ORGANOTIN COMPOUNDS 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 plastics. Therefore, ASR can play a role as a potential source of hazardous chemicals such as brominated frame retardants (BFRs)[1]. On the other hand, we found significant amount of organotin compounds in some household plastics[2]. Detailed analysis of organotin compounds as well as other hazardous chemicals in ASR should be required to assess their risk in the recycle process and to establish suitable treatment methods.

In this study, mono- to trisubstituted butyl-, phenyl- and octyltin compounds were analyzed in ASR in which heavy metals, BFRs and dioxin-related compounds were analyzed in our related study[1]. 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 dioxins in the thermal treatment for the wastes including ASR[1] and TV casing[3] with a benefit to produce *slag* and *metal* as incombustible byproducts that can be used as resources. In this study, behavior of organotin compounds in the high-temperature melting treatment of ASR by DMS was investigated using a full-scale testing plant.

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"[4]. 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. The result of material component analysis in ASR was shown in our related study[1].

Direct Melting System

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

Eight species of organotin compounds such as mono-(MBT), di-(DBT) and tributyltin (TBT), mono-(MOT), di-(DBT) and trioctyltin (TOT) and di-(DPT) and triphenyltin (TPT) were analyzed in ASR, *slag*, *metal*, fly ash and flue gas samples following the methods described elsewhere[5] with some modifications. In this study, concentrations of organotin compounds were calculated in ng/g or ng/Nm^3 based on each chloride forms. Analytical results on major elements, heavy metals, BFRs and dioxin-related compounds in these samples were reported in our related study[1].

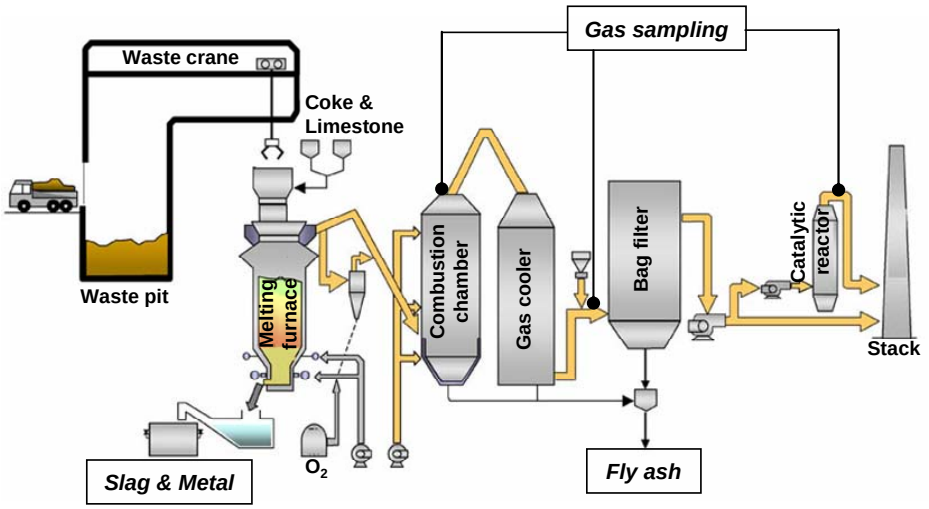

Figure 1. Flow chart of testing plant of coke-bed gasification DMS and sampling points of flue gas, *slag*, *metal* and fly ash

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 *slag*	kg/t -ASR	260
Production rate of *metal*	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

Table 2 shows concentrations of organotin compounds in ASR and in fly ash, *slag* and *metal* that were produced in the ASR treatment. All the butyl- and octyltin compounds analyzed were detected in ASR. To

our knowledge, this is a first report on the detection of organotin compounds in ASR.

Concentrations of monosubstituted organotins, MBT and MOT, were the highest in ASR and followed by the rest in the order DBT > DOT >> TOT >TBT. The concentration levels and patterns in ASR were similar to the results reported on household plastic materials made from polyvinyl chlorides (PVC), silicone resins and polyurethane foams[1,6]. Mono- and disubstituted alkyltins have been widely used as PVC stabilizers and synthetic catalysts for silicone resins and polyurethane foams. The detection of trisubstituted alkyltins, TBT and TOT, in ASR is not surprising because their detection have been reported in other plastic materials[1,6] and even in house dusts[7] with apparently higher concentrations of DBT and DOT. Therefore, TBT and TOT may be included in alkyltin-based stabilizers and/or catalysts as byproducts.

Concentrations of all the organotin compounds analyzed were below the detection limits in fly ash and byproducts, *slag* and *metal*. In the flue gas sample at the end of the combustion chamber, mono- and disubstituted alkyltins were detected at significant concentrations (Table 2), indicating their transfer to the flue gas from the treated ASR during the high-temperature melting process. However, only MBT and MOT were detected at the end of the catalytic reactor, suggesting effective removal and/or degradation of disubstituted alkyltins during the gas treatment processes by a bag filter and a catalytic reactor in DMS. A mass balance analysis to estimate decomposition rates of organotin 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 results showed that more than 99.996% of organotin compounds in ASR treated were decomposed.

All the results in this study indicate effectiveness of coke-bed gasification DMS for the decomposition of organotin compounds and recyclability of byproducts, *metal* and *slag*, resulting from the melting treatment of ASR. Despite our findings on ASR, available information on the concentrations of organotin compounds in other wastes is very limited. Further monitoring and development of proper techniques to remove organotin compounds in various plastic wastes are required to establish their recycling by safer methods.

Table 2. Concentrations of organotin compounds in ASR and in fly ash, *slag* and *metal* that were produced in the ASR treatment by DMS

Compound	ASR ng/g	Fly ash ng/g	Slag ng/g	Metal ng/g	Flue gas [a] ng/Nm^3	Flue gas [b] ng/Nm^3
MBT	51000	<1.0	<1.0	<1.0	47	140
DBT	25000	<1.0	<1.0	<1.0	410	<10
TBT	420	<1.0	<1.0	<1.0	<10	<10
MOT	54000	<2.0	<2.0	<2.0	77	210
DOT	8000	<2.0	<2.0	<2.0	230	<20
TOT	890	<2.0	<2.0	<2.0	<20	<20
DPT	<0.5	<0.5	<0.5	<0.5	<5.0	<5.0
TPT	<0.5	<0.5	<0.5	<0.5	<5.0	<5.0

[a] at the end of the combustion chamber, [b] at the end of the catalytic reactor

References

1. Sakai S, Takahashi S, Tanigaki N, Takamiya K, Osada M, Miyazaki T. *Organohalogen Compounds* 2006; 68: in press.
2. Takahashi S, Tanabe S. *Endocrine Disrupter News Letter* 2003; 5: 7 (in Japanese).
3. Sakai S, Osada M, Miyazaki T. *Book of Abstracts in BFR2004 workshop (Toronto, Canada)* 2004; 225.
4. Japanese Industrial Standard. JIS K0060 (1992) “Sampling Method of Industrial Waste”.
5. Iwamura M, Kadokami K, Jinya D, Tanada K. *Bunsek-ikagaku* 2000; 49: 523 (in Japanese).
6. Kawamura Y, Maehara, T, Suzuku T, Yamada T. *Shokueishi* 2000; 41: 246 (in Japanese).
7. Fromme H, Mattulat A, Lahrz T, Ruden H. *Chemosphere* 2005; 58: 1377.