

Ammonium Thiosulfate Leaching of Gold, Silver, and Copper from waste PCBs: Effects of Ammonia- and Chloride-based Pretreatments on the Improvement of Metal Extraction Efficiency

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Abstract: The present study describes the leaching of gold (Au), silver (Ag), and copper (Cu) from waste printed circuit boards (PCBs) of personal computers by ammonium thiosulfate leaching, and its pretreatment study for improving the extraction efficiency by ammonia or ferric chloride leaching was carried out. About 95%, 68%, and 90% of Au, Ag, and Cu leaching efficiency were obtained under the following conditions: 1 M of $\text{Na}_2\text{S}_2\text{O}_3$, 10 mM of CuSO_4 , 1 M of ammonia/ammonium concentration, 1% of pulp density, and a 24 h of leaching time in the presence of oxygen. When the pulp density was increased to 10%, however, the precious metal leaching efficiency significantly decreased showing 0.1% and 0.9% of Au and Ag extraction efficiency, respectively, and this may be due to the re-deposition of the dissolved metal ions to the base metals (especially Cu) in PCBs via electrochemical/galvanic interactions. To improve the leaching efficiency, pretreatment leaching by ammonia or chloride leaching was carried out and results showed that over 99% of Cu was dissolved by both of ammonia and ferric chloride leaching, and Au and Ag leaching efficiency increased to 9.6% and 14.4% in ammonium thiosulphate leaching in subsequent to ammonia leaching while increased to 31% and 34% in ammonium thiosulphate leaching in subsequent to ferric chloride leaching with the 10% of pulp density.

Keywords: Ammonium thiosulphate leaching, Gold, Silver, Copper, Printed circuit board, Ammonia leaching, Ferric chloride leaching

1. INTRODUCTION :

The rapid advance in electronic technologies makes early obsolescence of the devices thereby generating discarded gadgets, generating the fastest increase in waste electronics (i.e., E-waste) worldwide yearly. Printed circuit boards (PCBs) are essential part in all sorts of electronic equipment, and it generally composed of epoxy resin, fiber glass, cellulose and phenolic paper coated with copper layers, and silver (Ag) and/or gold (Au) are mainly present in the form of thin films on the PCBs [1]. The amount of those precious metals in PCBs contains much higher than in typical ores. For example, Au, Ag, and Cu content in PCBs were about 20–300 folds, 2–5 folds, and 400–650 folds higher than in typical ores, E-waste recycling thus has been steadily in the limelight worldwide [2–4].

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In recycling hydrometallurgy, thiosulfate solution has been extensively studied as an alternative method for the traditional technologies (e.g., cyanide or halides (aqua regia)) due to its environmental advantages such as non-toxic and mildly corrosiveness as well as high selectivity for the precious metals. The present study aims to carry out the leaching of Au, Ag, and Cu from waste PCBs, and pretreatment leaching was then studied to increase the leaching efficiency of precious metals, especially Au and Ag.

2. MATERIALS AND METHODS

2.1. PCB sample

Waste PC-PCBs were first crushed by a cutting mill (VH16, Seishin Enterprise Co., Ltd., Japan) and freeze crusher (TPH-02, As One, Japan) followed by a vibratory disc mill (RS 100, Retsch Co., Ltd., Germany) to obtain particles with D50 of 85 μ m (Figure 1). Chemical composition was checked by ashing furnace to burn the combustible materials, and the resulting ashing residue was then dissolved in aqua regia (1:3 by volume mixture of concentrated nitric and hydrochloric acids) at 90 °C for 2 h and the leachate was analyzed by ICP-AES (ICPE-9820, Shimadzu Corporation, Japan) (margin of error = \pm 2%). The results are summarized in Figure 2 and Table 1.

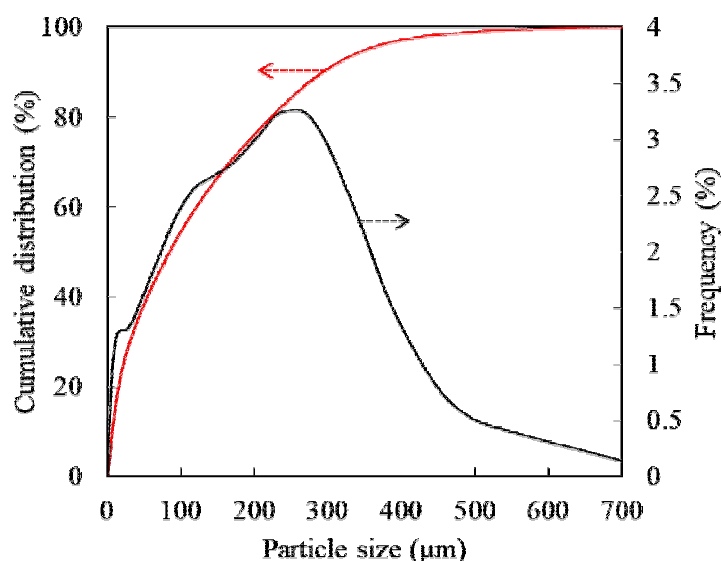


Figure 1. Particle size analysis of crushed waste PCBs.

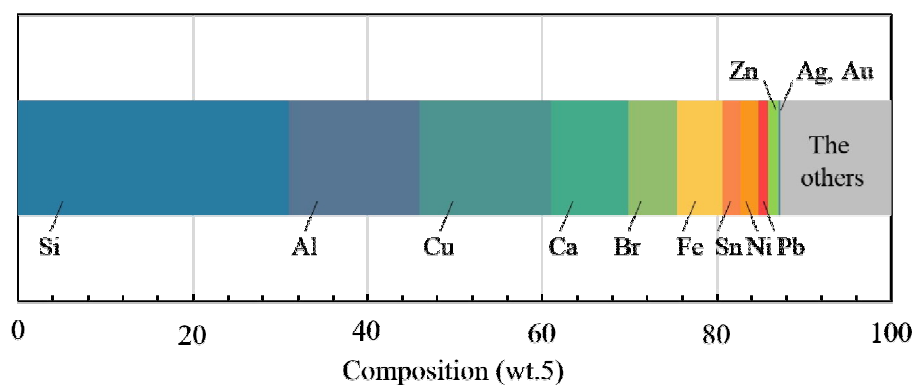


Figure 2. Elemental composition of PCBs.

Table 1. Elemental composition of PCBs in detail.

Elements	Wt. %
Si	31
Al	15
Cu	15
Ca	8.8
Br	5.6
Fe	5.2
Sn	2.1
Ni	2
Pb	1.2
Zn	1.1
Ag	0.17
Au	0.02
Others	12.81

2.2. Ammonium thiosulfate leaching experiments

Ammonium thiosulfate leaching experiments were conducted to investigate the effects of dissolved oxygen in the solution, leaching time, thiosulfate concentration, Cu (II) concentration, ammonia concentration, and pulp density on the Au, Ag, and Cu extractions. Leaching experiments were carried out in 50-ml Erlenmeyer flasks, and the flask containing solution with PCB samples were shaken a thermostat water bath shaker at a shaking speed of 120 rpm and amplitude of 40 mm at 25 °C. After shaking duration, the suspensions were separated by 0.2 µm membrane filters and the extracted metal ion concentrations were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES, ICPE-9820, Shimadzu Corporation, Japan) while residues were observed by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX, Superscan SSX-550, Shimadzu Corporation, Japan).

2.3. Ammonia leaching experiments

Ammonia leaching was carried out with solution containing 0.5 M of NH_4OH and 0.25 M of $(\text{NH}_4)_2\text{SO}_4$ (1:1 of molar ratio) with pH 9–10. All leaching experiments were carried out in 50-ml Erlenmeyer flasks, and the flask containing solution with PCB samples (10% of pulp density) were shaken a thermostat water bath shaker at a shaking speed of 120 rpm and amplitude of 40 mm at 25 °C. After leaching and solid-liquid separation, the leachate was analyzed by ICP-AES while residues were thoroughly washed with deionized water, then proceeded to ammonium thiosulfate leaching under the following conditions: 1 M of $\text{Na}_2\text{S}_2\text{O}_3$, 10 mM of CuSO_4 , 1 M of ammonia/ammonium concentration, 10% of pulp density, and a 24 h of leaching time in the presence of oxygen.

2.4. Ferric chloride leaching experiments

Ferric chloride solutions containing 0.5 M FeCl₃ and 0.5 M HCl with pH of around 1 were used in the leaching experiments. All leaching experiments were carried out in 50-ml Erlenmeyer flasks containing PCBs with ferric chloride solutions having 10% pulp density, and the flasks were shaken in a thermostat water bath shaker at a shaking speed of 120 rpm and amplitude of 40 mm at 25 °C. The subsequent procedure (i.e., ammonium thiosulfate leaching) was the same as the above explanations.

3. RESULTS AND DISCUSSION

3.1. Leaching of gold, silver, and copper from waste PCBs

Figure 3(a) presents the effects of dissolved oxygen in ammonium thiosulfate solution on leaching efficiency of Au, Ag, and Cu from waste PCBs. The results show that metal extractions were higher in the presence of the dissolved oxygen than in the absence system, indicating that oxygen is essential parameters in the oxidative leaching of metals as many previous authors reported on studies treating natural ores as well as E-waste in ammonium thiosulfate system [5]. In an ammonium thiosulfate system with O₂ condition, Au can be slowly dissolved into the ammonium thiosulfate solution as described in Eq. 1. If Cu(II) ammonia complex (Cu(NH₃)₄²⁺) is present in the solution, however, the leaching rate of precious metals further increased by about 18-20 fold generating Cu (I) thiosulfate complex (Cu(S₂O₃)₃⁵⁻) (Eq. 2). When the dissolved oxygen is present in the system, then it can be converted from Cu(I) complex to Cu(II) complex which is able to continuously leach target metals, leading to high leaching efficiency of precious metals as described in Eq. 3 [5]. This also could affect Ag dissolution (Eq. 4), and Cu dissolution efficiency is also further increased under the presence of oxygen conditions forming both ammonia and thiosulfate complexes as described in Eqs. 5 and 6 [6].

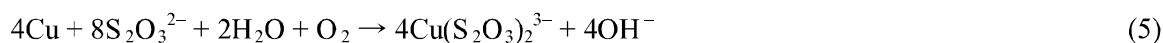
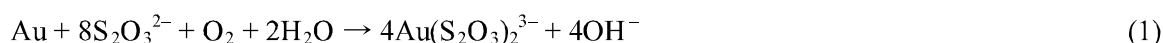
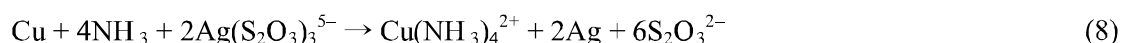
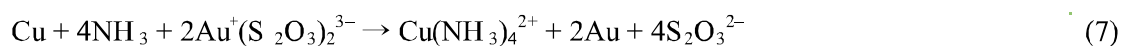


Figure 3(b) shows the leaching efficiency of Au, Ag, and Cu from waste PCBs in the ammonium thiosulfate solution varying extraction time. The results show that 95%, 69%, and 90% of Au, Ag, and Cu extractions, respectively were achieved for 24 h of leaching time. Figure 3 (c) shows the effects of thiosulfate concentration on Au, Ag, and Cu extractions from waste PCBs in ammonium thiosulfate system, and results show that the effects of thiosulfate concentration on metal extractions were negligible at below 0.1 M but increased above 1 M of thiosulfate concentration by the Eqs. 1, 4, and 5. Leaching of Au, Ag, and Cu also increased with increasing CuSO_4 concentration since Cu (II) complex acts as a strong oxidant known to catalyze the oxidative dissolution of metals in the ammonium thiosulfate system as mentioned in the previous part (Figure 3 (d)). Also, the effects of NH_3 concentration on metal extraction showed that extraction efficiency enhanced as NH_3 concentration increased. This could be elucidated by the fact that PCBs contain metallic Cu (about 15%) which is readily dissolved in the ammonium thiosulfate solvent generating higher concentration of catalyst (i.e., $\text{Cu}(\text{NH}_3)_4^{2+}$), leading to enhanced extraction of Au, Ag, and Cu (Figure 3(e)). Figure 3 (f) shows the effects pulp density on metal extractions in ammonium thiosulfate system, and results show that the increase in pulp density from 1% to 10% resulted in the significant decrease of metal extraction; Au, Ag, Cu extractions were decreased from 95% to 0.1%, 68% to 0.9%, 90% to 8.8%, respectively. There are several reasons for the results including lack of reagents, decomposition of thiosulfate, adsorption to organic material, or reductive deposition to base metals. The previous researcher focused on the leaching of gold from E-waste reported that one of the main reasons can be a reductive deposition of dissolved metal ions onto base metals forming galvanic cells according to the PCBs structure i.e., Cu and Al layers in PCBs [5,4]. For the identification, the leaching residue was observed by SEM-EDX. Figure 4 (a) and (b) show SEM photomicrographs with corresponding elemental maps of the leaching residue, and the results showed that Au was deposited onto the Cu and/or Al layers on PCBs after leaching, and compared with Au morphology in the residue and in the PCB samples, the morphology is different from it in PCB samples, implying that extracted precious metal ions were likely re-deposited onto the metals during the leaching as described in Eqs. 7 and 8. Jeon with co-authors also mentioned that Au was preferentially re-deposited on Cu and/or Al in crushed PCBs during leaching based on the residue characterization as well as cementation study [5].



To limit the antagonistic effect of Cu and Al coexistence on precious metal extraction, there was a previous study on separating Au concentrates and Cu-and/or Al-bearing parts in E-waste employing the physical separation techniques including gravity separation (e.g., Jig separation as well as hybrid-jig separation), magnetic separation, and flotation, and results showed that Au extraction was improved about 3-fold [7]. Although the extraction efficiency enhanced, there is a limitation in physically separating Au from Cu- and

Al-fractions as well as limitation in an increase in extraction efficiency due primarily to the PCBs structure such as layer or alloy form of the base metals forming galvanic cells that could enhance the reductive deposition of the precious metal ions during leaching. The subsequent research thus attempted to firstly leach Cu as a pretreatment which is the main component of PCBs and could be a main cause that increases the reductive deposition of the precious metal ions during leaching.

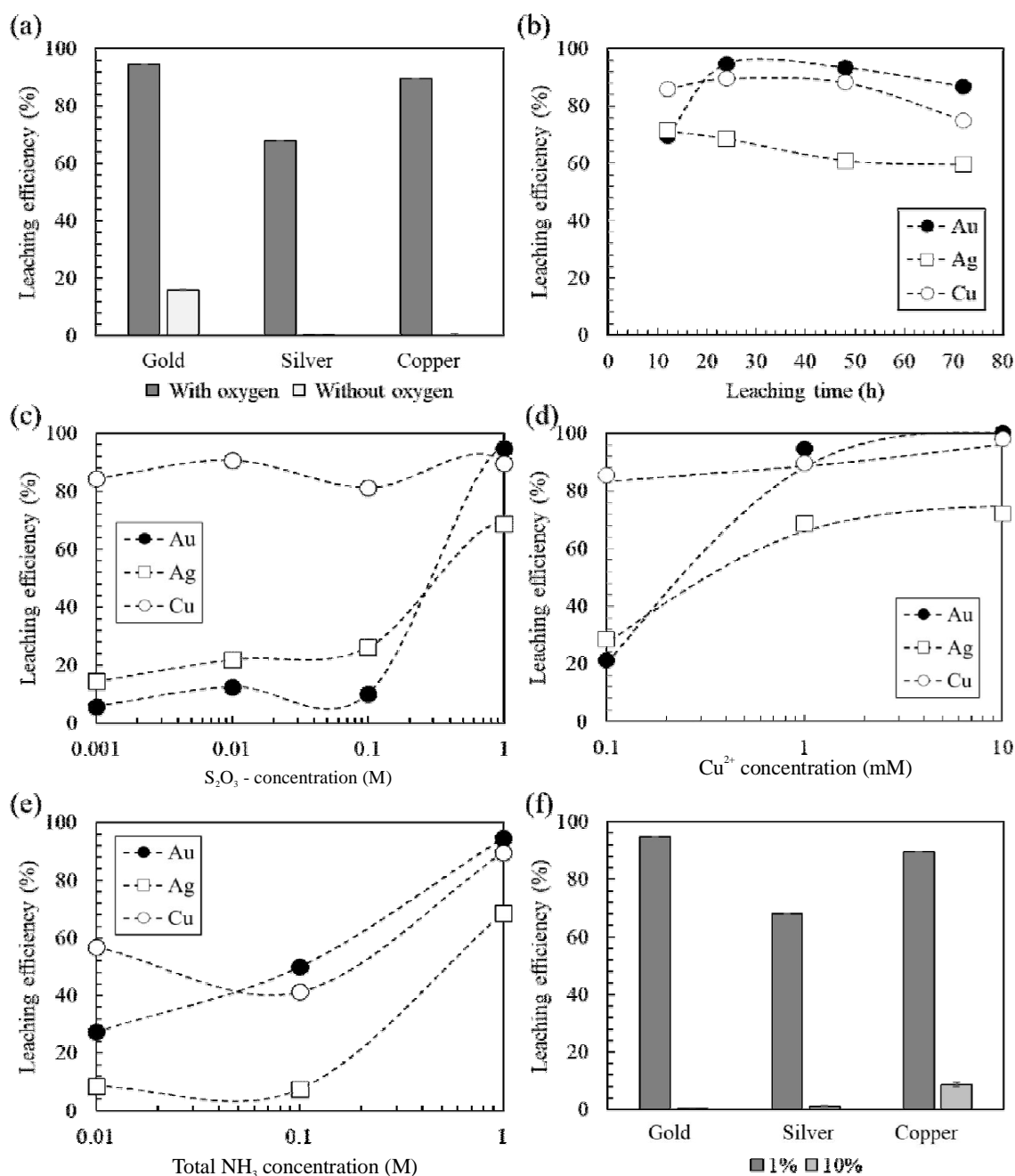


Figure 3. Leaching of gold, silver, and copper from waste PCBs with varying parameters including (a) with and without oxygen, (b) leaching time, (c) thiosulfate concentration, (d) Cu^{2+} concentration, (e) NH_3 concentration, and (f) pulp density in ammonium thiosulfate system.

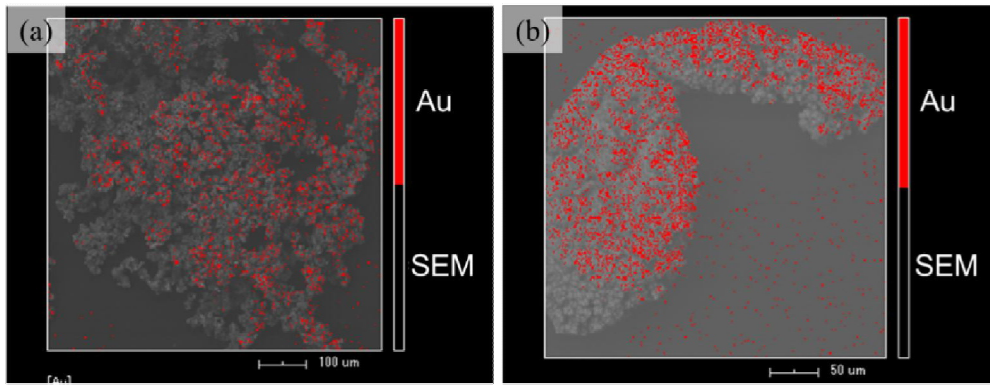
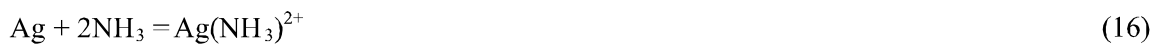
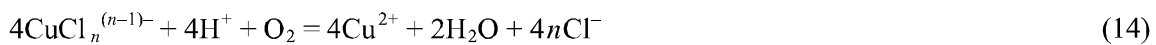
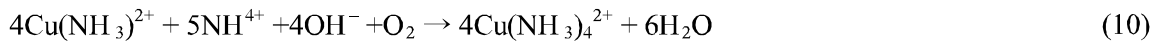


Figure 4. Gold deposition on the (a) Cu and (b) Al in PCBs.

3.2. Pretreatment leaching

Figure 5(a) shows the Au, Ag, and Cu extraction in ammonia as well as ferric chloride system. The results showed that about over 99% of Cu could be leached from the PCBs with both of ammonia (Eqs. 9 and 10) as well as ferric chloride solvent (Eqs. 11–15) while Au extraction was negligible in both solutions [8,9]. Silver also can be dissolved slowly in ammoniacal solutions with Eq. 16. In the leaching of PCBs in ammoniacal solution, the bulk of Cu can be dissolved in the solution forming Cu(II) complexes ($\text{Cu}(\text{NH}_3)_4^{2+}$), and this is able to enhance the Ag dissolution as described in Eq. 17 [10]. Moreover, Ag is also solubilized in the ferric chloride system and re-precipitated in the form of AgCl. The precipitates undergo partial dissolution, forming AgCl_3^{2-} and AgCl_4^{3-} complexes as shown in Eqs. 18 and 19 [11].



The residues containing Au then proceeded with the ammonium thiosulfate leaching and results showed that Au leaching efficiency after ammonia leaching or ferric chloride leaching pretreatment was enhanced to about 10% and 30%, respectively at 10% of pulp density, indicating that both pretreatments could enhance the

leaching efficiency of precious metals by successfully removing the interfering metal, Cu (Figure 5(b)). Furthermore, the results showed that the leaching efficiency after ammonia leaching pretreatment is relatively lower than after ferric chloride leaching pretreatment. Both pretreatments successfully extracted Cu from the PCBs, but the difference in Au leaching efficiency examined as having effect on Au in the pretreatment process. For the reason, ammonium thiosulfate leaching residues after ammonia and ferric chloride leaching pretreatments were observed by SEM-EDX, and results showed that the ammonia leaching of PCBs could readily make the surface coating on the Au fraction with oxygen, making the sulfur oxide components which leads to a decrease in Au extraction in subsequent ammonium thiosulfate leaching (Figure 6 a & b).

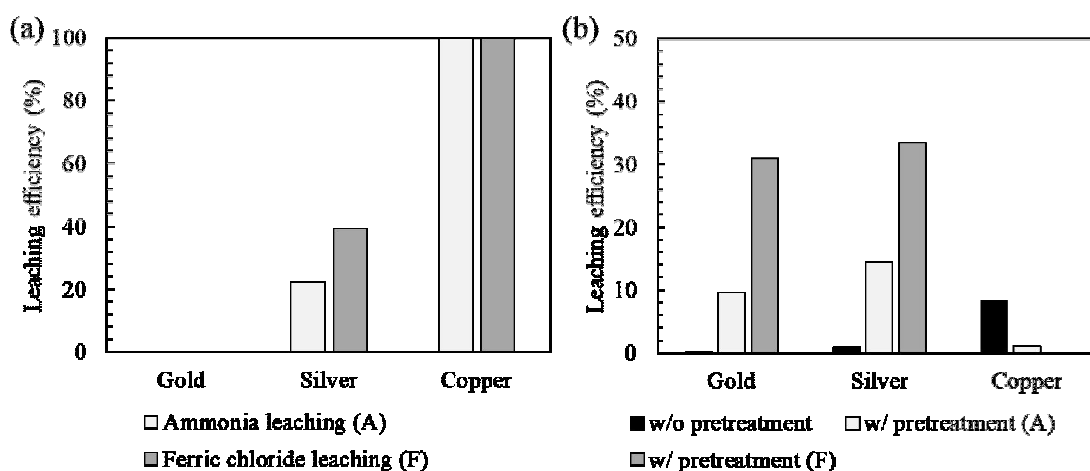


Figure 5. (a) metal extraction from PCBs in ammonia and ferric chloride leaching, and (b) effects of ammonia and ferric chloride leaching pretreatment on ammonium thiosulfate leaching efficiency of gold, silver, and copper.

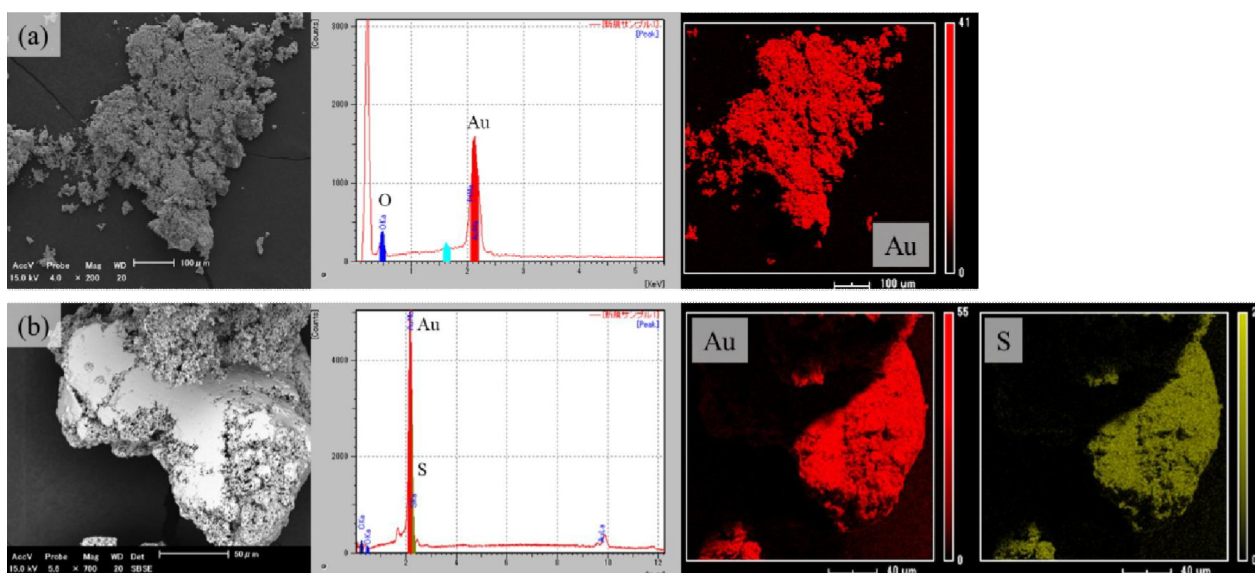


Figure 6. SEM photomicrographs of (a) chloride and (b) ammonia pretreatment leaching residue with corresponding elemental maps.

4. CONCLUSIONS

The present research was focused on the ammonium thiosulfate leaching of Au, Ag, and Cu from crushed waste PC PCBs and on the pretreatment study to further enhance the extraction efficiency by ammonia and ferric chloride solvents.

The maximum extraction was achieved at 24 h of the leaching time, and higher concentrations of CuSO_4 , ammonia, and thiosulfate enhanced the metal extractions. Also, dissolved oxygen is a critical parameter in ammonium thiosulfate system mainly due to the re-generation of catalyst. In comparison, highest metal extractions were achieved under the following conditions in the system: 1 M of $\text{Na}_2\text{S}_2\text{O}_3$, 10 mM of CuSO_4 , 1 M of ammonia/ammonium concentration, 1% of pulp density, and a 24 h of leaching time in the presence of oxygen. When the pulp density was increased to 10%, however, the precious metal leaching efficiency significantly decreased showing 0.1% and 0.9% of Au and Ag extraction efficiency, respectively, and one of the reasons may arise due to the re-deposition of dissolved metal ions to the base metals (especially Cu) in PCBs via electrochemical/galvanic interactions. To improve the leaching efficiency, pretreatment leaching by ammonia or ferric chloride leaching was carried out. The results showed that over 99% of Cu was dissolved by both of ammonia and ferric chloride leaching, and Au and Ag leaching efficiency increased to 9.6% and 14.4% in ammonium thiosulfate leaching in subsequent to ammonia leaching while increased to 31% and 34% in ammonium thiosulfate leaching in subsequent to ferric chloride leaching with the 10% of pulp density.

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