

## Heavy metals removal from automobile shredder residues (ASR)

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### Abstract

The fate of heavy metals during a separation process for automobile shredder residues (ASR) was investigated. A washing method to remove heavy metals from the ASR was also investigated. Although the separation process was not designed for removal of heavy metals, but for the recovery of reusable materials, the heavy metal content in the ASR was efficiently decreased. The concentrations of Pb, Cr and Cd in ASR were effectively reduced by a nonferrous metals removal process, and the As concentration was reduced by the removal of light dusts during the separation process. Five heavy metals (As, Se, Pb, Cr, Cd) remaining in the ASR after the separation process satisfied the content criteria of the Environmental Quality Standards for Soil (EQSS), while the concentrations of As, Se, Pb in the leachate from the remaining ASR did not satisfy the elution criteria of the EQSS. After additional washing of the remaining ASR with a pH 1 acid buffer solution, the As, Se, and Pb concentrations satisfied the EQSS for elution. These results indicate that an ASR residue can be safely recycled after a separation process, followed by washing at acidic pH.

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### 1. Introduction

The number of vehicles in Japan has been linearly increasing since 1975 and was approximately 72.5 million in 2002 [1]. Approximately 5 million vehicles are wasted every year. Approximately 9.09 million t of automobile shredder residue (ASR) are produced and disposed of every year after the separation of reusable metals and parts from end-of-life-vehicles (ELV) [2].

Most ASR is directly disposed of in landfill sites. In Japan, the residues area of landfill sites has been reduced every year, so that as of 2004, the landfill capacity for industrial and domestic waste could only be sustained for less than 2 and 8 years, respectively [3]. Therefore, recycling and reuse of ASR is urgently required, and many investigations are being conducted to develop technologies for recycling of plastics [4,5].

There are three methods of plastic recycling that include thermal recycle (energy recycle), chemical recycle (feed stock recycle) and material recycle (mechanical recycle). Material

recycling of ASR is generally difficult. One of major reasons for this is the contamination of ASR by heavy metals. The heavy metals in ASR may pose a threat to the environment by leaching from the ASR [6]. The leaching of heavy metals from ASR has become an object of public concern in Japan, so that since 1976, ASR is classified as a hazardous waste and must be disposed of in controlled landfill sites. The heavy metals originate from some residual metal pieces, solder, plasticizers and paints present in ASR [7–9]. The regulations for heavy metals in plastics are not defined in Japan, because the contamination of heavy metals into plastics is not generally assumed, and the recycling and reuse of waste plastics is not yet developed.

Some of the most probable products for material recycle of ASR are equipment used outdoors, e.g. containers, benches, fences and blocks, because the satisfactory production of this type of equipment has been achieved with material recycle of industrial waste plastics. Therefore, in the case of recycled products used outdoors, the elution of heavy metals should be prevented. In Japan, the Environmental Quality Standards for Soil (EQSS) regulate the toxicity and environmental impact of heavy metals eluted from soil. If the toxicities and environmental impact of heavy metals eluted from recycled products are lower

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than the EQSS levels, they can be estimated as being harmless. Therefore, one criterion for the material recycle of ASR is to satisfy the EQSS.

In some commercial plants, the residual reusable materials (e.g. iron and nonferrous metals) are additionally recovered from the ASR by separation processes in order to recycle them. After the recovery of reusable materials, the ASR residue is mainly composed of plastics; therefore, there is a possibility that the heavy metal content has been significantly decreased and will satisfy the EQSS. An evaluation of each separation process for reusable materials is important for the control of heavy metals in ASR for recycle.

In this study, main purpose is to evaluate the possibility of ASR recycling as a resource to remove heavy metals after separation process in comparison with EQSS. EQSS levels for the content in the residue and elution content were used to evaluate the safety of recycling ASR in regard to the effect on soil.

The heavy metal removal was studied in order to promote plastic recycling. An evaluation of heavy metal contamination was performed after each commercial separation process, and the fate of heavy metals in each separation process was investigated.

The performance of several washing methods, used to remove heavy metals from residual ASR after the separation process, was also studied.

## 2. Experimental

### 2.1. Separation process

A flow chart of the commercial separation process studied is shown in Fig. 1. Double circles represent reusable commercial materials in Japan. Residue-A, which is ASR in general, is the residue after the removal of iron from the shredded ELV using a permanent magnet. The percentage of ASR is normally 8% of the ELV. Large light plastics (mainly urethanes), large nonferrous metals (aluminum and copper wire) and large light dust (woods, fibers, urethanes and sediments) are removed from residue-A after shredding (particle diameter = 15–20 cm) using an eddy current separator (ECS) and a wind force separator. The light fraction and heavy fraction are separated by a mechanical wind force separator based on the specific gravity of both fractions. The ECS is based on a rotor comprised of magnetic blocks, either standard ferrite ceramic type or the more powerful rare earth magnets, depending on the application. The blocks are spun at high revolution (over 3000 rpm) to produce an ‘eddy current’ that reacts with different metals, according to their specific density and electrical conductivity, creating a repelling force on the charged particle. If a metal is light and conductive, such as aluminum, it is easily levitated and ejected from the normal flow of the product stream, making separation possible. After these

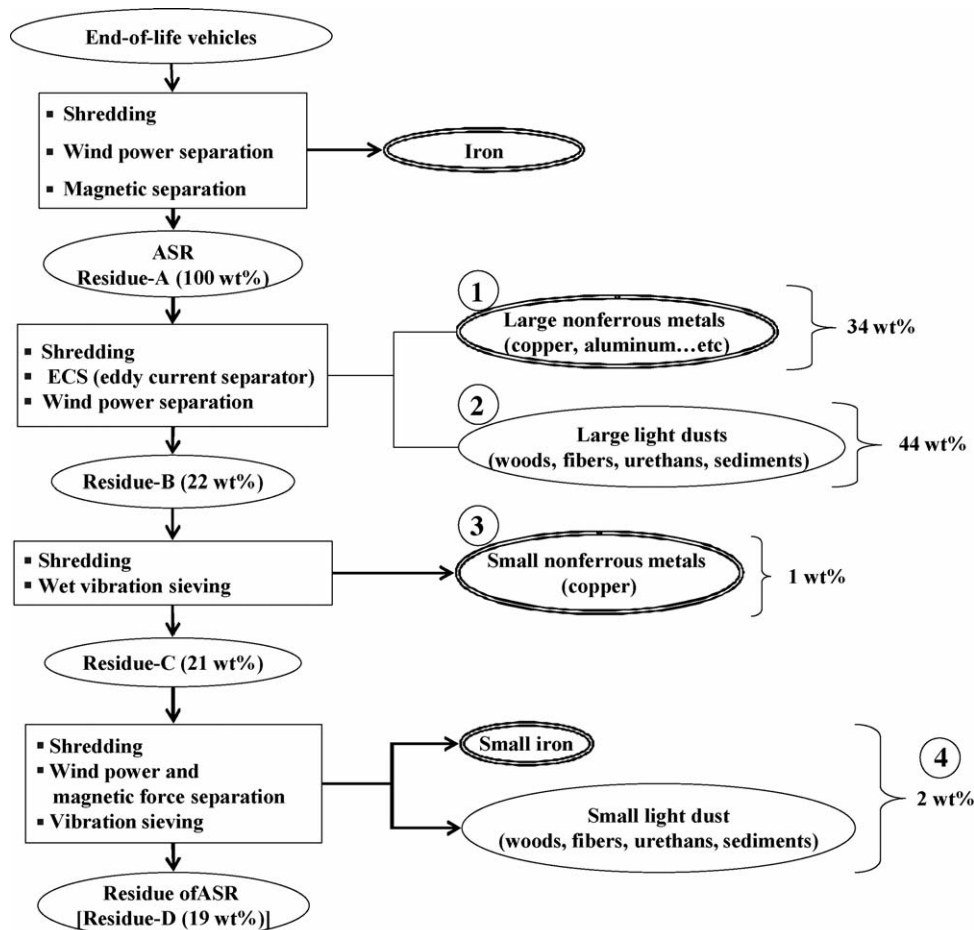


Fig. 1. Flow diagram for the separation process.

separation processes, the residues are mainly composed of small fractions, denoted as residue-B in this paper.

Residue-B is then shredded (particle diameter = 1–5 cm) and nonferrous metals (copper wires) are removed using a vibration sieve machine to leave residue-C on the basis of based on particle size. Residue-C is further shredded (particle diameter = 2–4 mm) and small iron and other light dusts are removed by both wind force and magnetic force separation followed by vibration sieving. The final residue is represented as residue-D (residue of ASR), which is mainly composed of small particles (approximately 2–4 mm) of heavy plastics.

## 2.2. Heavy metal contents in ASRs

The heavy metal content in ASR after each separation process was investigated in order to understand the fate of heavy metals during the separation processes. The EQSS content levels were used to evaluate the heavy metal content in ASR.

Heavy metal content in the ASR and subsequent residues was determined using the EQSS procedure [10,11]. Heavy metals were extracted from ASR using 1 M. HCl at room temperature for 2 h, with a liquid/solid (L/S) ratio of 100/3. Insoluble residues were removed by filtration with a 0.45  $\mu\text{m}$  membrane filter (Millipore HA), then the concentrations of As, Se, Pb, Cr and Cd in the filtrate were determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES; ICAP-575II, Nippon Jarrell-Ash Co. Ltd.). The detection limits of these five metals were approximately 0.001 mg/kg. The results of the heavy metal contents were expressed as an average value of three measurements. All coefficients of variation (CV) were less than 10%.

## 2.3. Leaching test (elution) of heavy metals from ASRs

To evaluate the safety of each ASR, the concentrations of heavy metals in ASRs after each separation process were compared with the EQSS criteria for elution.

Japanese leaching test No. 46 (JLT. 46) [12] was used to evaluate the concentrations of elutable heavy metals in ASR and residues. Heavy metals were eluted at room temperature for 6 h in an HCl solution with an initial pH ranging from 5.8 to 6.3. The L/S ratio was adjusted to 10. Insoluble residues were removed by filtration using a 1  $\mu\text{m}$  membrane filter (Whatman GF/B). Concentrations of As, Se, Pb, Cr and Cd in the filtrate were determined by ICP-AES. The detection limits of all five heavy metals were approximately 0.001 mg/L for. The results of the leaching test were expressed as the average value of three measurements. Each CV value was less than 10%.

## 2.4. Washing procedure

The concentrations of As, Se, and Pb in the eluate of residue-D did not satisfy the EQSS requirements for elution. Additional washing was required to decrease the concentration of heavy metals in ASR to levels that satisfy the EQSS for elution.

Additional washing of residue-D was also required to decrease the concentration of heavy metals. Several solutions,

Table 1  
Conditions for washing solutions

Washing solution	Concentration (mM)	Initial pH	Final pH
HCl	1.0	3.03	8.47
NaOH	0.01	11.85	9.52
Potassium chloride–hydrochloric buffer solution (HCl/KCl)	200	1.00	1.00

such as 1 mM HCl or 1 mM NaOH, were used for washing, and the efficiency of each solution was compared. Potassium chloride–hydrochloric (HCl/KCl) buffer solution (pH 1) was also used. Each washing was conducted at room temperature for 6 h using the same conditions as for the JLT-46 procedure. After washing, the residual solid was separated using a 1- $\mu\text{m}$  membrane filter (Whatman GF/B) that was rinsed with water, and then dried at 60 °C for 24 h. The results of the leaching test after washing were expressed as an average value of three measurements. Each CV value was less than 10%. The conditions for the different washing solutions are summarized in Table 1.

## 3. Results and discussion

### 3.1. Fate of heavy metals in the separation process

The heavy metal content in residue-A to D was determined by the EQSS procedure and is shown in Fig. 2. The dotted line corresponds to the EQSS content limits (EQSS-c) for each heavy metal. The As and Pb contents in residue-A were 1.7 and 8.4 times higher than EQSS-c, respectively. The contents of all five metals in residue-B were lower than those in residue-A. Large light fractions and/or nonferrous metals that were removed from residue-A should contain large amounts of heavy metals. The contents of As and Pb became lower less than EQSS-c in residue-B and residue-C, respectively, while the contents of Se, Cr and Cd was already lower in residue-A. The contents of As, Se and Cd were mainly removed by the separation between residue-A and residue-B, and those of Pb and Cd were mainly removed until residue-C. The contents increasing of Se, Pb and Cd were obtained between residue-C and residue-D, indicating that materials, which did not contain these heavy metals were mainly removed in this separation. Although the separation process was not designed for heavy metal removal, but for the recovery of reusable materials, the heavy metal contents in ASR were decreased mainly by the separation between residue-A and residue-C. The percentages of As and Pb removed by the separation process from residue-A to D were 100 and 92 wt.%, respectively.

Concentrations of heavy metals in the leachate of ASR residues are shown in Table 2. The concentrations for As, Se, Pb, Cr and Cd in the leachate from the residue-A were 108, 146, 127, 2.4, and 142 times higher, respectively, than the EQSS for elution (EQSS-e). The concentrations of As, Se and Pb in residue-D were still approximately 3, 4 and 8 times higher than the EQSS-e, respectively. This indicates that further processing

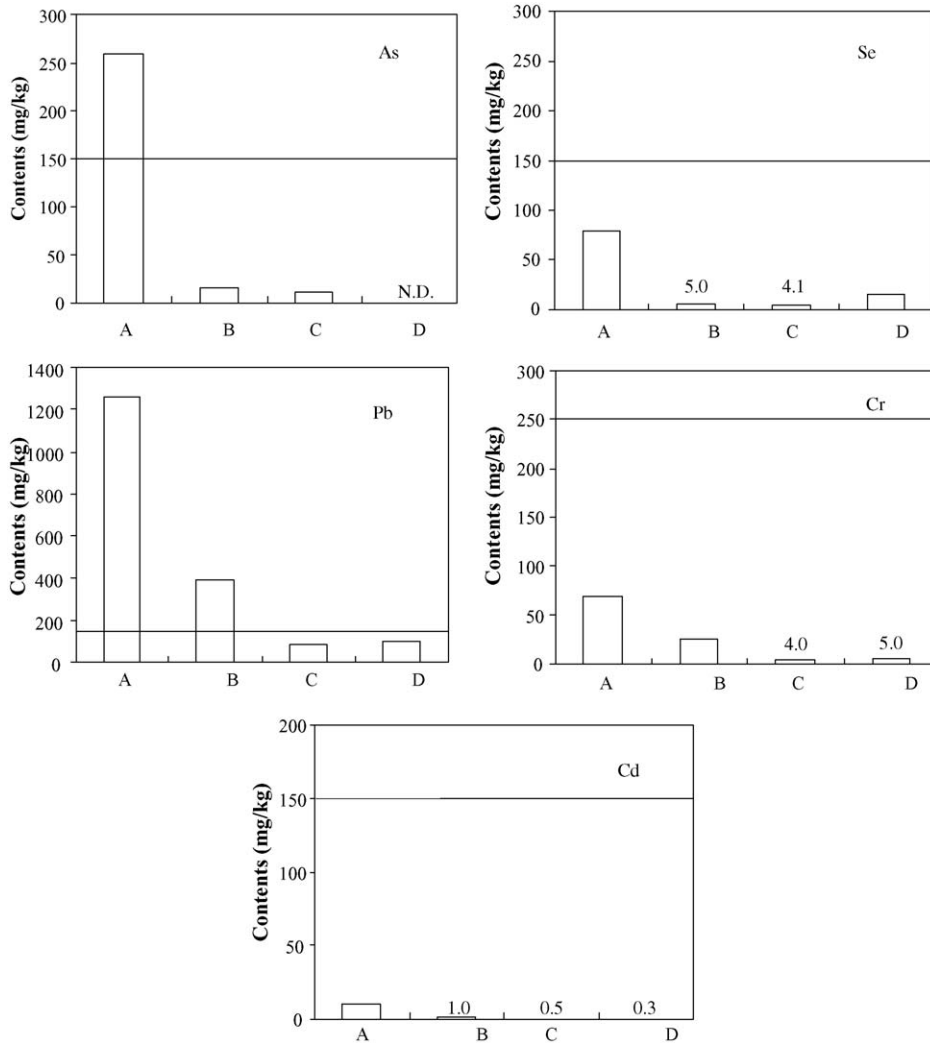


Fig. 2. Heavy metal content in residues-A, B, C and D (dotted line indicates EQSS-e).

for heavy metal removal is necessary to satisfy the EQSS-e for As, Se and Pb.

To clarify the distribution and fate of heavy metals in ASRs, the mass balance of five heavy metals in residue-D and four fractions ((1)–(4) in Fig. 1) were calculated and are summarized in Fig. 3. The weight percentage of each heavy metal in each fraction was calculated by the heavy metal content determined by the EQSS contents analysis given in Fig. 1. The weight percentage of ASR itself in each fraction is shown in the “ASR” column of Fig. 3.

Table 2  
Elution of heavy metals from residues-A, B, C and D

	As	Se	Pb	Cr	Cd
A	1.08	1.46	1.27	0.12	1.42
B	0.18	0.06	0.15	0.02	0.03
C	0.13	0.06	0.04	<i>N.D.</i>	<i>N.D.</i>
D	0.03	0.04	0.08	<i>N.D.</i>	<i>N.D.</i>
EQSS-e (mg/L)	0.01	0.01	0.01	0.05	0.01

N.D.: not detected (less than 0.001 mg/L) Italics mean to satisfy with EQSS-e.

The weight percentages (wt.%) of all heavy metals were widely distributed in the five fractions. Approximately 60 wt.% As was detected in fraction-(1), which was higher in comparison with ASR itself (approximately 35 wt.%). Pb, Cr, and Cd were detected at approximately 75–90 wt.% in fraction-(2). These

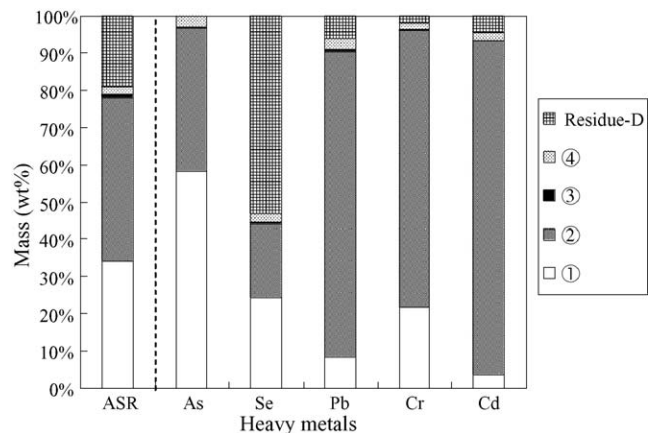


Fig. 3. Mass balance data for the separation process.

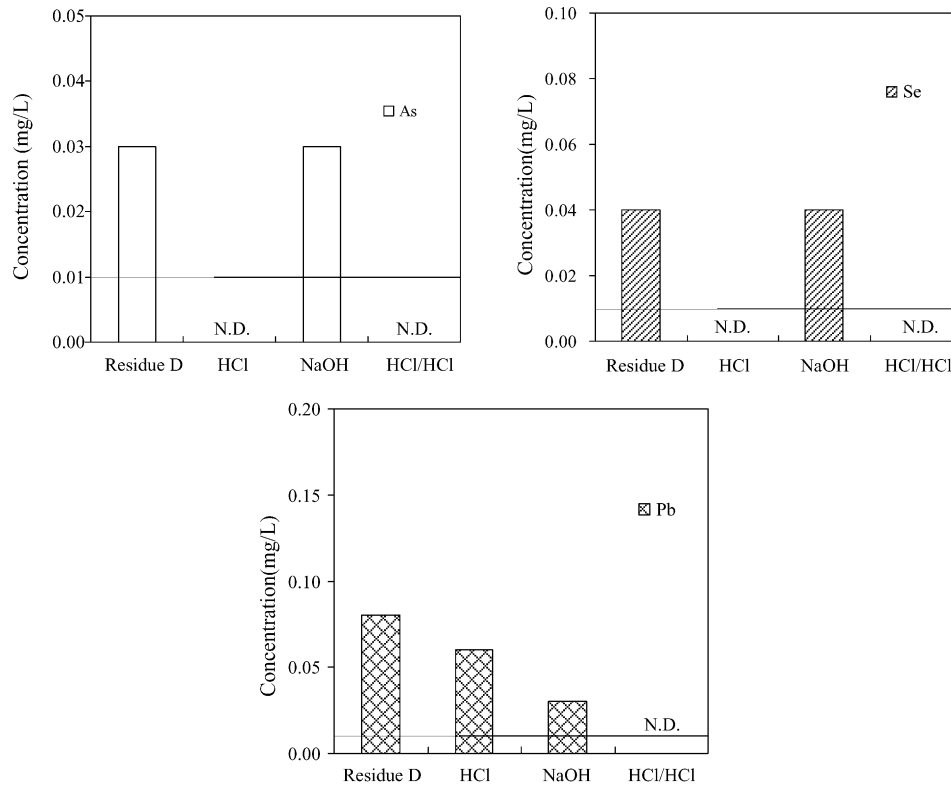


Fig. 4. Concentrations of heavy metals after washing (dotted line indicates EQSS-e).

results indicate that the separation of fraction-(1), containing light dusts (woods, fibers, urethanes, sediments), decreased the concentration of As in ASR, and the removal of fraction-(2) containing nonferrous metals (aluminium, copper wire) decreased the concentration of Pb, Cr, and Cd. The Pb contained in fraction-(2) resides in the “sediments” as powder and ingots derived from solder, and alloy metals that contain As contribute to the As content in fraction-(1). The concentrations of As, Se and Pb eluted from residue-D also could not satisfy the EQSS-e content, even though a large percentage of these metals were removed by the separation process. The As, Se and Pb remaining in residue-D would be described as easily elutable.

### 3.2. Removal of heavy metals from residue-D by washing

The concentrations of As, Se and Pb in the leachate of residue-D could not satisfy the EQSS-e as shown in Table 2. Washing methods with several different solutions were applied in order to reduce the concentration to a level lower than the EQSS-e. Fig. 4 shows the concentrations of As, Se and Pb in residue-D after washing with three different washing solutions. Washing with 1 mM sodium hydroxide solution did not decrease the concentration of all three heavy metals to EQSS-e levels. Hydrochloric acid washing significantly decreased the concentrations of all three heavy metals; however, the resulting concentration of Pb did not satisfy the EQSS-e. It is known that the amount of extracted heavy metals depends on the pH of the solution [12]. The solution pH was increased to higher than 8, even for washing with 1 mM hydrochloric acid solution. Therefore, potassium chloride-hydrochloric buffer solution was used to maintain a pH

of approximately 1.0 during the washing. The concentrations for all three metals did satisfy the EQSS-e levels after washing with the buffer solution. These results indicate that residue-D can be recycled safely after washing at pH 1.0.

## 4. Conclusions

The fate of heavy metals in the separation processes and washing methods of ASR were studied. Although the separation process was not designed for heavy metal removal, but for the recovery of reusable materials, the contents of heavy metals in ASR were efficiently decreased. The contents of As and Pb became lower less than EQSS-c in residue-B and residue-C, respectively, while the contents of Se, Cr and Cd was already lower in residue-A. The contents of As, Se and Cd were mainly removed by the separation between residue-A and residue-B, and those of Pb and Cd were mainly removed until residue-C. The percentage of As, Se and Pb removed by the separation process from residue-A to D were 97, 97 and 93 wt.%, respectively.

The concentrations of Pb, Cr and Cd in ASR were reduced by the removal of nonferrous metals (aluminium, copper wire), and As was reduced by the removal of light dusts (woods, fibers, urethanes, sediments) in the separation process.

The concentrations of As, Se and Pb in the leachate from the ASR residue that was separated from reusable fractions were still approximately 3, 4 and 8 times higher than the respective levels of EQSS for elution. However, the concentrations for all three metals did satisfy the EQSS for elution after washing at a pH of 1.

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