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Utillization of automobile shredder residue (ASR) as a reducing agent for the recovery of black copper

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Abstract–The physicochemical characteristics of automobile shredder residue (ASR) and its melting slag were investigated: In particular, the applicability of ASR as a reducing agent to the black copper recovery process. ASR is classified into three types after the shredding process: heavy fluff, light fluff and glass and soil. In this study, the portions of heavy fluff, light fluff and glass and soil in the ASR were 89.2 wt%, 8.1 wt% and 2.7 wt%, respectively. Physicochemical analysis revealed that moisture and fixed carbon content were low in heavy and light fluffs, and combustible content was the highest. The higher heating value (HHV) of light fluff was 6,607 kcal/kg, and the HHV of heavy fluff was 5,312 kcal/kg. To sum up, the separation of black copper and discard slag mostly seems to be affected by the melting temperature. Therefore, if basicity and melting temperature are properly controlled, the ASR can be used as a reducing agent in the smelting process of black copper recovery. Moreover, the possibility of black copper recovery from ASR and heavy metal poisoning is evaluated.

Keywords: Automobile Shredder Residue (ASR), Melting, Black Copper, End-of-life Vehicles (ELVs), Recovery

INTRODUCTION

Until the late 1990s, a variety of metals and nonmetals were still incorporated in automobiles. The laws for emission of air pollutants such as CO, NOx, particulate matter and hydrocarbon became more stringent than the laws for recycling and resource recirculation of end-of-life vehicles (ELVs) [1]. However, beginning in the 2000s, people began to recognize the significance of recycling and resource recirculation for ELVs. These changes were inevitable because the volume of ELVs had increased significantly along with the concerns regarding the environment and energy usage. For this reason, many countries reinforced regulations to promote the recycling of ELVs [2], and some focused specifically on disposal of automobile shredder residue (ASR) in an environmentally friendly way [3]. For example, in the EU, the government undertook a major effort to lead the systematic recirculation of ELVs through an end-of-life vehicle directive [4], and the landfill deposition rate of ELVs consequently decreased. Further, Asian countries, including Japan and China, reinforced their environmental regulations for ELVs since July 2002 [5-7]. In Italy, although the recycling rate of ELVs increased from 71 wt% (in 2005) to 85 wt% (in 2011), further effort is still required to meet EU targets because the number of vehicles continues to steadily increase [8,9].

In South Korea, the vehicle market has grown rapidly, with the discharge rate of ASR amounting to 150,000 tons/year in 2010. The ASR generated from the disposal process of ELVs consists of plastics (PP, PUR, PVC, ABS, etc.), glass and soil, iron, nonferrous metals, etc. [10]. Until the present, a significant portion of ASR had been incinerated, but most of the ASR was not incinerated completely because of noncombustible materials in the ASR. Moreover, according to chloride components and heavy metals in the ASR, hazardous air pollutants (HAPs) were generated and discharged during the incineration process [11]. Hence, the Korean government established a specific ASR recycling law. The target recycling rate was set to 85 wt% based on new vehicles, including energy recovery of 5 wt%, until 2014 and 95 wt% after 2015, including energy recovery of 10 wt%, by the ELV Directive [12, 13]. This is in accordance with the Korean regulation regarding the resource recycling of electrical and electronic products and automobiles. However, the recycling rate is still low, approximately 84 wt% in 2010, and the number of registered shredder residue recyclers is low compared with other dealers for dismantling, crushing, waste gases, etc. Hence, to meet the goal of 95 wt%, the ASR recycling industry in Korea must expand and develop innovative recycling technology. Therefore, basic research such as physicochemical analysis of the ASR is very important. In Italy, physicochemical analysis of the ASR was carried out with respect to lower heating value (LHV), particle size, heavy metal content and ultimate analysis by Fiore et al. [12]. The LHV of the ASR is 5,735 kcal/kg, and the size of most particles is greater than 20 mm. Moreover, in case of light fluff, carbon is 46 wt% in the ASR. In particular, light fluff contains a large amount of Cr, Mn, Ni and Pb [14]. According to Hwang et al. [15], the ASR produced in Japan is mainly composed of plastics, rubber, and urethane, but also contains metal and electrical

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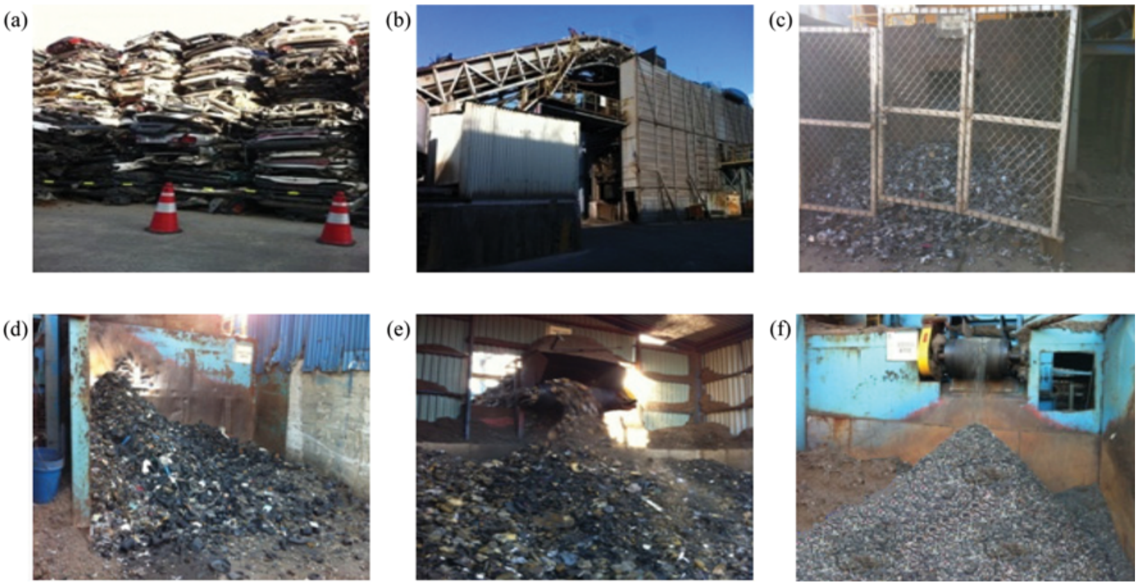


Fig. 1. Products from shredding process. (a) Compressed vehicle fluff. (b) Shredding vehicle fluff. (c) Non-ferrous metal. (d) Heavy fluff. (e) Light fluff. (f) Glass & soil.

wire, which are unrecovered during air classification and magnetic separation. Volatiles in the ASR are 85 wt%, and HHV is 8,571 kcal/kg. Rigid plastics are major constituents of the ASR, and particles smaller than 5.6 mm comprise 18 wt% of the ASR. Moreover, soil, grit, glass and miscellaneous materials are included [15]. In contrast, in South Korea, systematic analysis of the characteristics of ASR is rare [16]. Hence, we analyzed the physicochemical and thermal characteristics of ASR. In addition, to identifying a recycling method for ASR, we performed melting experiments. In the waste copper recycling process, lump coal is used as a reducing agent in the melting furnace. Because the LHV of the ASR is approximately 6,000 kcal/kg and a small amount of copper is also contained in the ASR, the lump coal can be substituted by the ASR as a reducing agent. Moreover, copper in ASR can be recovered. Hence, the possibility of recovering black copper and the environmental effects of discard slag were scrutinized by lab-scale experiments.

EXPERIMENTAL

1. Physicochemical Characteristics

1-1. Materials

The ASR used in this study was sampled from a domestic shredding company (KYUNGHAN). According to the shredding process, the ASR is generally classified into three types: heavy fluff, light fluff and glass and soil. Generally, heavy fluffs and light fluffs can be used as alternative fuel for cement kilns. In this case, most ASR is incinerated and may cause environmental hazards. For example, heavy metal concentration may exceed the standard concentration in the cement kiln [17]. Nonferrous materials can be recovered from glass and soil by mechanical sorting, and then the remnants are disposed into landfills.

Table 1 shows the results of the ASR classification. For reference, sampling was carried out five times per day for three days. The portion of heavy fluffs, light fluffs and glass and soil in the ASR was 89.2 wt%, 8.1 wt%, and 2.7 wt%, respectively. Heavy fluff includes thermoplastics, rubbers, resins, etc. The light fluff contains mainly resins, thermoplastics and thermosetting plastics that come from car sheets and relatively lightweight materials. The materials in glass and soil consist of glass, thermoplastic, soil, wires, etc.

Table 1. ASR classification

Materials	Heavy fluff (wt%)	Light fluff (wt%)	Glass & soil (wt%)
Metals	0.8	1.5	0.2
Rubbers	22.1	3.8	5.8
Resins	16.6	37.5	6.4
Wires	14.0	2.9	11.5
Thermosetting plastics	7.2	21.3	0.3
Thermoplastics	33.8	24.1	27.3
Woods	0.1	0.2	0.1
Papers	2.1	1.0	0.0
Soils	1.8	6.9	17.2
Glass	1.5	0.8	31.2

1-2. Analysis Methods

Table 2 shows the analysis methods adopted in the present study. Particle size distribution and apparent density were measured by using a sieving machine with standard sieves (1.0-53.0 mm) and a mass cylinder, respectively. Apparent density was measured using the following method. First, an empty container was filled with the sample. The container was then dropped several times from a height of 30 cm until the minimum porosity of the sample particles was achieved. Proximate analysis was carried out using TGA (LECO, TGA-701) based on ASTM (American Society for Testing and Material) D 3172. The composition of the sample was classified into fixed carbon, volatile matter, moisture and ash.

Table 2. Analysis methods for physicochemical characteristics of ASR

Item	Analysis instrument	Analysis methods
Particle size	Sieving machine	ASTM D 422-63
Apparent density	Mass cylinder	ASTM D 1895
Proximate analysis	TGA-701 LECO	ASTM D 3172
Calorific value (HHV)	AC-600 LECO	ASTM D 4809
Ultimate analysis	EA 1112 Thermo Fisher Scientific EA 1110 CE Instrument	ASTM D 5373
Thermo gravimetric analysis	TGA-701 LECO	ASTM E 1131

To measure calorific value, the ASR sample was milled into small particles because the diameters were less than 1 mm. Higher heating values were measured by a bomb calorimeter (LECO, AC-600). The ultimate analysis was to examine the elemental composition of the sample and calculate the material balance for thermochemical processes. Elemental analyzers EA 1112 and EA 1110 were used. EA 1112 adopted the Porapak PQS column (2 m×6 mm ×5 mm), and the oven temperature was initially held at 65 °C. The oven temperature was then increased to 900 °C and run for 680 s. Helium gas was used as the carrier gas, and the flowrate was set to 140 ml/min. EA 1110 used the molecular sieve 5A column (1 m×3 mm×5 mm), and the oven temperature was initially held at 65 °C. The oven temperature was then increased to 1,040 °C and run for 300 s. Helium gas was used as a carrier gas, and the flowrate was set to 120 ml/min. Thermogravimetric analysis (TGA) involved the TGA-701 LECO (precision: ±0.02% RSD) instrument to examine the thermal degradation characteristics of the ASR. The temperature was increased from 25 °C to 950 °C at a heating rate of 10 °C/min in the presence of nitrogen.

2. Lab-scale Melting Experiment

Fig. 2 shows the process of the waste copper recovery plant. Briquetted raw material and fuel are supplied into the melting furnace through the inlet and lance pipe, respectively. They then melt together at approximately 1,300 °C in the melting furnace, and the molten mass is moved every 4 h into a refining furnace. Molten mass is separated into black copper and slag depending on the specific gravity of each component, and then discharged from the refining furnace. In a boiler, heat is recovered from high-temperature gas, which is generated during the melting process, and air pollutants are removed by air pollution control facilities such as a bag filter, wet scrubber or electrostatic precipitator. In a commercial plant, coal is used to heat the melting furnace. Substances that contain copper such as secondary copper, C-slag, waste foundry sand and lump coal (or ASR) were used as raw materials for waste copper recovery. Here, secondary copper and C-slag are the residues generated from the nonferrous smelting process. The secondary copper and C-slag are critical to the operation of a copper refinery. The former is used as the main raw material for recovering black copper, and the latter improves the fluidity in the melting furnace.

As mentioned, lump coal is used as the reducing agent in the melting furnace. We conducted melting experiments to judge

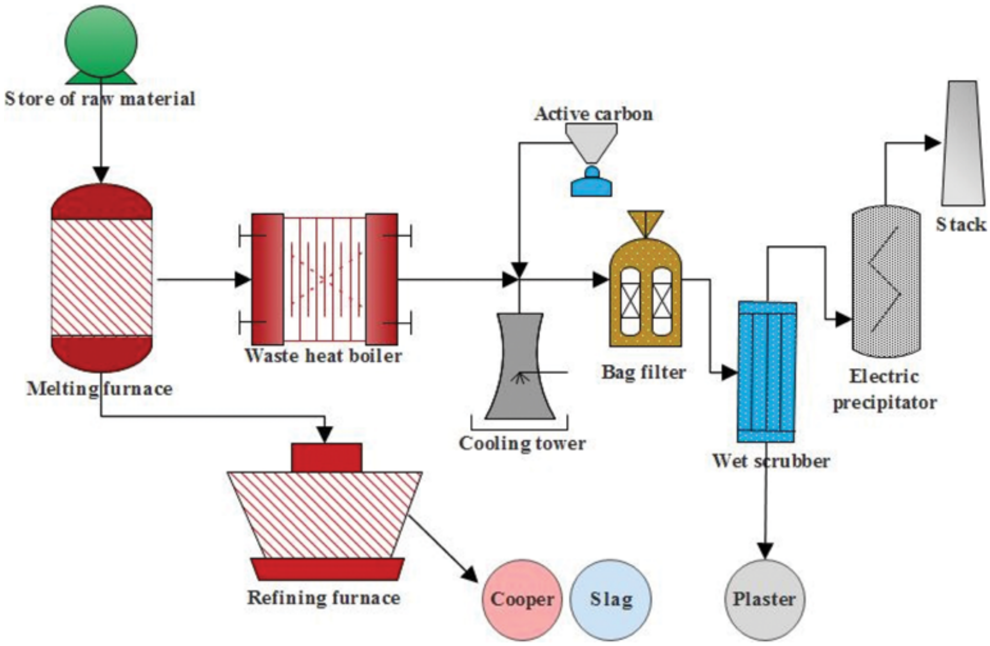


Fig. 2. Schematic diagram of waste copper recovery process.

Fig. 3. Photo of lab-scale melting furnace.

whether replacement of lump coal by ASR is possible and to examine the amount of copper recovered from ASR. The melting experimental furnace is described in Fig. 3. In a commercial facility, a small quantity of oxygen is used for refining of metals, and in lean oxygen conditions, the reduction reaction of metals is carried out with lump coal such as charcoal and bituminous coal. Therefore, here, oxygen was supplied to drive the reduction reaction, and ASR was used as a reducing agent instead of lump coal. In addition, heat was supplied directly by using electric heaters unlike at a commercial facility.

The primary role of the ASR here was as a reducing agent in the melting process. Hence, instead of lump coal, the ASR was placed at the top of a crucible. After samples were made, they were mixed in a ball mill for more than 4 h. Next, a sample was placed in a 300 cc alumina crucible (at a purity 99.99%), and heat was supplied to melt the sample. The melted sample then slowly cooled in the air, and the black copper (BC) and discard slag (DS) were separated. Table 3 shows the melting experiment conditions such as mixing ratio, reaction temperatures and time. To perform X-ray diffraction (XRD) and copper content analysis, the samples were pulverized using 100 mesh (254 μm).

After the melting experiment, BC and DS were separated from melting slag, and the content of the copper was analyzed. The analysis method was iodometric titration, and each sample was analyzed three times to determine the representative copper contents. The calculation formula of copper content is given as follows:

$$\mathrm{Cu}(\%)=\frac{\mathrm{M}\times\mathrm{V}\times\mathrm{f}}{\mathrm{W}}\times 100$$

Table 3. Condition of melting experiment

Item		Experimental condition
Mixing ratio of sample material (wt%)	ASR	9.1
	Secondary copper	63.6
	C-slag	21.8
	Waste foundry sands	5.5
Melting temperature (°C)		1300, 1350, 1400
Melting time (min)		120

where

M=the equivalent copper in 1 mL of approximately 0.08 N $Na_2S_2O_3$ standard solution (g)

V=the usage of 0.08 N standard solution (ml)

f=factor (standard solution titer)

W=the amount of sampling (g)

RESULTS AND DISCUSSION

1. Physicochemical Characteristics of ASR

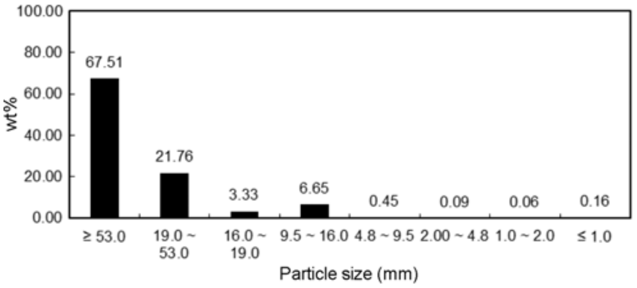
The physicochemical characteristics of ASR are very important for deciding how to reuse, recycle or recover ASR efficiently and economically. Hence, in the present study, the physicochemical characteristics of domestic ASR were determined as follows.

1-1. Particle Size

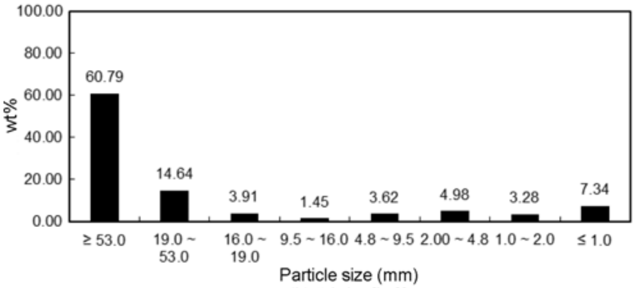
The particle size distribution of the samples is shown in Fig. 4. The particle size in heavy and light fluffs generally exceeded 53.0 mm. A particle size of less than 4.8 mm is very rare in heavy fluff. However, small particles still exist in light fluff, although their weight percent is low. Most glass and soil particles are of medium size, approximately 2.0-19.0 mm.

1-2. Apparent Density

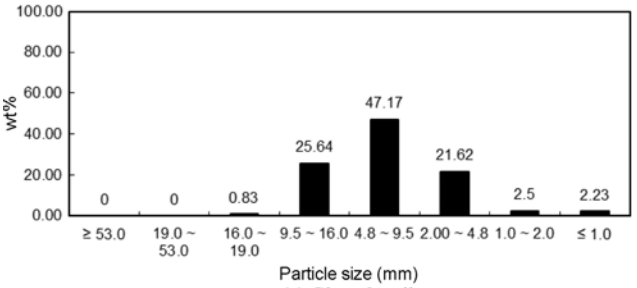
The apparent density of each component of the ASR is pre-



(a) Heavy fluff.



(b) Light fluff.



(c) Glass & soil.

Fig. 4. Particle size distribution for each ASR component.

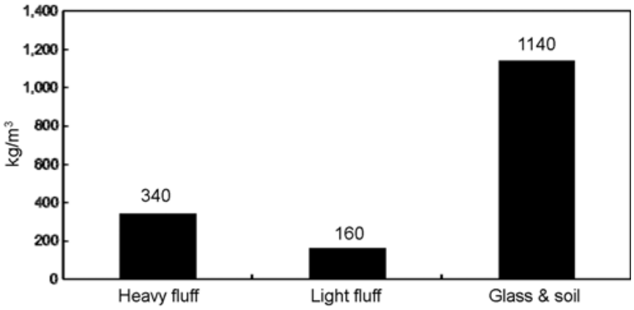


Fig. 5. Apparent density for each ASR component.

Table 4. Apparent density of total ASR

ASR density (kg/m³)	Present study	Menad Nourreddine (2007)	Mirabile et al. (2002)
	347	405	359

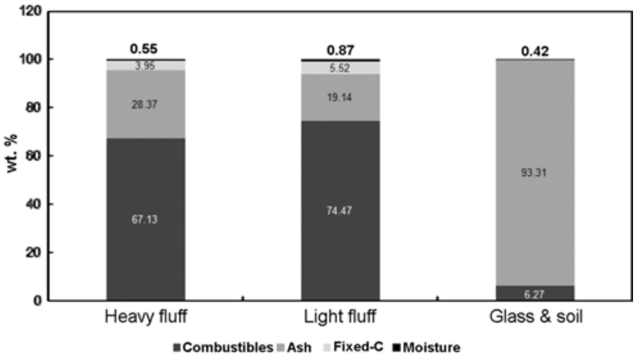


Fig. 6. Proximate analysis for each ASR component.

sented in Fig. 5. As shown, the density of glass and soil is the highest, and the density of light fluff is the lowest. In glass and soil, heavier solid particles are dominant, such as sand and glass, which have relatively smaller diameters. However, large particles that are comparatively lighter such as rubbers and plastics are very rare. Table 4 shows the apparent density of total ASR and compares these data with those of other studies [17,18]. The density of the ASR examined by Nourreddine [18] was 405 kg/m³, and the result from the study by Mirabile et al. [19] was 359 kg/m³. The total apparent density analyzed by the present study is 347 kg/m³, a value very similar to the data from Mirabile et al. [19]. However, it is much lower than that of the data from Nourreddine [18].

1-3. Proximate Analysis

Fig. 6 shows the results of proximate analysis for the ASR. Moisture and fixed-C (fixed carbon) content are very low for the three components. Note that the moisture content is less than 1 wt% for all three components. The content of combustible materials in heavy and light fluffs is higher, but the ash content of heavy and light fluffs is lower than that of glass and soil. Table 5 shows the data of proximate analysis for each material in ASR. Thermo plastics have the highest wt% of combustibles and resins, and thermosetting plastics also have higher values. With respect to water content, woods and papers have higher values. Metals, glass and soils have a higher content of ash. For fixed carbon, rubber has the highest content. Table 6 shows the proximate analysis of total ASR by comparing these data with those of other studies. For reference, other literature observations were recalculated on the basis of total ASR. In Table 6, in the present study, moisture is 0.57 wt%, combustibles are 66.08 wt%, fixed carbon is 3.97 wt%, and ash is 29.38 wt% of total ASR. The results of combustibles and ash are similar, but the moisture and fixed carbon are lower than the literature data [13,20-25].

Table 5. Proximate analysis for each material of ASR

Materials	Moisture (wt%)	Combustibles (wt%)	Ash (wt%)	Fixed-C (wt%)
Metals	0.12	0.00	99.88	0.00
Rubbers	1.26	58.81	13.61	26.32
Resins	0.93	84.53	14.13	0.41
Wires	0.32	58.85	40.83	0.00
Thermosetting plastics	0.22	84.30	9.67	5.81
Thermo plastics	0.13	94.16	5.55	0.16
Woods	26.37	54.33	9.58	9.72
Papers	19.80	50.05	27.94	2.21
Soils	3.01	33.00	63.99	0.00
Glass	0.17	0.05	99.78	0.00

1-4. Calorific Value

Fig. 7 shows the results of caloric values of the ASR components. The caloric value of light fluff is the highest among the three components at 6,607 kcal/kg. Light fluff has the highest HHV because it consists of highly calorific materials such as rubber, resins, thermosetting plastics and thermoplastics, as shown in Table 1. The caloric values of heavy fluff and glass and soil are 5,312 kcal/kg and 571 kcal/kg, respectively. Generally, ASR has a relatively high caloric value compared with other refuse-derived fuels (RDF) [27]. Table 7 shows the calorific value of each material. Thermoplastics, thermosetting plastics, rubber and resin have higher calorific values in ascending order. Table 8 shows the caloric value of total ASR compared with other studies. In Table 8, HHV varies from 3,548

Table 6. Proximate analysis for total ASR

Contents (wt%)	Present study	Zolezzi et al. (2004)	Galvagno et al. (2001)	Day et al. (2001)	Rausa and Pollesel (1997)	Roy and Chaala (2001)	Kondoh et al. (2000)	Mancini et al. (2010)
Moisture	0.57	2	14.9	6	1.27	0.6-6.6	0.8	15.41
Combustibles	66.08	62.5	48.8	45	74.37	41.3-82.3	61.3	-
Fixed-C	3.97	10.2		-	-	-	15	-
Ash	29.38	27.3	37.1	-	12.11	18.3-58.2	23.6	44.7

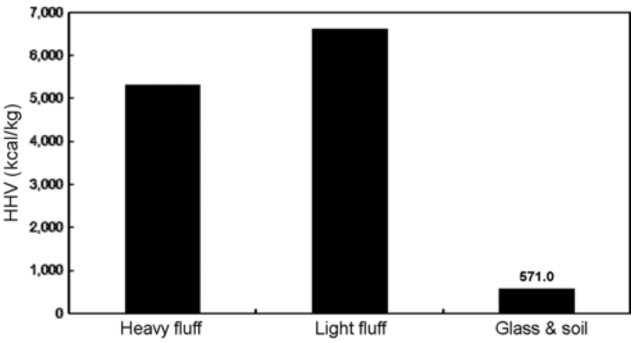


Fig. 7. Calorific value for each ASR component.

Table 7. Calorific value for each material of ASR

Materials	HHV (kcal/kg)
Metals	-
Rubbers	7,587.9
Resins	7,184.8
Wires	1,860.4
Thermosetting plastics	6,679.9
Thermo plastics	8,036.0
Woods	3,600.1
Papers	2,415.7
Soils	1,922.1
Glass	-

to 7,310 kcal/kg, and the average HHV of the data from other literature is 5,400 kcal/kg. The HHV of the present study is 5,300 kcal/kg, which is very close to the result of Zolezzi et al. and Mancini et al. [12,20].

1-5. Ultimate Analysis

Fig. 8 shows the result of the ultimate analysis of ASR components. Carbon content is 52.4 wt% in heavy fluff, 52.9 wt% in light fluff, and 5.4 wt% in glass and soil. Hydrogen content is 7.3 wt% in heavy fluff and 6.9 wt% in light fluff, and 0.5 wt% in glass and soil. Nitrogen content is 10.7 wt% in heavy fluff, 18 wt% in light fluff and 0.27 wt% in glass and soil. Oxygen and sulfur content are very low in all components. In particular, the carbon content is the highest among the ASR components because each material has the highest carbon content as shown in Table 9, where thermoplastics have the highest carbon and hydrogen content, and woods and papers have the highest oxygen content. The nitrogen content of thermosetting plastics is the highest, but the nitrogen content in the other materials is less than 1 wt%. With the exception of rubber, sulfur is not detected in all materials. Table 10 shows the ultimate analysis of total ASR compared with other studies. The values from each study are different, but the pattern of wt% is very

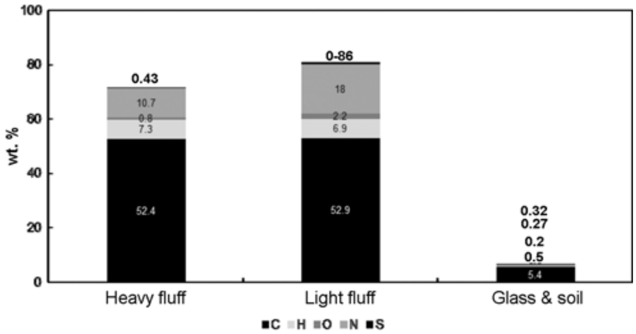


Fig. 8. Ultimate analysis for each ASR component.

Table 9. Ultimate analysis for each material of ASR

Materials	C	H	O	N	S
Rubbers	75.29	6.85	3.78	0.13	0.34
Resins	53.27	4.48	27.36	0.76	0.00
Wires	37.26	4.41	17.50	0.00	0.00
Thermosetting plastics	55.67	8.02	22.29	4.35	0.00
Thermo plastics	80.59	13.52	0.34	0.00	0.00
Woods	43.88	5.55	40.78	0.21	0.00
Papers	30.92	4.17	36.81	0.16	0.00

similar. The data from the present study also show similarity to other studies. However, the results of the present study show a large amount of oxygen and nitrogen compared to those of other studies. This may be due to the ASR materials as described in Table 8 [12,20-25].

1-6. Thermogravimetric Analysis

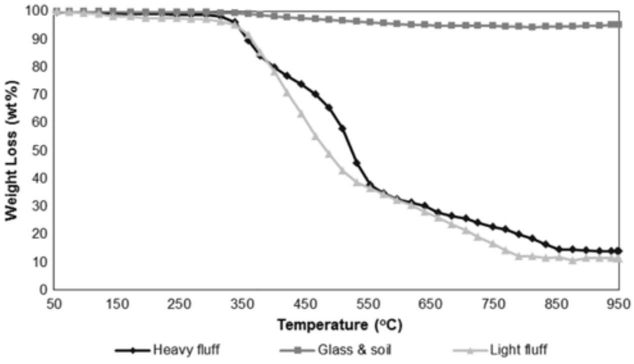
Fig. 9 shows the thermogravimetric analysis (TGA) results of ASR components. As shown in Fig. 11(a), heavy and light fluffs exhibit very similar patterns of weight loss, and significant weight loss begins to occur at 300 °C. However, glass and soil do not exhibit meaningful weight loss with increasing temperature. Further, Fig. 11(b) shows that most of the materials begin to lose weight at approximately 300-500 °C. Papers and woods start to decompose at lower temperatures, and most weight is reduced at approximately 300-400 °C. The weight of thermoplastics (TP), thermosetting plastics (TSP) and resins sharply decreased at approximately 400-600 °C. High temperature is required for complete thermal degradation of rubber. The weight decrease of soil is very slow, and soil contains relatively low combustible materials. Thus, the amount of remaining ash is approximately 90 wt%, which is higher than that of other materials. In the case of plastics, the amount of remaining ash at 950 °C, which is the final temperature, is less than 20 wt%. Considering each component of ASR, the thermal degradation range is as wide as 300-800 °C. The remaining ash is

Table 8. Caloric value for total ASR

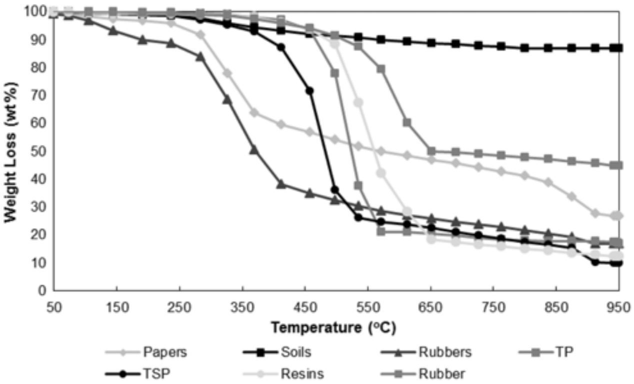
	Present study	Zolezzi et al. (2004)	Galvagno et al. (2001)	Day et al. (2001)	Rausa and Pollesel (1997)	Roy and Chaala (2001)	Kondoh et al. (2000)	Mancini et al. (2010)
HHV (kcal/kg)	5,316	5,000	4,643	3,429	6,738	3,548-7,310	6,833	4,699

Table 10. Ultimate analysis for total ASR

Element (wt%)	Present study	Zolezzi et al. (2004)	Galvagno et al. (2001)	Day et al. (2001)	Rausa and Pollesel (1997)	Roy and Chaala (2001)	Kondoh et al. (2000)	Mancini et al. (2010)
C	49.77	47	37.2	30	56.61	32.8-45.1	60	36.3
H	5.07	5.8	4.8	3.7	7.89	4.1-6.2	6.6	4.67
O	19.52	19.5	1.5	7	21.35	-	7.8	-
N	2.42	1.2	2.1	1.7	2.72	0.6-2.1	1.7	-
S	0.62	0.3	0.4	0.3	0.23	0.2-1	-	0.280



(a) ASR components



(b) ASR materials

Fig. 9. TGA analysis for ASR.

distributed between 10 and 98 wt% according to the ASR materials, and remaining ash of soil is the highest.

TGA analysis data of total ASR from the present and other studies are summarized in Fig. 10. Both the present and the reference [27] studies were in the presence of nitrogen with increasing temperature up to 950 °C. Although ASR concentrations were different between the two samples, two thermal degradation curves show very similar patterns. As clearly seen, the major weight loss occurs near 250-500 °C. However, the amount of final residue is 40 wt% for the reference and 25 wt% for the present study.

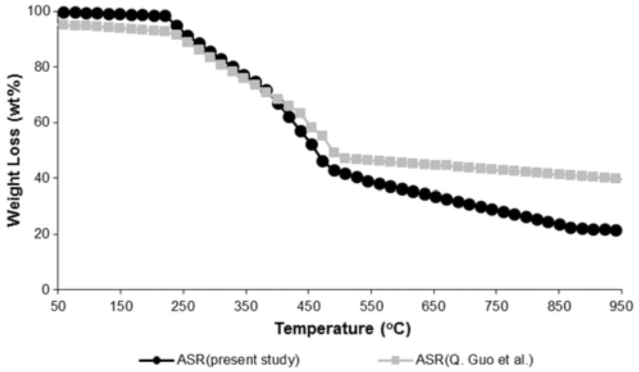
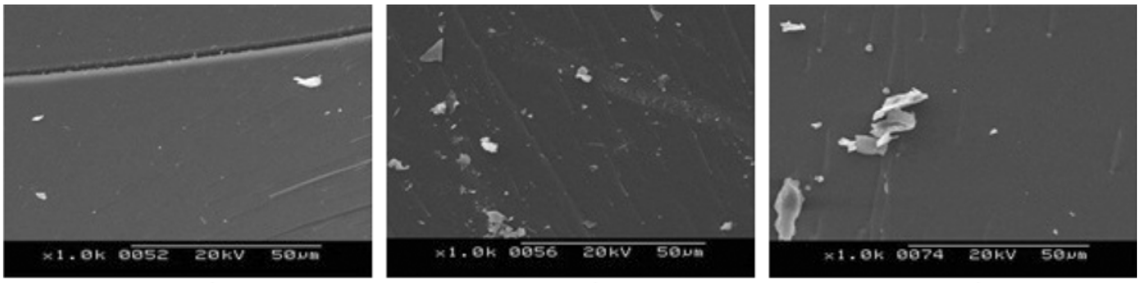


Fig. 10. TGA analysis of total ASR compared with Guo et al.

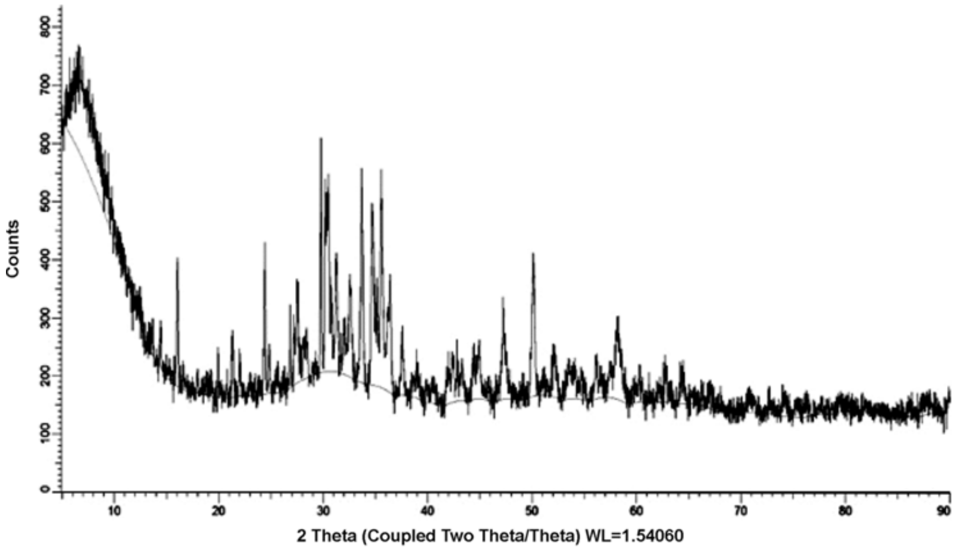
2. Result of Lab-scale Melting Experiment

In the melting experiment, the ASR was used as a reduction agent instead of lump coal, and the secondary copper, C-slag and waste foundry sands were used as sample materials. Here, C-slag refers to copper slag, which is generated by the copper smelting process as waste. For reference, secondary copper, which is critical to the operation of a copper refinery, was used as the main raw material. Recently, materials that contain copper such as PCB substrate have also been used. C-slag improves the fluidity in the melting furnace, and the role of the waste foundry is to separate the raw material into black copper and discard slag. Fig. 11 presents the surface of slag observed by using SEM for ASR slag. As

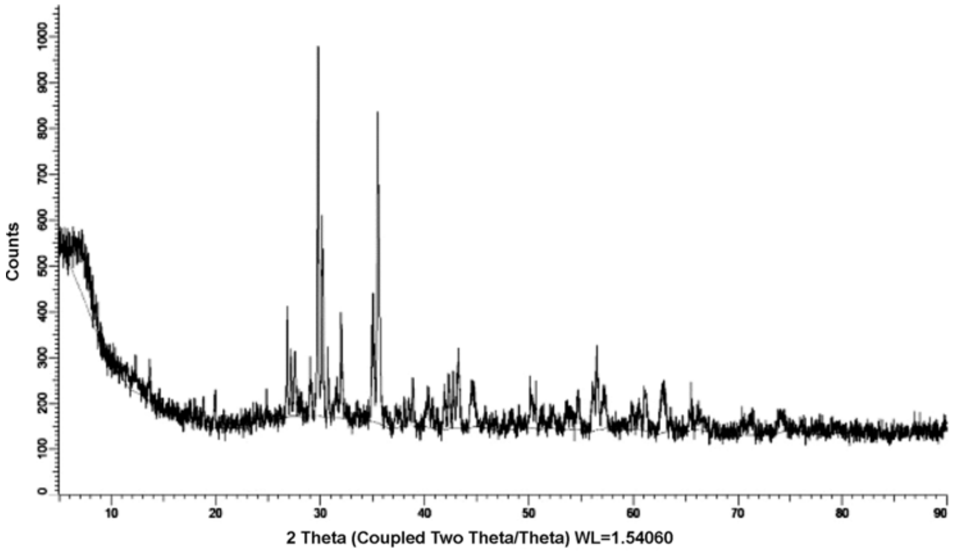


1300 ℃ 1350 ℃ 1400 ℃

Fig. 11. SEM results of the surface of melting slag depending on the temperature conditions.



(a) Lump coal



(b) ASR

Fig. 12. XRD Results of melting slag at 1,300 °C depending on reducing agents. (a) Lump coal. (b) ASR.

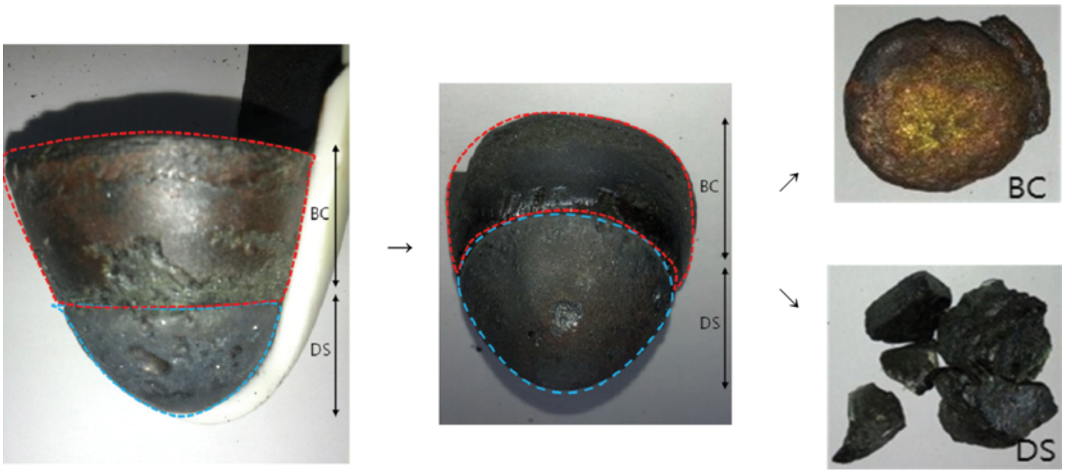


Fig. 13. Experiment result as separating BC and DS.

shown, crystal was not formed on the surface of the slag. The precipitation process of melting slag is different according to the existence of a crystal nucleus. If a nucleating agent (material) exists, precipitation occurs homogenously from the inside [17,28]. However, in some cases, a glassy state is achieved inside the slag because the growth rate of crystal on the surface is very slow. XRD analysis results of the melting slag at 1,300 °C as a function of reducing agents are presented in Fig. 12. As shown, a few peaks of crystalline structure appear, but an amorphous state is observed in both cases. In addition, there is no significant difference between the XRD results of the two cases; hence, the replacement of lump coal by ASR does not affect the molecular structure of the melting slag. This means that lump coal can be substituted by ASR as a reducing agent, satisfying the smooth discharge from the furnace during the actual recovery process.

3. Result of Copper Content in Melting Slag

To determine whether copper can be additionally recovered from ASR, the following experiment was performed. Fig. 13 shows black copper (BC) and discard slag (DS) after separation via the melting experiment involving the replacement of lump coal by ASR. Fig. 14 shows the copper content in the raw material, BC and DS. The values were divided by the initial weight of the sample. As the melting temperature increases, the copper content in BC increases, but the copper content in DS is reduced. It is considered that copper in DS migrates to BC in the lower part of a crucible as the temperature increases. By comparing the results based on the reducing agent, the copper content is slightly higher in the sample with ASR than lump coal, because there is copper in the ASR but not in the lump coal. However, as mentioned, it is almost negligible. Second, under the same temperature conditions, the copper content of BC is higher when ASR was used as a reducing agent.

4. Heavy Metal Content and Leaching Concentration of Melting Slag

Various heavy metals have been used as materials in vehicles. In particular, bronze, hexavalent chrome, mercury, cadmium, etc., are contained in bearing cells, anticorrosive coating materials, dashboards and batteries. Heavy metals in melting slag have stable oxidized structures because they melt at fairly high temperature. Hence, it is difficult for heavy metal to leach from melting slag. However, in melting slag, which is produced under reduction conditions, heavy metals cannot bond completely. Therefore, heavy metals are able to be leached as elements or metallic oxides. To evaluate environmental hazards, the heavy metal content in ASR-slag and the leaching concentration of heavy metals were analyzed. Leaching experiments were performed using the Korea Standard Leaching Test (KSLT). Organic compounds in the leached liquid were then decomposed according to the EPA Method 7471A. After filtering (Whatman 41) the sample, heavy metals were measured by using ICP (Inductively coupled plasma emission spectroscopy, Varian, Model: Ultramass 700). The results are presented in Table 11.

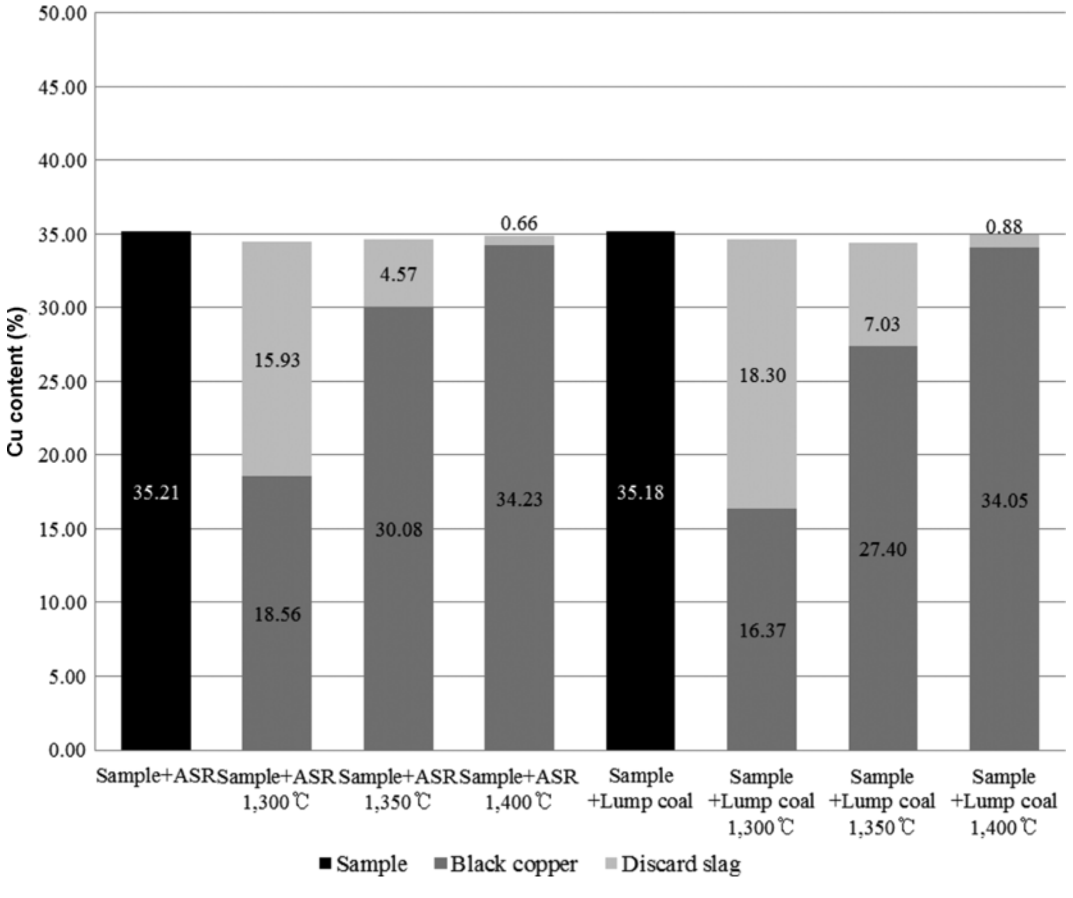


Fig. 14. Copper content in the sample and products depending on the temperatures.

Table 11. Heavy metal content and leaching concentration of melting slag

Analyte	Total heavy metal (mg/kg)			Heavy metal leaching concentration (μg/*l*)		
	1300 °C	1350 °C	1400 °C	1300 °C	1350 °C	1400 °C
Al	109,320.830	99,004.166	92,002.254	ND	ND	ND
Fe	178,234.250	135,589.498	157,295.641	0.021	0.016	0.002
Ag	1.717	ND	1.006	ND	ND	ND
Be	1.281	1.021	ND	ND	ND	ND
Cd	2.975	1.351	1.982	0.002	0.023	0.007
Co	13.716	11.742	11.564	ND	ND	ND
Cr	7,000.984	5,095.396	6.845.561	0.012	0.029	0.07
Cu	798.766	500.431	489.412	ND	0.001	ND
Mn	1,751.175	1,093.629	1.495.236	ND	ND	ND
Mo	14.942	5.128	8.641	ND	ND	ND
Ni	94.806	147.700	ND	0.003	ND	ND
Pb	4.746	ND	2.644	ND	ND	ND
Sb	ND	ND	ND	ND	ND	ND
Sn	ND	1.391	ND	ND	ND	ND
Ti	4,441.577	2,732.798	2.541.368	ND	1.307	ND
V	24.194	15.700	11.654	ND	ND	ND
Zn	20.733	9.576	18.764	ND	46.965	38.553
Hg	0.031	ND	ND	ND	ND	ND

Although leaching concentrations of As, Cd, Cr, Fe, etc. are higher than those of other heavy metals, they do not exceed Korean standards.

CONCLUSION

The status quo of ELV management in Korea was investigated, and the physicochemical and thermal characteristics of ASR were analyzed.

1. ASR is the final product of the shredding process of ELVs. In Korea, ASR is generated at a rate of approximately 20-30 wt% based on the weight of new cars through the shredding process. Most ASR is disposed of by landfill or incineration. Korean domestic vehicle industries should aim for a 95 wt% recycling rate until 2015 according to the law regarding resource recycling of electrical and electronic equipment and vehicles.

2. ASR is generally classified into three types: heavy fluff, light fluff and glass and soil. In Korea, the portions of heavy fluffs, light fluffs and glass and soil in ASR are 89.2 wt%, 8.1 wt% and 2.7 wt%, respectively. As a result of the physicochemical analysis, the apparent density of ASR was computed to be 347 kg/m^3. The particle size in heavy and light fluffs generally exceeded 53.0 mm. However, most of the glass and soil particles were generally of medium size at approximately 2.0-19.0 mm. From proximate analysis of each component of ASR, combustible content was 67.13 wt% in heavy fluff, 74.47 wt% in light fluff and 6.27 wt% in glass and soil. In the three ASR components, the moisture content was less than 1 wt%. The caloric value of light fluff was 6,607 kcal/kg, which is the highest value among the three components. In addition, the caloric values of heavy fluff and glass/soil were 5,312 kcal/kg and 571 kcal/kg, respectively. From the ultimate analysis of each ASR component, carbon content was 52.4 wt% in heavy fluff, 52.9 wt% in light fluff, and 5.4 wt% in glass and soil. Hydrogen content was 7.3 wt% in heavy fluff, 6.9 wt% in light fluff, and 0.5 wt% in glass and soil. Nitrogen content was 10.7 wt% in heavy fluff, 18 wt% in light fluff and 0.27 wt% in glass and soil. Oxygen and sulfur content was very small for all cases. From TGA, for the heavy and light fluffs, significant weight loss started at 300 °C. However, glass and soil did not show meaningful weight loss with increasing temperature.

3. To sum up, when ASR was used instead of lump coal as a reducing agent in the copper recovery, molten states were very similar to that of lump coal. Moreover, the heavy metal content and leaching did not exceed Korean government mandates on pollution. In conclusion, the replacement of lump coal by ASR does not affect the process of separating BC and DS and the slag discharge characteristics.

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