

DIOXIN-RELATED COMPOUNDS, BROMINATED FLAME RETARDANTS AND HEAVY METALS IN AUTOMOBILE SHREDDER RESIDUE (ASR) AND THEIR BEHAVIOR IN HIGH-TEMPERATURE MELTING PROCESS

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Introduction

In Japan, approximately 4 million cars are disposed every year. About 75 to 80 % wt of the end-of-life vehicle (ELV) is recycled, but the final remainder called automobile shredder residue (ASR) is mostly disposed in landfills. The problem is that limited availability of landfill causes costly and even illegal disposal of ASR. Such a concern prompted a review of the current recycling system, and the government implemented "Automobile Recycling Law", which was enforced on January 1st, 2005. Accordingly, automobile and recycle companies have made various efforts to reduce amount of ASR in the recycling processes of ELV. On the other hand, ASR constitutes many complex materials including heavy metals and various flame-retarded plastics. Therefore, ASR can play a role as a potential source of hazardous chemicals including brominated flame retardants (BFRs), and may have the potential to produce dioxin-related compounds such as brominated dioxins in thermal treatment processes¹. Detailed analysis of hazardous chemicals in ASR should be required to assess their risk in the recycle process and to establish suitable treatment methods.

In this study, BFRs, dioxin-related compounds and heavy metals in ASR were analyzed with the material component analysis to understand its properties. In addition, Direct Melting System (DMS), shaft furnace type high-temperature gasification and melting technology, was applied for the treatment of ASR. DMS has been reported to be effective to decompose BFRs and to suppress the formation of dioxin-related compounds in the thermal treatment for municipal solid wastes (MSW) with a benefit to produce *slag* and *metal* as incombustible byproducts that can be used as resources². In this study, behavior of dioxin-related compounds, BFRs and heavy metals in the high-temperature melting treatment of ASR by DMS was investigated using a full-scale testing plant, and the result was compared with those reported in the treatment of MSW including waste TV casing².

Materials and Methods

Collection of ASR

Approximately 15 tons of ASR was collected from a recycle company and stored in the stockyard of the testing plant. For the material component and chemical analysis, total 107 kg of ASR samples were collected by a sampling shovel (~35 L of capacity) from 15 points in the stockyard following the method of JIS K0060 "Sampling Method of Industrial Waste"³. Then, the ASR sample was sieved by 5-mm mesh screen and manually separated into individual components such as plastics, rubber, polyurethane foam, textile, wire, metals, etc. Each component was weighed and crushed into <1.0 mm. Then, the sub-samples from each component were mixed together based on the weight % of each component. This remixed sample was again crushed into <0.25 mm and employed for chemical analysis.

Direct Melting System

Melting treatment of ASR was performed at more than approx. 1500 °C with a coke-bed gasification

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furnace (Figure 1). In this system, the addition of small amounts of coke and limestone flux to the melting furnace makes it possible to directly melt the wastes containing incombustibles at high temperatures, allowing all *slag* and *metal* byproducts to be effectively utilized as resources. The gas generated from thermal decomposition in the melting furnace is completely combusted in a downstream combustion chamber. The waste gas is then discharged from a stack after rapid cooling by a gas cooler, dedusting by a low-temperature bag filter, and waste gas decomposition in a catalytic reactor. Operating data in the melting treatment of ASR are shown in Table 1. During the experiment, flue gas, *slag*, *metal* and fly ash samples were collected (sampling points of these products are shown in Figure 1).

Chemical Analysis

Major elements (e.g., Cl, Br, S, Ca, Si, Al, Na, K) and heavy metals (e.g., Pb, Cd, As, Se, Fe, Cu, Zn, Sb,) in ASR, *slag*, *metal* and fly ash were measured by AAS, ICP-AES and ICP-MS. Moisture, combustible and ash contents and low heat value (LHV) in ASR were also analyzed. Hydrochloric (HCl) and bromic acids (HBr), NO_x, SO_x and CO were analyzed in flue gas samples with heavy metals. BFRs such as polybrominated diphenyl ethers (PBDEs) and tetrabromobisphenol-A (TBBP-A) and dioxin-related compounds including polychlorinated (PCDDs/DFs), polybrominated (PBDDs/DFs) and monobromo-polychlorinated dibenzo-*p*-dioxins and dibenzofurans (MoBPCDDs/DFs) and polychlorinated biphenyls (PCBs) were analyzed in ASR, *slag*, *metal*, fly ash and flue gas samples following the method described elsewhere⁴.

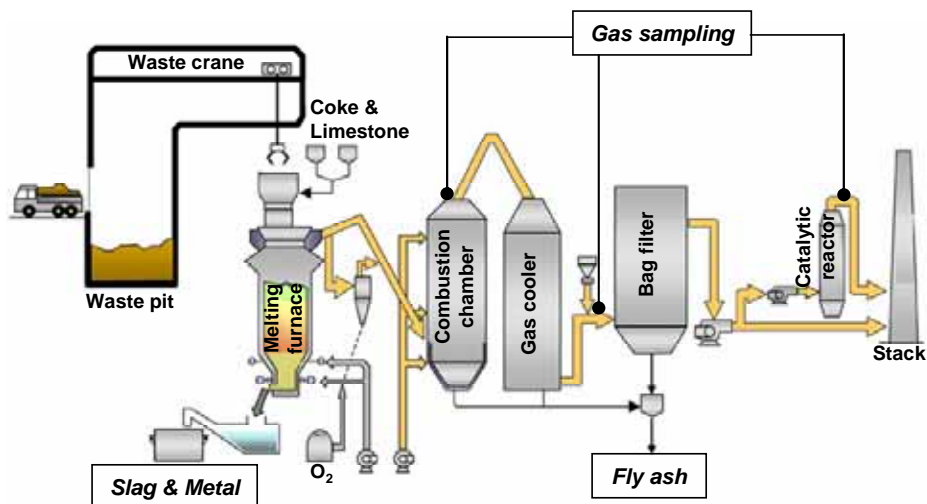


Figure 1. Flow chart of testing plant of coke-bed gasification DMS and sampling points of flue gas, *slag*, *metal* and fly ash

Table 1. Operating data for the treatment of ASR by DMS (data averaged over 24-hours in stable state)

	Unit	Data
Treated amount of ASR	t/24h	9.4
Production rate of incombustible materials	kg/t -ASR	390
Production rate of <i>slag</i>	kg/t -ASR	260
Production rate of <i>metal</i>	kg/t -ASR	120
Production rate of fly ash	kg/t -ASR	44
Production rate of exhaust gas	m ³ N (12%O ₂ dry) /t -ASR	11000
Temperature at combustion chamber	°C	960
Concentration of oxygen in flue gas	% dry	14

Results and Discussion

Material component of ASR

After sieving by 5-mm mesh screen, 70.1 % of total weight of the ASR sample remained above the screen. The ASR sample above 5-mm consisted of plastics (41.6 %), inseparable complexes (20.9%), rubbers (13.4 %), urethanes (7.1 %), textiles (5.2 %), wires (5.0 %), metals (3.2 %), papers (1.3 %), and other unclassified material (2.3%). ASR showed high LHV (5170 kcal/kg = 21500 kJ/kg) with high combustible (68.1 %) and ash contents (30.7 %).

Concentrations and behaviors of major elements and heavy metals

Table 2 shows concentrations of major elements, heavy metals, dioxin-related compounds and BFRs in ASR and in fly ash, *slag* and *metal* that were produced in the ASR treatment.

Although ASR contained considerable amount of halogens and some heavy metals, their concentrations in the byproduct *slag* were apparently lower than those in ASR and fly ash. Concentrations of toxic heavy metals detected in *slag* were below the environmental guidelines for soil in Japan. Toxic or less valuable elements, halogens, sulfur, Pb, Cd and Zn, were enriched into fly ash (non-recyclable material), while valuable metals, Fe and Cu, were retained in the byproduct *metal*.

In the flue gas sample collected at the end of the catalytic reactor, concentrations of all the heavy metals, SO_x and HBr were below the detection limits, and concentrations of HCl, NO_x and CO were detected at 13 ppm, 111 ppm and 4 ppm, respectively.

Concentrations and behaviors of BFRs and dioxin-related compounds

As shown in Table 2, concentrations of PBDEs were the highest in ASR and followed by the rest in the order TBBP-A > PCBs > PBDDs/DFs = coplanar PCBs > PCDDs/DFs. Among the congeners of PBDEs and PBDDs/DFs detected in ASR, higher brominated congeners such as decabromodipheylether (DeBDE) and octabrominated dibenzofurans (OBDF) showed the highest proportions. Such congener patterns of BFRs and PBDDs/DFs in ASR were similar to those reported in BFR-treated plastics like waste TV casings collected in Japan¹⁻³. In addition, a relatively high concentration of PCBs and its congener profile (higher proportions of tetra- and pentachlorobiphenyls) in ASR suggest that its potential sources are technical PCB mixtures (i.e. KC-400 and KC-500) used in electrical equipments such as capacitors.

Concentrations of BFRs, PBDDs/DFs and PCBs in byproducts *slag* and *metal* and in fly ash were apparently lower than those in ASR, suggesting their decomposition in the treatment of ASR by DMS. Concentrations of PCDDs/DFs and MoBPCDDs/DFs in *slag* and *metal* were also lower than those in ASR. On the other hand, concentrations of PCDDs/DFs and MoBPCDDs/DFs in fly ash were higher than those in ASR, suggesting the *de novo* formation of these dioxins during the cooling process. A similar result was also observed in a previous study on the melting treatment of MSW including waste TV casing (and only MSW) by DMS².

At the end of the catalytic reactor, concentrations of PCDDs/DFs, coplanar-PCBs, PBDDs/DFs, TBBP-A and PCBs in the flue gas were detected at values of 0.15 ng/Nm³ (0.0014 TEQ ng/m³), 0.16 ng/Nm³ (0.000026 TEQ ng/Nm³), 0.20 ng/Nm³, 28 ng/Nm³ and 2.6 ng/Nm³, respectively. Concentrations of MoBPCDDs/DF and PBDEs in the flue gas were below the detection limits. A mass balance analysis to estimate decomposition rates of BFRs and dioxin-related compounds through the ASR treatment was conducted based on the concentrations in the samples and production rates of byproducts, fly ash and exhaust gas. The result showed that more than 99.9% of PBDEs, TBBP-A and PBDDs/DFs and more than 99 % of PCBs (including coplanar-PCBs) in the treated ASR were decomposed, while the *de novo* formation of PCDDs/DFs and MoBPCDDs/DFs, that were enriched into fly ash (non-recyclable material),

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were confirmed through the DMS process.

All the results in this study indicate effectiveness of coke-bed gasification DMS for the decomposition of BFRs, PCBs and PBDDs/DFs in ASR and recyclability of byproducts *metal* and *slag* resulting from the melting treatment of ASR. However, relatively high production rates of PCDDs/DFs and MoBPCDDs/DFs through the ASR treatment were noted compared to the result in a previous study on MSW including waste TV casing². This may due to a higher production rate of fly ash through the treatment and higher concentrations of halogens and heavy metals (particularly Cu) in ASR than in case of MSW treatment². Development of 'pre'-separation technique to remove heavy metals and halogens from ASR before any thermal treatment is required.

Table 2. Concentrations of major elements, heavy metals, dioxin-related compounds and BFRs in ASR and in fly ash, *slag* and *metal* that were produced in the ASR treatment by DMS

Element/Compound	Unit ^a	ASR	Fly ash	Slag	Metal
Total chlorine (Cl)	mg/kg	29000	360000	5600	920
Total bromine (Br)	mg/kg	300	4100	<20	<20
Total Sulfur (S)	mg/kg	3600	15000	4500	2200
Calcium (Ca)	%	12.4	16.1	21.8	2.98
Silica (Si)	%	12.9	3.44	16.2	7.64
Aluminum (Al)	%	5.37	0.65	12.5	1.86
Sodium (Na)	%	1.89	8.23	0.07	<0.01
Potassium (K)	%	0.53	1.97	<0.01	<0.01
Lead (Pb)	mg/kg	1700	16200	19	550
Mercury (Hg)	mg/kg	0.08	0.1	<0.01	<0.01
Cadmium (Cd)	mg/kg	6.2	18	<0.5	<0.5
Arsenic (As)	mg/kg	3.5	13	<1.0	10
Selenium (Se)	mg/kg	0.2	5.1	0.5	<0.1
Chromium-VI (Cr-VI)	mg/kg	<1.0	<1.0	<1.0	<1.0
Iron (Fe)	%	2.83	1.69	0.73	33.5
Copper (Cu)	%	3.4	1.03	0.51	41.2
Zink (Zn)	%	0.88	8.0	0.01	0.06
Antimony (Sb)	%	0.04	0.18	<0.01	0.27
PCDDs/DFs ^b	ng/g	0.97	99	0.27	1.1
Coplanar-PCBs	ng/g	30	4.6	0.027	0.03
TEQs ^c	ng/g	0.027	1.7	0.0011	0.004
PBDDs/DFs ^d	ng/g	30	0.26	n.d.	n.d.
MoBPCDDs/DFs ^e	ng/g	n.d.	44	n.d.	0.03
PBDEs ^f	ng/g	310000	2.8	0.1	0.2
TBBPA	ng/g	15000	0.29	0.07	0.05
PCBs ^g	ng/g	270	22	0.091	0.15

^a dry weight basis, ^b sum of tetra- to octachlorinated congeners, ^c sum of individual TEQs of PCDD/DF and coplanar-PCB isomers (based on WHO-TEFs), ^d sum of tetra- to octabrominated congeners, ^e sum of tri- to heptachlorinated congeners, ^f sum of mono- to decabrominated congeners, ^g sum of mono- to decachlorinated congeners

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