A STUDY OF BROMINATED COMPOUND RELEASE FROM APPLIANCE-RECYCLING FACILITY

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Introduction

Japan put into effect its "Electric Household Appliance Recycling Law" (Appliance Recycling Law) in April of 2001. Braun tubes TV sets, refrigerators, washing machines and air-conditioners that were discarded by the household must be recycled to achieve a certain recycling rate (TV: 55 %, refrigerators: 50 %, washing machines: 50 % and air-conditioners: 60 %. These % mean not less than numbers.). The possibility of appliance-recycling facilities releasing brominated compounds that are contained in the back cover of TV sets, etc., has become a matter of concern.[1-3)] We, therefore, have undertaken to check such release from an appliance-recycling facility, and an adjoining waste incineration plant that was burning the residues from appliance recycling facility.

Methods and Materials

For the study, we have chosen a recycling facility built in 2000 with the throughput of 75T/10.5H and an adjoining incineration plant of 150T/24H capacity.

The first study (2000) was centered on the brominated compound release from the appliance recycling facility. The neighboring incinerator was burning residues and Refuse Derived Fuel(RDF) from the recycling facility, and was using the exhaust from the recycling facility as its combustion air, and treating it at a high temperature. Therefore, the bottom ash, fly ash and flue gas of the incinerator were also analyzed. At the second test (2001), TV back covers and the dust collected from inside the TV sets were analyzed, and sorted according to the period of manufacture (second half 80's, first half 90's, and second half 90's). Figure 1 shows the flow sheet of the appliance recycling facility and the waste incineration plant.

Extraction and clean up

All samples were used for determination of polybrominated diphenyl ethers (PBDEs), polybrominated dibenzo-*p*-dioxins (PBDDs), polybrominated dibenzofurans (PBDFs) and tetrabromo bisphenol A (TBBPA) by HRGC/HRMS. Flue gas, fly ash, bottom ash, and dust sample was subjected into Soxhlet extraction for 16 hrs using toluene with accordance to JIS K 0311 which is standard method for PCDD/DF analysis, with only exception of extraction conducted under dark conditions. In case of TV casing samples, it was melted by toluene for overnight and extracted.

The extracted solvent was further subjected into column chromatography after spiking individual congeners of $^{13}C_{12}$-labled PBDEs, PBDD/DFs or TBBPA as internal standards. Additionally plastic samples were added with hexane for solidifying resin and subjected into H_2SO_4 digestion prior to column chromatography. For separations, multi layer silicagel, alumia and carbon column

chromatograms which is similar to PCDD/DF analytical method with slight modification of elution solution was prepared to further separate PBDEs and PBDD/DFs. In case of TBBPA analysis, trimethylsilyl (TMS) derivative procedure by BSTFA was followed.

Analysis

Analysis of samples were conducted in HRGC/HRMS Micromass Autospec Ultima with a Hewlett Packard HP 6980 series with a DB-5 MS (60 or 30m, 0.32 or 0.25mm, 0.25 or 0.1μm) capillary column for all the brominated chemicals. The MS was operated in selected ion monitoring mode (SIM) at a resolution >10, 000. Two or more predominant ions were monitored for each congener group.

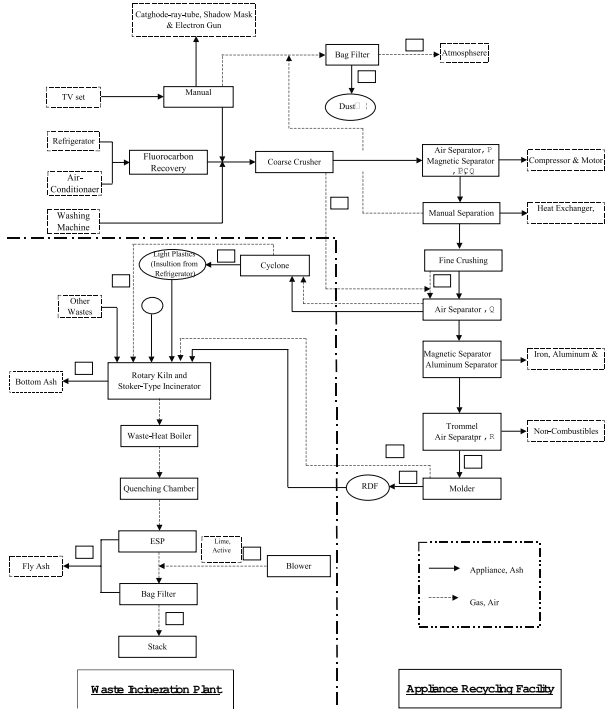


Figure 1. Flow Chart of Appliance Recycling Facility and Waste Incineration Plant

Results and Discussion

1. *TV set back cover and the dust inside TV set*

The results of analysis according to the period are shown in Table 1. For reference, dust from indoor units of air conditioners was also analyzed.

- The amounts of dust inside TV sets varied by each unit, with older sets generally containing more.
- The back cover analysis averaged 280μg/g of PBDDs/DFs4-8, and 68,000μg/g of PBDE. The dust likewise showed 4.1μg/g and 230μg/g, respectively.
- The TBBP-A contents of TV set back covers increased as the period of manufacture became more recent. They were 11μg/g for 2nd half of 1980's, 340μg/g for 1st half of 1990's and 21,000μg/g for 2nd half of 1990's. Similarly, those of the dust rose, 4.1μg/g, 11μg/g and 37μg/g, respectively.

Table 1. Analyses of TV Back Cover and Dust from inside TV set

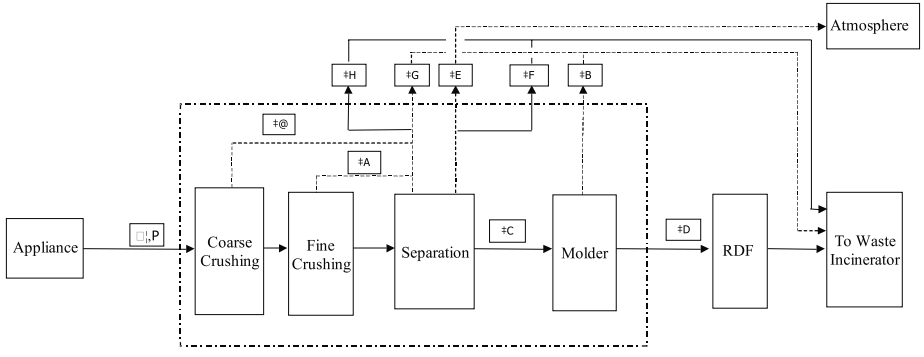
Sample		Dust from inside TV set				Dust from A/C	TV Back Cover			
Period		2nd Half 80's	1st half 90's	2nd half 90's	Average		2nd half 80's	1st half 90's	2nd half 90's	Average
Brand x Units		Brand Ax4	Brand Ax3	Brand Cx1		Brand Bx1	Brand Ax4	Brand Ax3	Brand Cx1	
		Brand Bx4	Brand Bx2	Misc.x8		Misc.x1	Brand Ax4	Brand Bx2	Misc.x8	
		Brand Cx1	Brand Cx1				Brand Cx1	Brand Cx1		
	,	R	Misc.x					Misc.x3		
Amount of Dust	g/Unit	2.78	1.75	1.60	2.05	1.16				
PBDD, fDF, 4-8	ng/g	8,500	1,600	2,100	4,100	7.7	100,000	240,000	510,000	280,000
PBDD, fDF, 4-8	ng/g	8,500	1,600	2,100	4,100	5.9	100,000	240,000	510,000	280,000
PBDEs	ng/g	200,000	160,000	320,000	230,000	4,200	36,000,000	91,000,000	77,000,000	68,000,000
TBBP-A	ng/g	4,100	11,000	37,000	17,000	150	11,000	3,400,000	21,000,000	8,100,000

2**.** *Material Balance at the Facilities*

The material balance of PBDDs/DFs4-8, PBDEs and TBBP-A derived from the results of analyses at the recycling facility and at the incineration plant are shown in Fig.2 and Fig.3, respectively. The gas volume and treated volume are based on the design values. The input at the recycling facility was based only on TV sets, and other wastes incinerated at the incineration plant was presumed to be MSW.

2-1 *Appliance Recycling Facility*

• The exhaust (3) from the molder produced higher concentrations and larger amounts of PBDDs/DFs, PBDE and TBBP-A compared with others [1, 2, B and G]. This seems to indicate that the grinding, abrasion and heating (heater temp:160 ºC)in the molder caused evaporation of brominated compounds.



		INPUT	OUTPUT										OUT/IN Ratio
		□¦,P Appliance	‡@ Rough Crusher Exhaust	‡A Fine Crusher Exhaust	‡C Waste Plastics	‡F BF Dust	‡G Air to Incinerator	‡E BF Outlet	‡H Light Plastics	‡B Molder Exhaust	‡D RDF	Total	
Gas Volume, Throuput	m^3N/h □(/h	0.35	1,120	560	1.53	0.000072	4,200	24,000	0.0045	4,470	1.53		
PBDDs/DFs4-8 Concentration	ng/m^3N □(ng/g	180,000	0.46	3.2	1.0	11	2.3	0.019	6.4	7.5	10,000		
PBDDs/DFs4-8 Content	mg/h	63,000	0.00052	0.0018	1.5	0.00079	0.01	0.00046	0.03	0.034	15,000	15,000	0.24
PBDEs Concentration	ng/m^3N □(ng/g	59,000,000	39	83	350	8,300	280	2.4	7,600	1,100	540,000		
PBDEs Content	mg/h	21,000,000	0.044	0.046	540	0.6	1.2	0.058	34	5	830,000	830,000	0.040
TBBP-A Concentration	ng/m^3N □(ng/g	3,000,000	32	99	680	4,300	600	5.5	740	4,500	140,000		
TBBP-A Content	mg/h	1,100,000	0.036	0.055	1,000	0.3	2.5	0.13	3.3	20	210,000	210,000	0.19

(□¦,P□fV Cover only □Each concentration data is calculated by weighted average of each piriod numbers □j

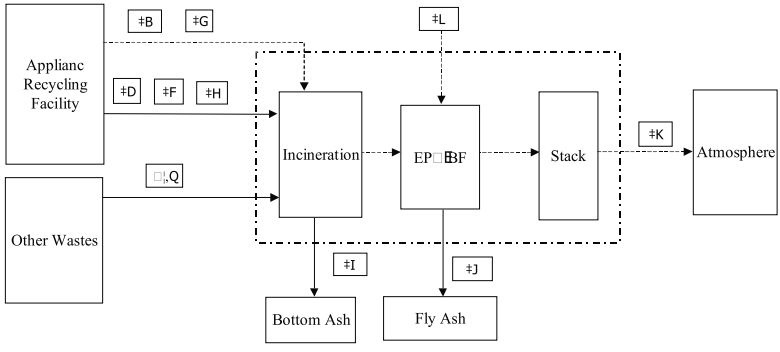
Figure 2. Brominated Compound Material in Appliance Recycling Facility

2-2 *Waste Incinerator*

• The input for the incinerator included RDF, exhaust gas frow Molder and other residues from the recycling facility. However, the throughput and discharge from the recycling facility vary widely,

not as constant as those of the incinerator. Judging from the operational record, therefore, the maximum amount of RDF was set at the design value and the minimum at one-twentieth of the same.

• The input of PBDDs/DFs in the incinerator material balance was within 330~6,700mg/h while its output was 0.61mg/h, showing decreases of 1/500~1/11,000. Similarly, PBDE declined by 1/80~1/1,600 and TBBP-A by 1/500~1/9,000. These facts indicate that the incinerator doubles as a disintegrator of brominated compounds.



		INPUT								OUTPUT				OUT/IN Ratio
		‡D RDF	‡F BF Dust	‡H Light Plastics	‡B Molder Exhaust	‡G Combustion Air	‡L Blower Outlet	□¦,Q Other Waste	Total	‡I Bottom Ash	‡J Fly Ash	‡K Flue Gas	Total	
Gas Volume, Throughput	m^3N/h □@h	0.033 □ 0.67	0.0000315	0.002	1,960	4,200	1,920	5.58		0.34	0.26	49,700		
PBDDs/DFs4-8 Concentration	ng/m^3N □@g/g	10,000	11	6.4	7.5	2.3	N.D	0.16		1.7	0.12	0.014		
PBDDs/DFs4-8 Content	mg/h	330 □ 6,700	0.00035	0.013	0.015	0.01	0	0.89	330 □ 6,700	0.58	0.031	0.0007	0.61	0.00009 1 □ 0.0018
PBDEs Concentration	ng/m^3N □@g/g	540,000	8,300	7,600	1,100	280	38	9.4		300	470	3.5		
PBDEs Content	mg/h	18,000 □ 360,000	0.26	15	2.2	1.2	0.073	52	18000 □ 360000	100	120	0.17	220	0.00061 □ 0.012
TBBP-A Concentration	ng/m^3N □@g/g	140,000	4,300	740	4,500	600	2.0	280		20	1.3	8		
TBBP-A Content	mg/h	4,600 □ 94,000	0.14	1.5	8.8	2.5	0.0038	1,600	6,200 □ 96,000	6.8	3.4	0.40	11	0.00011 □ 0.0018

□¦,Q□Other wastes incinerated at the incineration plant was presumed to be MSW.

Figure 3. Brominated Compound Material Balance in Waste Incinerator

Acknowledgements

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