

A Novel Process for Extracting Precious Metals from Spent Mobile Phone PCBs and Automobile Catalysts

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A novel process to simultaneously extract the precious metals such as gold, silver, platinum, palladium and rhodium from spent mobile phone printed circuit boards (PCBs) and honeycomb-type auto catalysts by smelting using waste-copper slag without adding any collector metals or by-products such as dross, matte and slime has been developed. In the process, waste-copper slag which is an industrial waste discharged from copper smelter is used not only as a flux for controlling slag composition, but also as a collector metal for capturing precious metals, and a plastic component contained in spent mobile phone PCBs is done as a reducing agent of iron oxides contained in the waste-copper slag. Using the developed process, up to 95% of gold, silver, platinum, palladium and rhodium contained in the raw materials were extracted in a Cu–Fe–Sn alloy phase, respectively. [doi:10.2320/matertrans.M2013051]

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1. Introduction

Large amounts of spent printed circuit boards (PCBs) and honeycomb-type auto catalysts are generated, respectively, from mobile phones and automotive catalytic converters. The environmental pollution caused thereby becomes a social issue. However, the spent PCBs and auto catalysts contain precious metals such as gold, silver, platinum, palladium and rhodium that can be recovered. It has been known that the total amount of precious metals contained in spent mobile phone PCBs is 700–4,000 ppm, and that in spent auto catalysts is 1,000–2,000 ppm.^{1–5)} In addition, the spent PCBs contains significant amounts of valuable metals like copper, tin and iron.^{1–5)} Thus, recovering such precious metals is strongly required in terms of effective utilization of resources and environmental conservation. Currently, a number of processes for extracting precious metals from the solid wastes have been suggested and developed. These are largely divided into gas phase volatilization, hydrometallurgical and pyrometallurgical processes.

In the gas phase volatilization process, precious metals from spent auto catalysts are volatilized by selective chlorination and condensed in a cooler zone. Most of the volatilization reactions are carried out in the temperature range of 523–873 K.^{6,7)} The hydrometallurgical process is to leach precious metals from spent PCBs and auto catalysts by using acid or alkali solutions and concentrate them from the leach solution by using various methods like precipitation, cementation and solvent extraction.^{6,7)} In the pyrometallurgical process, spent auto catalysts are melted with flux components and contact the molten slag containing precious metals with a molten metal pool, into which the precious metals dissolve and accumulate. The molten metal is called a collector metal. Iron, copper, nickel, lead-copper and nickel matte are commonly used as collector metals.^{6,7)} The extracted precious metals must be further treated in order to individually separate and purify them. Recently, several

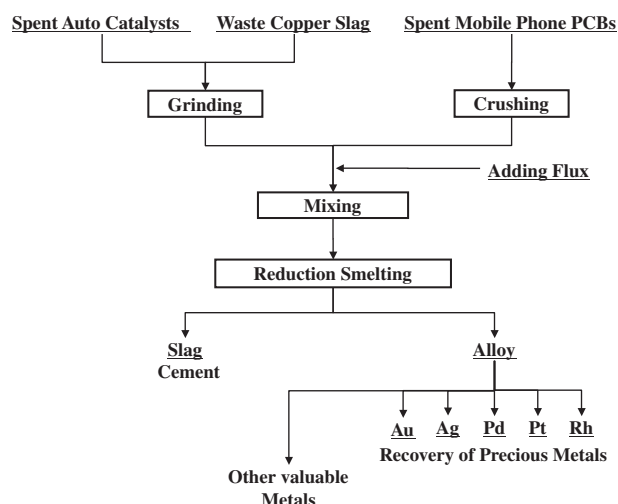


Fig. 1 Flow sheet of the process developed in the study.

pyrometallurgical processes that employ the nonferrous metal smelting furnaces are developed and commercialized. The processes are to extract precious metals as a nonferrous metal phase from spent PCBs and auto catalysts charging in the furnaces them together with nonferrous concentrate or byproducts such as dross, matte and slime.^{8,9)} In the processes, the extracted precious metals are also further treated in order to individually separate and purify them.

Among the above processes, the pyrometallurgical processes are effective for extracting precious metals from the solid wastes in a large-scale treatment. However, a process that can extract precious metals from spent PCBs and auto catalysts by using waste nonferrous slag without adding any collector metals or byproducts such as dross, matte and slime has not yet been developed. The present research is concerned with developing such a new process. Figure 1 shows the flow sheet of the developed process. In the present process, waste-copper slag which is an industrial waste discharged from copper smelter can be used not only as fluxes for controlling slag composition, but also as a collector

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Table 1 Chemical composition of spent mobile phone printed circuit boards (PCBs).

Element	Concentration (mass%)
Au	0.1359
Ag	0.2262
Pd	0.0096
Pt	0.0036
Rh	0.0005
Cu	42.8
Fe	4.6
Sn	2.6
Ni	0.6
Pb	0.06
Zn	0.01
Co	0.01
Al ₂ O ₃	4.2
SiO ₂	10.0
CaO	2.7
MgO	0.4

Table 2 Chemical composition of spent honeycomb-type auto catalysts.

Element	Concentration (mass%)
Pd	0.08
Pt	0.07
Rh	0.01
Al ₂ O ₃	37.8
SiO ₂	34.6
CaO	0.8
MgO	9.2

metal for capturing precious metals, and a plastic component contained in spent PCBs can be used as a reducing agent. It was thus thought that the developed process is simple and economic compared with the conventional pyrometallurgical processes.

2. Experiment

2.1 Choice of slag system

Tables 1 and 2 present the chemical compositions of the spent mobile phone PCBs and auto catalysts, used in the work. The samples were respectively obtained from spent mobile phones and automotive catalytic converters. Figure 2 shows the liquidus line at 1673 K of the ternary slag system consisting of the three main slag components contained in the spent PCBs. The dot in the figure represents the weight-percent composition based on the total mass of just the three main slag-forming oxides contained in the spent PCBs. As shown in Fig. 2, the melting temperature of the spent PCBs is expected to be over 1673 K. It was reported by previous researchers that the melting temperature of the spent auto catalysts is over 1873 K.⁵⁾ Such high melting temperature means that a lot of energy is necessary to dissolve and accumulate the precious metals contained in the spent PCBs and auto catalysts into a molten metal pool. Thus, suitable

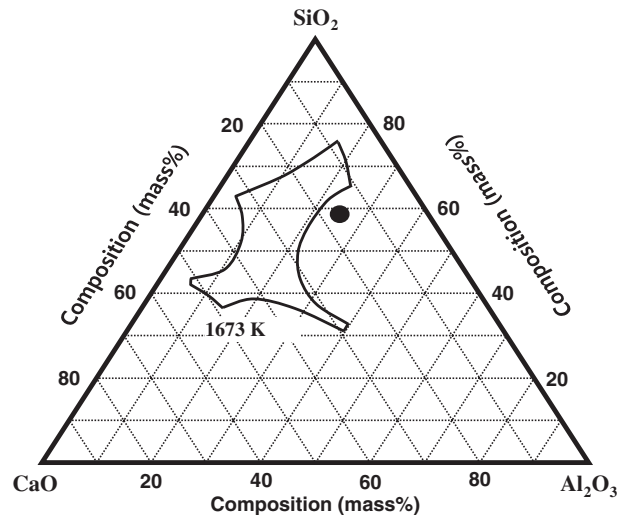


Fig. 2 Liquidus line at 1673 K of the Al₂O₃-CaO-SiO₂ slag system used to predict the melting temperature of the spent mobile phone PCBs. The dot represents the mass% composition based on the total mass of just the three main slag-forming oxides contained in the used PCBs (Table 1).

Table 3 Chemical composition of waste-copper slag.

Element	Concentration (mass%)
Cu	0.7
FeO	47.9
Al ₂ O ₃	4.1
SiO ₂	34.5
CaO	3.4
MgO	1.2

fluxes are needed to lower their melting temperatures. However, the additional amounts of fluxes must be as small as possible, because it is undesirable to generate large amounts of waste solids that require disposal.

With this in mind, an FeO-CaO-SiO₂ slag system was chosen to simultaneously extract precious metals such as Au, Ag, Pd, Pt and Rh from the spent PCBs and auto catalysts by smelting with adding waste-copper slag as a slag formative while minimizing the additional amount of fresh slag formatives. Table 3 presents the chemical composition of the waste-copper slag used in this work. The waste slag was obtained from LS-Nikko copper smelter INC. in Korea. Currently, large amount of the waste slag has been discarded from the slag cleaning furnace of copper smelting furnace. It is thus desirable to reuse the waste-copper slag in the viewpoint of resource recycling. Figure 3 shows the liquidus line of the waste-copper slag system at 1573 K. Also displayed in this figure is the target composition region that will be used to calculate the input ratio of spent PCBs, spent auto catalysts, and fluxes in the reduction smelting step.

2.2 Experimental procedure

Reduction smelting experiments were carried out in a box type furnace described in previous paper.⁵⁾ Waste-copper slag and spent auto catalysts were first crushed into small particles with a diameter of from 0.5 to 1.0 cm, respectively. Spent

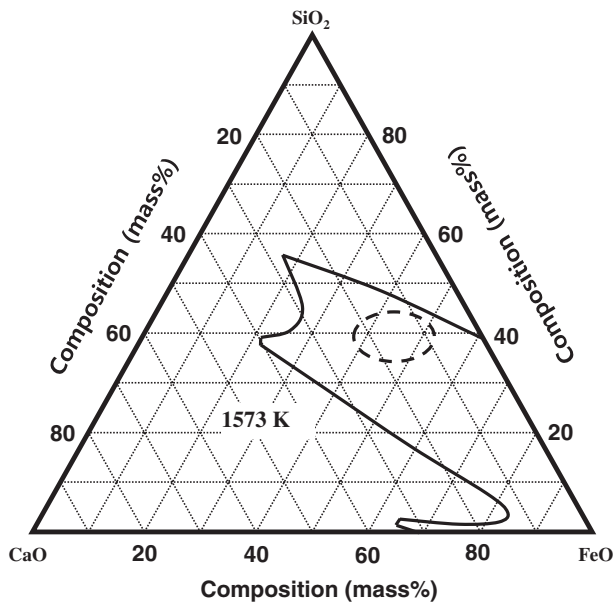


Fig. 3 Liquidus line at 1573 K of FeO–CaO–SiO₂ slag system which is the waste-copper slag system. Circle with dotted line represents the target composition region that will be used to calculate the input ratio of spent mobile phone PCBs, spent auto catalysts and waste-copper slag in the reduction smelting step.

Table 4 Input amounts of raw materials tested for the reduction smelting.

Sample No.	Amount of species (g)			
	Spent mobile phone PCBs	Spent auto catalyst	Waste-copper slag	CaO
A	100	30	150	30
B	100	50	150	50
C	100	100	150	70

PCBs are also crushed under 5 cm to insert easily into a melting crucible. The waste-copper slag, spent PCBs and auto catalysts were then mixed with CaO which is a flux as an agent for controlling slag composition. Here, CaO used in the experiments was analytical grade manufactured by Junsei Chemical Company. The addition amounts of CaO were calculated by considering the chemical compositions of FeO, CaO and SiO₂ contained in the spent PCBs, auto catalysts and waste-copper slag to achieve the target slag composition region shown in Fig. 3. Here, the reduction agents such as coal and coke were not added because spent PCBs contains considerable amount of plastic which can be used to maintain the reduction atmosphere of furnace during the smelting. The mixture was charged in an alumina crucible (10 cm height and 7 cm inner diameter), and fed to the reactor in the furnace. In the experiment, the range of 310–420 g (\pm 2 g) of the mixed solids was used for each run. Table 4 presents the input amount of raw materials tested for the reduction smelting. The mixture started melting at around 1473 K, and was fully melted at 1573 K for 1200 s. And then, the reduction smelting was carried out at the range of 1623–1698 K for 3600 s to obtain a melt. After that, the melt was cooled in air. During the experiments, it was not possible to avoid partial erosion of the crucible.

Table 5 Average chemical compositions of slags obtained from the charge materials under the reduction smelting temperature between 1623 and 1698 K.

Sample No.	Temp. (K)	Concentration (mass%)					
		Al ₂ O ₃	CaO	FeO	Fe ₂ O ₃	MgO	SiO ₂
A	1623–1698	11.1	17.2	18.2	7.4	2.0	32.8
B	1673	12.0	22.7	14.2	6.5	2.8	33.3
C	1673	15.1	24.3	11.8	5.2	3.7	30.4

Table 6 Mass and chemical compositions of alloys obtained from the charge materials under the reduction smelting temperature between 1623 and 1698 K.

Sample No.	Temp. (K)	Mass of Alloy (g)	Concentration								
			Cu	Fe	Sn	Ni	Au	Ag	Pd	Pt	Rh
			mass%				ppm				
	1623	65.1	64.1	23.1	4.4	2.2	1880	3300	450	440	110
A	1673	68.4	60.1	30.8	4.0	2.1	1800	2350	450	380	120
	1698	69.1	60.5	30.3	3.9	2.4	1800	2900	440	380	95
B	1673	65.8	59.5	32.2	5.0	2.3	1600	3450	930	430	170
C	1673	70.6	57.0	33.7	5.2	2.4	1400	3400	1350	780	310

Samples before and after the reduction smelting were analyzed for Au, Ag, Pd, Pt, Rh, Cu, Sn, Ni, Al, Ca and Mg by the inductively coupled plasma (ICP) method (JY-38 Plus, Jobin-Yvon Equipment Co., London, UK). Also, the total iron and divalent iron contents in the slag specimens were determined by titration with K₂Cr₂O₇, the SiO₂ content by a gravimetric analysis method.

In the present study, the extraction ratios of gold, silver, platinum, palladium and rhodium were defined as:

$$E_M = \frac{A_M}{(A_M + S_M)} \times 100 \quad (1)$$

where, E_M is the extraction ratio of M metal, A_M is the weight (g) of M metal concentrated into the molten metal phase (alloy phase), and S_M is the weight (g) of M metal remained in the slag phase.

3. Results and Discussion

Table 5 presents the chemical composition of the slags obtained from the experiments. Although the viscosity of the slag was not measured in this study, it was estimated to be about 4 poise at 1673 K based on previously reported data.¹⁰⁾ Thus, all the molten phases obtained in this work were easily separated into slag and alloy phases.

Table 6 presents the mass and chemical compositions of the alloy phases obtained from the experiments. As shown in Table 6, the alloy phase was mainly composed of copper, iron and tin with small amounts of Au, Ag, Pt, Pd and Rh. Here, most iron in the alloy phase was reduced from iron oxide compounds contained in the waste-copper slag by a plastic component contained in the spent PCBs. It was verified that the average reduction ratio of the iron oxide compounds is about 29.5%.

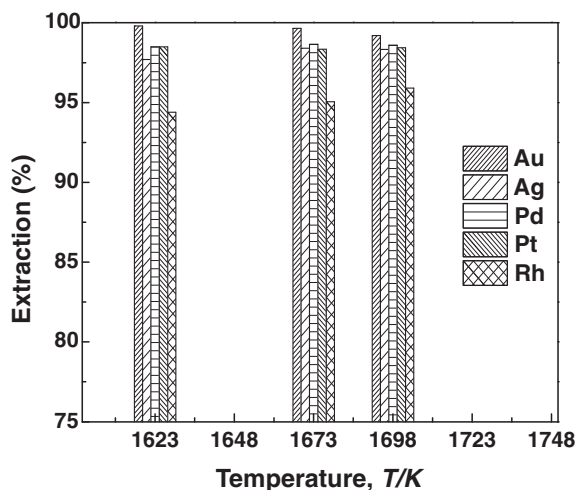


Fig. 4 Average recovery percentage of Au, Ag, Pd, Pt and Rh extracted from the charge material of A in Table 4.

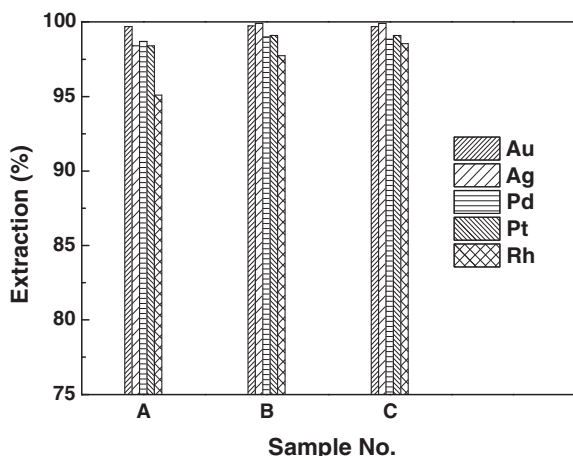


Fig. 5 Average recovery percentage of Au, Ag, Pd, Pt and Rh extracted from the charge materials in Table 4 under a reduction smelting temperature of 1673 K.

The effect of reduction smelting temperature on the recovery percentages of Au, Ag, Pt, Pd and Rh was examined by varying the temperature between 1623 and 1698 K, while the mixing ratio was kept constant. Figure 4 presents the effect of reduction smelting temperature on the recovery percentages using sample A shown in Table 4. It is seen in the figure that the recovery percentages were over 95% for all precious metals considered at over 1673 K and recovery percentages is relatively steady at the considered temperature range.

The effect of the input amount of auto catalysts on the recovery percentages of Au, Ag, Pt, Pd and Rh was examined by varying the input amount between 30 and 100 g, while the reduction smelting temperature was kept constant. Figure 5 presents the effect of the input amount on the recovery percentages of Au, Ag, Pt, Pd and Rh under a reduction smelting temperature of 1673 K. These results show that Au, Ag, Pt, Pd and Rh are predominantly collected in the alloy phase, and the recovery percentages are over 95% under all the mixing ratios considered. Also, it is noted that the

recovery percentages is not changed with increasing the input amount of auto catalysts.

It was thus verified that the novel process to extract precious metals contained in spent mobile phone PCBs and honeycomb-type auto catalysts by reduction smelting using waste-copper slag without adding any collector metals or byproducts such as dross, matte and slime is possible. The main feature of the process is that waste-copper slag is used not only as a flux for controlling slag composition, but also as a collector metal for capturing precious metals, and a plastic component contained in spent mobile phone PCBs is done as a reducing agent of iron oxides contained in the waste-copper slag.

Therefore, the proposed process is simpler than conventional processes, and has an additional benefit of recovering other valuable metals like copper, tin and iron from spent mobile phone PCBs and waste-copper slag.

4. Conclusions

In this study, a novel process to extract precious metals contained in spent mobile phone PCBs and honeycomb-type auto catalysts by smelting without collector metals with using only CaO as a slag formative was investigated. Based on the experimental results, a novel process flow-sheet was proposed. In the reduction smelting process over 95% of gold, silver, platinum, palladium and rhodium contained in the spent PCBs and auto catalysts were respectively extracted in a Cu-Fe-Sn alloy phase at the reduction smelting temperature of over 1673 K under all the mixing ratios considered. The proposed novel process is thus simpler than conventional processes as there is no requirement of collector metals like dross, matte and slime used in conventional pyrometallurgical processes.

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