 to 1997. PBDDs/DFs contaminated level peaked in early 1990s, and then the level was a bit on the decrease in late 1990s.

Behavior of PBDDs/DFs in full-scale municipal solid waste incineration plants

Table 2 shows the results of PBDDs/DFs measured in each full-scale municipal solid waste incineration plants. Facility A indicates that the concentration of released PBDDs/DFs was on the increase if the mixed rate of shredded bulky waste was up. By contrast, it shows that the concentration was lower if the rate of shredded bulky waste was low.

Table 2 PBDDs/DFs in Each Full-Scale Municipal Solid Waste Incineration Plant

		Input Waste (ng/g)	Flue Gas (ng/Nm^3)	Incineration Residues (ng/g)	
				Bottom Ash	Fly Ash
FacilityA	Domestic Waste Combustion	-	1.5	0.24	0.46
	Shredded Busky Waste mixed at 25%	-	3.3	7.0~8.8 *1	1.3~13 *1
	Crushed Electrical Appliances Waste mixed at 50%	-	19	27	12
FacilityB	Domestic waste mixed with a small amount of crushed bulky waste	0.53~1.4 / 2.9 *	0.39	0.0058	0.30
FailityC	Mainly Domestic Waste	0.030~0.40 *3	0.28	0.012	0.082

Values of Facility A and C are total oncentration of Mo-OcBDDs/Fs
Values of Facility B is total concentration of Mo-HxBDDs/DFs
*1 Measurements,two times (n=2)
*2 Concentration of Domestic Waste (n=2) /Crushed Waste (n=1)
*3 Concentration of DomesticWaste (n=3)

The input and output of PBDDs/DFs per ton waste were calculated from the concentrations of PBDDs/DFs measured at each facility (Table 3). However, PBDDs/DFs in the waste were not measured at Facility A, so that decomposition rate as system was not available. The high efficient flue gas system such as Facility B and C resulted in approximately 90% decomposition rates as system. In regard to Facility A, the increase of the output would keep pace with the input. Therefore, the further decomposition, including the high-temperature melting[6], would be worthwhile being considered positively, in case that the incineration residues were generated by mixed combustion of shredded bulky waste.

Table 3 Input and Output of PBDDs/DFs in the Municipal Waste Incineration Plants

		Input	Output				Decompostion Rate as System
			Total	Flue Gas	Bottom Ash	Fly Ash	
Facility A	Domestic Waste Combustion	550	64	21	28	15	-
	Shredded Bulky Waste mixed at 25%	1,000*	993-1,439	17	952-1,197	22-225	-
	Crushed Electrical Appliances Waste mixed at 50%	1,700,000 **	3,935	129	269	3,537	-
Facility B	Domestic Waste with a small amount of Bulky Waste	240-850	12	2.8	0.53	9.1	95-99%
Facility C	Mainly Domestic Waste	18-250	3.9	1.5	0.56	1.8	78-98%

Unit: μ g/ton waste, *Presumption values from Facility B

**Presumption in waste TV casings mixed for 10% within the crushed electrical appliances waste

Acknowledgements

This research was financially supported by the Health Science Research Grant of the Ministry of Health, Labour and Welfare, 1999, " Studies on behavior and control of dioxins in the process of waste management" as one of researches organized by the Japan Waste Research Foundation. The authors express a gratitude for the parties concerned.

References

1) WHO, Polybrominated dibenzo-*p*-dioxins and dibenzofurans, *Environmental Health Criteria,* **1998,** 205

2) Sakai, S. *Organohalogen Compounds*, **2000,** 47, 210.

3) Waste research association, *Studies of hazardous waste and chemical materials cycle,* **1998,1999,** (in Japanese).

4) Shibakawa, S., Tejima, H., Eguchi, K., Sakai, S., *Pro.of 11th National Conf. of Japan Society of Waste Management Experts*, **2000,** 703-705, (in Japanese).

5) Kawakami, I., Sano, E., Sakai, S., Yagi, Y., *Pro.of 11th National Conf. of Japan Society of Waste Management Experts*, **2000,** 697-699, (in Japanese).

6) Sakai, S. The Second International Workshop on Brominated Flame Retardants, **2001.**