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Author(s)	Jeon, Sanghee; Tabelin, Carlito Baltazar; Park, Ilhwan; Nagata, Yoshito; Ito, Mayumi; Hiroyoshi, Naoki
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Ammonium thiosulfate extraction of gold from printed circuit boards (PCBs) of end-of-life mobile phones and its recovery from pregnant leach solution by cementation

Sanghee Jeon^{1,*}, Carlito Baltazar Tabelin², Ilhwan Park¹, Yoshito Nagata³, Mayumi Ito¹,
and Naoki Hiroyoshi¹

¹Laboratory of Mineral Processing and Resources Recycling, Division of Sustainable Resources Engineering, Faculty of Engineering, Hokkaido University, Kita 13, Nishi 8, Kita-ku, Sapporo 060-8628, Japan

²School of Minerals and Energy Resources Engineering, The University of New South Wales, Sydney, NSW 2052, Australia

³Laboratory of Mineral Processing and Resources Recycling, Division of Sustainable Resources Engineering, Graduate School of Engineering, Hokkaido University, Kita 13, Nishi 8, Kita-ku, Sapporo 060-8628, Japan

*Corresponding author. Tel.: +81-11-706-6315

E-mail address: shjun1121@gmail.com (Sanghee Jeon)

Postal address: Division of Sustainable Resources Engineering, Faculty of Engineering, Hokkaido University, Kita 13, Nishi 8, Kita-ku, Sapporo 060-8628, Japan

Highlights

- ✓ Leaching mechanisms of metals in ammonium thiosulfate system were investigated
- ✓ Gold recovery by various cementation agents (e.g. Pb, Ni, Cu, Zn, Fe) was presented
- ✓ Effects of various factors on gold recovery from pregnant solution were discussed
- ✓ Selective recovery of Au from pregnant solution was obtained using Cu

Abstract

In this study, the ammonium thiosulfate leaching of gold (Au) from printed circuit boards (PCBs) of end-of-life mobile phones and the subsequent recovery of dissolved metals from pregnant leach solution via cementation were elucidated under various conditions. Over 99% of Au was extracted from crushed PCBs ($D_{50} = 85 \mu\text{m}$) 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, 0.1 g/10 ml of solid-to-liquid ratio, and a 24 h of leaching time in the presence of oxygen. In contrast, the recovery of Au ions via cementation was more favorable in the absence of oxygen. Among the various cementation agents evaluated, copper (Cu) was the most selective and recovered around 95% of extracted Au from the pregnant leach solution even in the presence of various coexisting metal ions. The cementation of Au exhibited two distinct kinetic regions: (1) an initially rapid rate, and (2) a more gradual and constant rate. Finally, the use of Cu plates to recover Au ions from ammonium thiosulfate pregnant solution of crushed PCBs is proposed, which could selectively recover about 80% of dissolved Au and is easier to handle and reuse compared with Cu powder.

Keywords: Ammonium thiosulfate leaching, Gold, Cementation, Printed circuit boards, Recycling

1. Introduction

Printed circuit boards (PCBs) essential in all sorts of electronic equipment and portable gadgets (e.g., laptop computers and mobile phones) contain substantial amounts of gold (Au), which oftentimes exceed those found in natural Au ores (Jeon et al., 2018a; Park et al., 2017). Jeon et al. (2018a), for example, reported that Au in PCBs of mobile phones from Japan was more than 300-fold higher than typical Au ores. Because 70% of the total metal price in PCBs is accounted for by Au, the recovery of this rare and precious metal from various types of electronic wastes (e-wastes) is not only economically viable but also profitable (Jeon et al., 2019a).

In Au hydrometallurgy, the first stage is to dissolve Au using suitable lixiviants followed by the recovery of extracted Au ions from pregnant leach solutions (Jeon et al., 2018b; Yoo et al., 2012). In the leaching stage, cyanide or the halides (e.g., aqua regia) are the most commonly used lixiviants to extract Au both from natural ores and e-wastes. Unfortunately, cyanide is highly toxic while the halides are extremely corrosive and unselective (Chu and Ko, 2018; Jeon et al., 2018b). Because of these limitations, several lixiviants like thiourea, iodine-iodide and ammonium thiosulfate have been proposed in recent years as alternatives (Arima et al., 2002; Hiskey and Lee, 2003; Molleman and Dreisinger, 2002). Among these alternatives, ammonium thiosulfate is very attractive because it is not only highly selective for Au but is also non-toxic and only mildly corrosive (Jeon et al., 2018b; Numluk and Chaisena, 2012). Even with these advantages, however, the industrial-scale application of ammonium thiosulfate especially in e-waste recycling remains challenging and the following issues still needed to be addressed: (1) in the leaching stage, the mechanisms involved in Au extraction in the presence of other metals like copper (Cu), zinc (Zn), aluminum (Al), iron (Fe), lead (Pb) and nickel (Ni), which are ubiquitous in PCBs, remain unclear, and (2) in the recovery stage, effective techniques to recover dissolved Au from the pregnant leach solutions are still elusive.

Gold extraction in ammonium thiosulfate medium from natural Au ores, which contains negligible amounts of unwanted and coexisting metals, is already well understood (Molleman and Dreisinger, 2002; Langhans et al., 1992). In Au extraction from e-wastes, however, the mechanisms involved during Au dissolution in ammonium thiosulfate medium in the presence of coexisting metals (e.g., Cu, Zn, Al, Fe, Pb and Ni), which are abundant in e-wastes and could interfere with Au extraction, remains unclear. The presence of Cu, for example, could improve Au extraction because its dissolution has been reported to stabilize Cu(II) and Cu(II)-ammonia complexes (Ha et al., 2010). Meanwhile, electrochemical interactions between coexisting metals (e.g., Cu and Al) has been shown to synergistically enhance Au cementation or precipitation reactions leading to limited Au extraction from PCBs especially at very high solid-to-liquid ratios (Choi et al., 2019; Jeon et al., 2018b; 2019b). Although the authors have published several papers on the leaching of Au from e-wastes (Jeon et al., 2018a) and crushed mobile phones (Jeon et al., 2018b; 2019a), their focus was mainly on Au extraction and the effects of various parameters like reagent concentrations and the presence/absence of oxygen were not elucidated in detail. Similarly, majority of studies on the use of ammonium thiosulfate in e-waste recycling focused only on the extraction of one or two target metals (e.g., Au and/or Cu) and the effects on Au extraction of other coexisting metals found in e-wastes like Zn, Al, Fe, Pb and Ni have largely been ignored (Ha et al., 2010; Petter et al., 2014; Tripathi et al., 2012).

The recovery of dissolved Au from various solutions is also well studied, and several conventional techniques developed for this purpose includes electrowinning (Aylmor, 2001), adsorption with activated carbon (Gallagher et al., 1990; Navarro et al., 2006), and cementation onto metals and magnetite (Arima et al., 2002; Calderon et al., 2019). Electrowinning and adsorption with activated carbon are very effective in cyanide and chloride media but are

ineffective when applied in ammonium thiosulfate pregnant solutions especially from e-waste recycling. Electrowinning is not ideal for ammonium thiosulfate pregnant solutions because of the abundance Cu in e-wastes and PCBs, the high concentration of dissolved Cu (i.e., $\text{Cu}(\text{NH}_3)_4^{2+}$), and various oxidation-reduction reactions of thiosulfate complexes, all of which interfere during the recovery process (Aylmor, 2001). Similarly, adsorption is inefficient in the recovery of Au from ammonium thiosulfate pregnant solutions because of the very low affinity of Au-thiosulfate complex to activated carbon (Aylmor, 2001; Gallagher et al., 1990; Guerra et al., 1990; Jeon et al., 2019b). Meanwhile, cementation using Zn, Al, Fe or Cu to recover Au ions from ammonium thiosulfate solution has been elucidated by several studies and most of them reported high Au recoveries (Arima et al., 2002; Guerra and Dreisinger, 1999; Hiskey and Lee, 2003; Karavasteva, 2010; Navarro et al., 2004). Arima et al. (2002), for example, evaluated the potential of various cementing agents (i.e., Cu, Zn, and Al) to recover dissolved Au from synthetic solutions similar to those obtained in the Hishikari gold deposit in Japan and found that about 93% of Au could be recovered by Cu powder having Cu/Au⁺ mass ratio of 200. Similarly, Navarro et al. (2004) reported over 90% Au recovery using Zn in model ammonium thiosulfate solutions containing only dissolved Au. Unfortunately, most of these previous cementation studies on Au recovery used single-component model experiments that are not representative of real pregnant leach solutions (Arima et al., 2002; Guerra and Dreisinger, 1999; Hiskey and Lee, 2003; Karavasteva, 2010; Navarro et al., 2004). One complication during cementation, for example, occurs when there are substantial amounts of Cu ions in thiosulfate solution because they raise the redox potential of solution and form catalysts (i.e., Cu(II)-ammonia complex) that make Au recovery difficult (Aymor, 2001; Hiskey and Lee, 2003). This means that although cementation is a promising approach to recover extracted Au after ammonium thiosulfate leaching of crushed PCBs, the mechanisms

involved in the recovery of Au ions from real pregnant leach solutions containing various coexisting metal ions are still not well understood.

In this study, the ammonium thiosulfate extraction of Au from PCBs of end-of-life mobile phones and the recovery of this precious metal from pregnant leach solutions were elucidated under various conditions. Specifically, the objectives of this study are three-fold: (1) to investigate the effects of various leaching parameters like extraction time, concentrations of CuSO_4 , $\text{Na}_2\text{S}_2\text{O}_3$ and total ammonium/ammonia, as well as the presence and absence of oxygen, (2) to determine the roles played by coexisting metals on Au extraction, and (3) to elucidate the cementation phenomenon of Au with base metal ions from PCB leached pregnant solution using various cementing agents (e.g., Zn, Fe, Ni, Pb and Cu). These objectives were achieved by conducting shaking flask extraction and cementation experiments under various conditions, monitoring the changes in leachate chemistry using inductively coupled plasma atomic emission spectroscopy (ICP-AES), and characterizing in detail the leaching/cementation residues by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS).

2. Materials and methods

2.1 Printed circuit boards of waste mobile phones

Printed circuit boards (PCBs) obtained from discarded mobile phones were crushed by a cutting mill (VH16, Seishin Enterprise Co., Ltd., Japan), freeze crusher (TPH-02, As One, Japan), and vibratory disc mill (RS 100, Retsch Co., Ltd., Germany) to obtain particles with D_{50} and D_{80} of 85 and 224 μm , respectively (Fig. S1). For the composition of the crushed product, it was first treated in an ashing furnace to burn the combustible materials (e.g., plastics), the resulting ash 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 = ± 2 %). The amounts of Au and major metals in the PCB sample, including combustible and residual/non-combustible components (e.g., ceramics and glasses), are summarized in Table 1.

2.2 Gold leaching experiments

Batch leaching experiments were conducted to investigate the effects of leaching time (12–72 h), the presence/absence of oxygen, solid-to-liquid ratio (0.1–1 g/10 ml), CuSO_4 concentration (0.1–10 mM), $\text{Na}_2\text{S}_2\text{O}_3$ concentration (0.001–3 M) and total ammonia/ammonium concentration (0.01–1 M) on the extractions of Au and other coexisting metals from crushed PCBs. The ammonium thiosulfate solution used in these experiments were prepared using deionized (DI) water (18 $\text{M}\Omega\cdot\text{cm}$, MilliQ[®] Integral Water Purification System, Merck-Millipore, USA) and reagent-grade chemicals ($\text{Na}_2\text{S}_2\text{O}_3\cdot 5\text{H}_2\text{O}$, NH_4OH , $(\text{NH}_4)_2\text{SO}_4$ and $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$) obtained from Wako Pure Chemical Industries, Ltd., Japan. All of the leaching experiments were carried out in 50-ml Erlenmeyer flasks containing a known amount of crushed PCBs and 10 ml of ammonium thiosulfate solution. 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 ammonium thiosulfate solution used for the leaching experiments with time or with and without O_2 was composed of 1 M of $\text{Na}_2\text{S}_2\text{O}_3\cdot 5\text{H}_2\text{O}$, 0.5 M of NH_4OH , 0.25 M of $(\text{NH}_4)_2\text{SO}_4$ and 10 mM of $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$. Prior to the leaching experiment without O_2 , dissolved O_2 was removed by purging 10 ml of ammonium thiosulfate solution for 30 minutes with N_2 (>99.99%). After this, crushed PCBs (0.1 g) was immediately added to the flask, the suspension was re-purged with N_2 for 15 more minutes to ensure that residual O_2 was removed from the system, and the flask was then completely sealed using a silicon cap and parafilm. Meanwhile, the

leaching experiments with O₂ were conducted without N₂ purging and were always open to the atmosphere. After the predetermined shaking duration, the suspensions were filtered through 0.2 μm membrane filters (Sartorius AG, Germany) and the metal ion concentrations of the filtrates were measured by ICP-AES. Meanwhile, the residues were washed thoroughly with DI water, dried in a vacuum drying oven at 40 °C and analyzed by SEM-EDS (Superscan SSX-550, Shimadzu Corporation, Japan).

2.3 Gold ion cementation experiments

The pregnant leach solutions were prepared by leaching 0.1 g of ground PCBs in a 10 ml solution containing 1 M of Na₂S₂O₃·5H₂O, 0.5 M of NH₄OH, 0.25 M of (NH₄)₂SO₄ and 10 mM of CuSO₄·5H₂O (Note that these concentrations were selected based on conditions of maximum Au extraction, which will be discussed in the succeeding sections). After 24 h, the leachates (i.e., pregnant leach solutions) were collected by filtration (0.2 μm membrane filters) for the cementation experiments.

To recover Au ions from the pregnant solutions, ultrapure (>99.9%) Pb, Ni, Cu, Zn and Fe powders were used as cementation agents. These experiments were carried out by putting 0.1 g of metal powder (<75 μm, Wako Pure Chemical Industries, Ltd., Japan) in 50 ml Erlenmeyer flasks containing 10 ml of N₂-purged pregnant solution to limit the unwanted effects of dissolved oxygen on cementation (Note that the purging procedure was the same as that outlined in Section 2.2). The sealed flasks were then shaken in a thermostat water bath shaker at a shaking speed of 120 rpm and amplitude of 40 mm at 25 °C for 1–72 h. After the predetermined shaking duration, the suspensions were filtered through 0.2 μm membrane filters and the metal ion concentrations of the filtrates were measured by ICP-AES. Meanwhile, the

residues were collected, washed thoroughly with DI water, dried in a vacuum drying oven and then analyzed by SEM-EDS.

3. Results and discussion

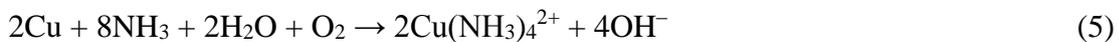
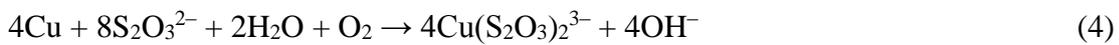
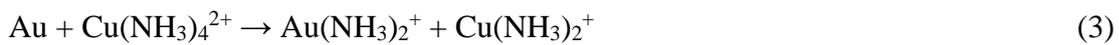
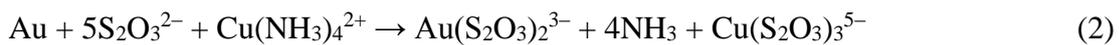
3.1 Leaching of gold and coexisting metals from printed circuit boards

3.1.1 Effects of leaching time

Fig. 1 shows the metal extraction of Au and other coexisting metals from crushed PCBs with time, which was calculated by the following equation:

$$\text{Metal extraction (\%)} = \frac{C_m \times V}{m \times M} \times 100\% \quad (1)$$

where C_m is the concentration of dissolved metal in mg/L, V is the volume of solution in L, m is the mass of sample (g) and M is the metal content of the sample (mg/g), respectively. The results showed that Au and Cu extractions were high at around 70-95%, which could be attributed to the formation not only of Au- and Cu-ammonia complexes but also of Au- and Cu-thiosulfate complexes as described by the following reactions (Aylmor and Muir, 2001; Jeon et al., 2018b):



Similarly, Ni, Zn, and Pb extractions were substantial at around 20–45% but were lower than those of Au and Cu because these metals could only form stable complexes with NH_3 (Yoo and Kim, 2012). In contrast, Al and Fe extractions were low at less than 20% because Al do not form stable complexes with either thiosulfate or ammonia (Jeon et al., 2018; Oh et al.,

2003) while Fe could be easily coated with a passivating S layer in thiosulfate solution (Fig. 1(b)). The maximum Au extraction was obtained after 24 h, so the leaching time was fixed at 24 h in the succeeding experiments.

3.1.2 Effects of oxygen

Fig. 2 shows the effects of oxygen on the extraction of Au and coexisting metals from crushed PCBs. Higher metal extractions were obtained in the presence of oxygen than in its absence. These results indicate that oxygen is essential in the continuous oxidative leaching of Au, which are consistent with the reports of other authors using natural ores and e-wastes (Aylmor, 2001). According to Eq. 2, the Cu(II)-ammonia complex ($\text{Cu}(\text{NH}_3)_4^{2+}$) is converted to Cu(I)-thiosulfate complex ($\text{Cu}(\text{S}_2\text{O}_3)_3^{5-}$) during the oxidative dissolution of Au and oxygen is essential to convert $\text{Cu}(\text{S}_2\text{O}_3)_3^{5-}$ back to $\text{Cu}(\text{NH}_3)_4^{2+}$ according to Eq. 6 (Jeon et al., 2018b). In other words, the continuous supply of oxygen ensured $\text{Cu}(\text{NH}_3)_4^{2+}$ regeneration that increased Au extraction from crushed PCBs in ammonium thiosulfate solution.



3.1.3 Effects of solid-to-liquid ratio

Leaching of the metals from PCBs was investigated with varying solid-to-liquid ratio in ammonium thiosulfate solution (Fig. 3). As can be seen that the increase in solid-to-liquid ratio from 0.1 g to 1 g/10 ml resulted in the decrease of metal extraction. At the maximum solid-to-liquid ratio in the present study (i.e., 1 g/10 ml), Au extraction was less than 5% due mainly to the lack of leaching reagent as well as the re-deposition of dissolved Au onto base metals like Al with Cu via electrochemical/galvanic interactions (Jeon et al., 2018b). The important roles played by electrochemical/galvanic interactions between materials with conductive/semi-

conductive properties on leaching and precipitation reactions have also been noted in mine tailings (Chopard et al., 2017; Li et al., 2019a, b; Park et al., 2018a, b), pyrite-rich waste rocks (Park et al., 2019; Tabelin et al., 2017b, c; Tomiyama et al., 2019), flotation (Barker et al., 2014; Mu et al., 2018) and mineral processing grinding circuits (Rabieh et al., 2018; Seng et al., 2019b). Based on the results, solid-to-liquid ratio of 0.1 g/10 ml might be considered as optimum for gold extraction under the present reagent condition at 25°C for 24 h.

3.1.4 Effects of CuSO₄ concentration

Fig. 4 illustrates the effects of CuSO₄ concentration on metal extractions from crushed PCBs. The leaching of Au, Cu, Pb, Ni and Zn increased with increasing CuSO₄ concentration while the effects of CuSO₄ on Fe and Al extractions were negligible. Addition of CuSO₄ had very dramatic effects on Au extraction, which increased to almost 100% at 10 mM of CuSO₄. This very strong effects of CuSO₄ on Au extraction could be attributed to the formation of Cu(II)-ammonia complex (Cu(NH₃)₄²⁺), a strong oxidant that is known to catalyze the oxidative dissolution rate of Au in ammonium thiosulfate medium by up to 18-fold (Eqs. 2 and 3) (Aylmor and Muir, 2001). The maximum Au extraction was obtained at 10 mM of CuSO₄, so this concentration was used in the succeeding experiments.

3.1.5 Effects of Na₂S₂O₃ concentration

Fig. 5 shows the effects of Na₂S₂O₃ concentration on the extractions of Au, Cu, Ni, Pb, Zn, Al and Fe from crushed PCBs. When Na₂S₂O₃ concentration was less than 1 M, Au extraction slightly increasing while extractions of Al and Fe were negligible. In case of Cu, it always showed a high extraction of up to 1M concentration of thiosulfate because of Eq. 4 and 5. The

leaching of all metals in 3 M Na₂S₂O₃ was lower than that in 1 M Na₂S₂O₃ because high concentrations of S₂O₃²⁻ could destabilize Cu(NH₃)₄²⁺ as explained by Eq. 7. The maximum Au extraction was obtained at 1 M of Na₂S₂O₃, so this amount was used in the succeeding experiments.



3.1.6 Effects of total ammonia/ammonium concentration

Fig. 6(a) shows the effects of total ammonia/ammonium concentration on metal extractions from crushed PCBs. In this series of experiments, the molar ratio of NH₄OH and (NH₄)₂SO₄ was kept constant at 2:1 while the total ammonia/ammonium concentration (i.e., the sum of the concentrations of ammonia species (NH₃ and NH₄⁺)) was varied from 0.01 to 1 M. At the maximum total ammonia/ammonium concentration (i.e., 1 M), extractions of Cu, Pb and Ni were higher than those of Al and Fe because the affinities of Cu, Pb and Ni for ammonia are stronger than Al and Fe (Yoo and Kim, 2012). In the leaching of Au from natural Au ores, Aylmore and Muir (2001) noted that the effects of total ammonia/ammonium concentration were negligible because the ability of NH₃ to form complexes with Au was weaker than that S₂O₃²⁻. The leaching results for PCBs, however, showed that Au extraction increased with increasing total ammonia concentration and the maximum extraction of Au was obtained at the highest total ammonia/ammonium concentration (Fig. 6(a)). This discrepancy could be explained by two possible mechanisms: (1) PCBs contain metallic Cu rather than Cu-sulfide or oxide minerals, so at higher total ammonia/ammonium concentration, metallic Cu is readily dissolved generating a higher concentration of Cu(NH₃)₄²⁺ that catalyzed Au dissolution (Eq. 2), and (2) Au in PCBs is generally present with Cu-bearing components (Fig. 6(b)) and/or reductively deposited onto Cu during leaching especially in the presence of Al (Fig. 6(c)) (Jeon

et al., 2018b), so the enhanced dissolution of Au-bearing Cu particles would also increase Au extraction.

3.2 Recovery of gold ions from ammonium thiosulfate pregnant solution

3.2.1 Effects of various cementing agents with/without oxygen

Fig. 7(a) and (b) shows the recovery of extracted metals from ammonium thiosulfate pregnant solution by Zn, Ni, Pb, and Cu with and without oxygen, respectively. Metal recovery (%) is defined as

$$\text{Metal recovery (\%)} = \frac{C_i - C_f}{C_i} \times 100\% \quad (8)$$

where C_i and C_f are the initial and final concentrations of metal ions, respectively. As discussed previously, oxygen enhanced the dissolution of Au in ammonium thiosulfate solution, hence higher recovery was obtained under the absence of oxygen (Fig. 7(b)) compared to the presence of the oxygen (Fig. 7(a)). The recovery results showed that Au recovery was high after adding either Cu or Zn, the bulk of which occurred via cementation (Fig. 7(b-1) and 7(b-2)). Between the two, Cu exhibited better selectivity for Au than Zn because of its higher standard redox potential (Cu: +0.339 V, Zn: -0.762 V). It is interesting to note that not only Au but also Al was recovered regardless of the cementing agent used. To clarify how Al is recovered, the residues were examined by SEM-EDS and the results showed that most of Al was precipitated/cemented on the metallic reductants (Fig. 8). Ni could also recover Au from the pregnant leach solution, but its efficiency was lower than those of Cu and Zn. In contrast, Au recovery by Pb was very low because Pb-carbonates/hydroxide could easily form on the surface of metallic Pb especially under circumneutral and alkaline conditions (Fig. 8(c-3)) (Tabelin and Igarashi, 2009; Tabelin et al., 2012, 2017, 2018; Tatsuhara et al., 2012). Although both Zn

and Cu could recover dissolved Au efficiently, Zn was unselective and recovered most of the coexisting metal ions in the pregnant leach solution. In contrast, Cu was more selective and preferentially recovered Au over the other coexisting metal ions due primarily to its high redox potential. (Fig. 7(b)). According to Hiskey and Lee (2003), Au recovered on Cu in ammonium thiosulfate solution is predominantly composed of a mixture of intermetallic alloys such as AuCu, Au₃Cu or AuCu₃ and not as pure metallic Au.

3.2.2 Kinetics of metal cementation on zinc, nickel, lead and copper

Kinetic data are shown in Fig. 9 for the first-order kinetics (i.e., $\ln([Au]/[Au]_0)$) of metal recovery (%) as a function of time for each cementing agents (i.e., Zn, Ni, Pb and Cu). In the cementation of Au using Zn (Fig. 9(a)), Ni (Fig. 9(c)) or Pb (Fig. 9(d)), two kinetic regions were observed. The initial region lasted for about 24 h (Fig. 9(c) and 9(d)) or 0-48 h (Fig. 9(a)) after which, the rate stabilized until the end of the experiment. This phenomenon could be explained by the rapid decrease in reaction area of cementation agents after they are covered by metals during cementation. Fig. 9(e) indicates the effect of various cementing agents on the reaction rate, especially Au recovery, and table 2 shows the differences of the first order rate constants with coefficient of determination obtained from pseudo-first-order kinetic model using various cementing agents on Au recovery. The experimental rate was observed that Pb and Ni, and Cu and Zn are quite similar, respectively. Although reaction rates of Zn and Cu are similar, Cu has more selectivity for Au recovery than Zn, hence Cu was selected for subsequent experiments.

3.2.3 Effects of copper dosage on dissolved gold recovery from pregnant leach solution

Fig. 10 shows the effects of dosage of Cu on metal recovery. The results showed that dissolved Au recovery as the dosage of Cu increased. When Cu dosage was less than 0.01 g/10 ml, Au recovery was about 20% because most of the Cu added simply dissolved in the ammonium thiosulfate system (Eq. 4 and 5) (Jeon et al., 2018). When Cu dosage was increased, Au recovery and Cu dissolution both increased. At 0.1 g/10ml, Au recovery and Cu dissolution both decreased because dissolved Cu were largely re-precipitated as $(\text{Cu}(\text{NH}_3)_4)(\text{Cu}(\text{S}_2\text{O}_3)_2)_2$ and/or $\text{Cu}_4(\text{SO}_4)(\text{OH})_6\text{H}_2\text{O}$, making Au concentration press inefficient (Jeon et al., 2018b). As discussed in previous studies, addition of cementing agent should be in excess to recover dissolved Au from ammonium thiosulfate solution via cementation (i.e., Cu/Au⁺ mass ratio > 100) (Arima et al., 2002; Jeon et al., 2018b).

Unfortunately, the recovery of very fine Au-loaded Cu powder will be difficult in practice, so the use of Cu plates that could easily be removed after cementation was evaluated. The cementation experiments with Cu plates was done in a similar way as outlined in section 2.3 but instead of Cu powder, a Cu plate with dimensions of 1 cm x 1 cm x 0.4 mm (length x width x thickness) was used.

3.2.4 Recovery of dissolved gold from pregnant leach solution using copper plate

Fig. 11 shows the recovery of Au, Cu, Ni, Pb, Zn and Al with time in ammonium thiosulfate pregnant solution using Cu plate. The maximum Au recovery of about 80% was obtained after 24 h, which was lower than that using Cu powder. SEM observation of the Cu plate after the cementation experiment also showed that Au was recovered via cementation similar to that observed with Cu powder (Fig. 11(b)). Although Au recovery with the Cu plate was lower than that of the Cu powder, using Cu plates eliminates the need for solid-liquid separation processes

like filtration. Moreover, Cu plates are easier to transport, handle and reuse during processing because of their relatively larger size.

4. Conclusions

The extraction of Au as well as various metals from crushed PCBs of discarded mobile phones and the recovery of these metal ions from the ammonium thiosulfate pregnant solution via cementation using various cementing agents were investigated. Apparent equilibrium in terms of Au extraction from crushed PCBs was achieved after 24 h. Higher concentrations of CuSO_4 and total ammonia concentration enhanced the leaching of Au because these conditions were more favorable for the formation of $\text{Cu}(\text{NH}_3)_4^{2+}$ that catalyzed Au extraction in ammonium thiosulfate medium. In comparison, the highest Au extraction was observed at around 1 M of $\text{Na}_2\text{S}_2\text{O}_3$ that rapidly decreased above this amount. Oxygen is also a critical parameter during Au extraction because of its role in the regeneration of $\text{Cu}(\text{NH}_3)_4^{2+}$. Over 99% of Au was extracted using 1 M of $\text{Na}_2\text{S}_2\text{O}_3$, 10 mM of CuSO_4 and 1 M of total ammonium concentration, a treatment time of 24 h and in the presence of oxygen. Although oxygen was crucial in the leaching of Au from crushed PCBs, removal of oxygen was more favorable for the recovery of Au ions from the pregnant solution. Among the various metals used as cementing agents, Cu was the most effective and could selectively recover dissolved Au in pregnant leach solutions even in the presence of various coexisting metal ions. The gold cementation reaction exhibited two distinct kinetic regions: an initially fast rate followed by a slow and constant rate. Aside from Cu powder, the use of Cu plates, a material that is easier to handle than fine powders, was also effective in the recovery of Au ions from ammonium thiosulfate pregnant solutions of crushed PCBs.

References

- Arima, H., Fujita, H., Yen, W., 2002. Gold cementation from ammonium thiosulfate solution using zinc, copper and aluminum powders. *Materials Transactions* 43(3), 485–493.
- Aylmor, M.G., Muir, D.M., Thiosulfate leaching of gold – A review, 2001. *Minerals Engineering* 14, 135–174.
- Barker, G.J., Gerson, A.R., Menuge, J.F., 2014. The impact of iron sulfide on lead recovery at the giant Navan Zn–Pb orebody, Ireland. *Int. J. Miner. Process.* 128, 16–24. <https://doi.org/10.1016/j.minpro.2014.02.001>.
- Calderon, A.R.M., Alorro, R.D., Tadesse, B., Yoo, K. and Tabelin, C.B., 2019. Evaluation of Maghemite-Rich Iron Oxide Composite Prepared from Magnetite as Adsorbent for Gold from Chloride Solution. *JOM*, 1-8.
- Choi, S., Yoo, K., Alorro, R.D., Tabelin, C.B., 2019. Cementation of Co ion in leach solution using Zn powder followed by magnetic separation of cementation precipitate for recovery of unreacted Zn powder. *Minerals Engineering* (In Press).
- Chopard, A., Plante, B., Benzaazoua, M., Bouzahzah, H., Marion, P., 2017. Geochemical investigation of the galvanic effects during oxidation of pyrite and base-metals sulphides. *Chemosphere* 166, 281-291
- Chu, C., Ko, T.H., Evaluation of Acid Leaching on the Removal of Heavy metals and Soil Fertility in Contaminated Soil, 2018. *Journal of Chemistry* 2018, 1–8.
- Gallagher, N.P., Hendrix, J.L., Milosavljevic, E.G., Nelson, J.H., Solujic, L., 1990. Affinity of activated carbon towards some gold (I) complexes. *Hydrometallurgy* 25, 305–316.
- Guerra, E., Dreisinger, D.B., 1999. A study of the factors affecting copper cementation of gold from ammonium thiosulfate solution. *Hydrometallurgy* 51 (2), 155–172.

- Ha, V.H., Lee, J., Jeong, J., Hai, H.T., Jha, M.K., 2010. Thiosulfate leaching of gold from waste mobile phones. *J. Hazard. Mater.* 178 (1-3), 1115–1119.
- Hiskey, J.B., Lee, J., 2003. Kinetics of gold cementation on copper in ammoniacal thiosulfate solutions. *Hydrometallurgy* 69, 45–46.
- Ilyas, S, Lee, J., 2018. *Gold Metallurgy and the Environment*. CRC Press, Taylor & Francis Group.
- Jeon, S., Ito, M., Tabelin, C.B., Pongsumrankul, R., Kitajima, N., Park, I., Hiroyoshi, N., 2018a. Gold recovery from shredder light fraction of E-waste recycling plant by flotation-ammonium thiosulfate leaching, *Waste Management*. 77, 195–202.
- Jeon, S., Tabelin, C.B., Takahashi, H., Park, I., Ito, M., Hiroyoshi, N., 2018b. Interference of coexisting copper and aluminum on the ammonium thiosulfate leaching of gold from printed circuit boards of waste mobile phones, 2018. *Waste Management* 81, 148–156.
- Jeon, S., Ito, M., Tabelin, C.B., Pongsumrankul, R., Tanaka, S., Kitajima, N., Saito, A., Park, I. and Hiroyoshi, N., 2019a. A physical separation scheme to improve ammonium thiosulfate leaching of gold by separation of base metals in crushed mobile phones. *Minerals Engineering*, 138, pp.168-177.
- Jeon, S., Tabelin, C.B., Takahashi, H., Park, I. Ito, M., and Hiroyoshi, N., 2019b. Enhanced cementation of gold via galvanic interactions using activated carbon and zero-valent aluminum: A novel approach to recover gold ions from ammonium thiosulfate medium. *Hydrometallurgy* (In press).
- Karavasteva, M., 2010. Kinetics and deposit morphology of gold cemented on magnesium, aluminum, zinc, iron and copper from ammonium thiosulfate-ammonia solutions. *Hydrometallurgy* 104(1), 119-122.

- Khaliq, A., Rhamdhani, M.A., Brooks, G., Masood, S., 2014. Metal extraction processes for electronic waste and existing industrial routes: A review and Australian perspective. *Resources*, 3, 152–179.
- Kim, E., Kime, M., Lee, J., Pandey, B.D., 2011. Selective recovery of gold from waste mobile phone PCBs by hydrometallurgical process. *J. Hazard. Mater.* 198, 206-215.
- Li, X., Gao, M., Hiroyoshi, N., Tabelin, C.B., Taketsugu, T. and Ito, M., 2019a. Suppression of pyrite oxidation by ferric-catecholate complexes: An electrochemical study. *Minerals Engineering* 138, 226-237.
- Li, X., Hiroyoshi, N., Tabelin, C.B., Naruwa, K., Harada, C. and Ito, M., 2019b. Suppressive effects of ferric-catecholate complexes on pyrite oxidation. *Chemosphere*, 214, pp.70-78.
- Langhans, J.W., Lei, Jr. K.P.V., Carnahan, T.G., Copper-catalyzed thiosulfate leaching of low-grade gold ores, 1992. *Hydrometallurgy* 29, 191–203.
- Molleman, E., Dreisinger, D., The treatment of copper-gold ores by ammonium thiosulfate leaching, 2002. *Hydrometallurgy* 66, 1–21.
- Mu, Y., Peng, Y., Lauten, R.A., 2018. The galvanic interaction between chalcopyrite and pyrite in the presence of lignosulfonate-based biopolymers and its effects on flotation performance. *Miner. Eng.* 122, 91-98. <https://doi.org/10.1016/j.mineng.2018.03.048>.
- Navarro, P., Alvarez, R., Vargas, C., Alguacil, F.J., 2004. On the use of zinc for gold cementation from ammoniacal-thiosulphate solutions. *Minerals Engineering* 17, 825–831.
- Navarro, P., Vargas, C., Alonso, M., Alguacil, F.J., 2006. The adsorption of gold on activated carbon from thiosulfate-ammonium solutions. *Gold Bulletin* 39(3), 93–97.
- Numluk, P., Chaisena, A., Sulfuric Acid and Ammonium Sulfate Leaching of Alumina from Lampang Clay, 2012. *Journal of Chemistry* 9, 1364–1372.

- Oh, C.J., Lee, S.O., Yang, H.S., Ha, T.J., Kim, M.J., Selective Leaching of Valuable Metals from Waste Printed Circuit Boards, 2003. *Journal of the Air & Waste Management Association* (53), 897–902.
- Park, I., Yoo, K., Alorro, R.D., Kim, M., Kim, S., 2017. Leaching of Copper from Cuprous Oxide in Aerated Sulfuric Acid, *Material Transactions*, 58(10), 1500–1504.
- Park, I., Tabelin, C.B., Seno, K., Jeon, S., Ito, M., Hiroyoshi, N., 2018a. Simultaneous suppression of acid mine drainage formation and arsenic release by Carrier-microencapsulation using aluminum-catecholate complexes. *Chemosphere*. 205, 414-425. <https://doi.org/10.1016/j.chemosphere.2018.04.088>.
- Park, I., Tabelin, C.B., Magaribuchi, K., Seno, K., Ito, M. and Hiroyoshi, N., 2018b. Suppression of the release of arsenic from arsenopyrite by carrier-microencapsulation using Ti-catechol complex. *Journal of hazardous materials*, 344, pp.322-332.
- Park, I., Tabelin, C.B., Jeon, S., Li, X., Seno, K., Ito, M. and Hiroyoshi, N., 2019. A review of recent strategies for acid mine drainage prevention and mine tailings recycling. *Chemosphere* 219, 588–606.
- Petter, P.M.H., Veit, H.M., Bernardes, A.M., 2014. Evaluation of gold and silver leaching from printed circuit boards of cell phones. *Waste Manage.* 34(2), 475-482.
- Seng, S., Tabelin, C.B., Kojima, M., Hiroyoshi, N., Ito, M., Galvanic microencapsulation (GME) using zero-valent aluminum and zero-valent iron to suppress pyrite oxidation, 2018. *Materials Transactions*, M-M2018851.
- Rabieh, A., Eksteen, J.J., Albijanic, B., 2018. Galvanic interaction of grinding media with arsenopyrite and pyrite and its effect on gold cyanide leaching. *Miner. Eng.* 116, 46-55. <https://doi.org/10.1016/j.mineng.2017.10.018>.

- Tripathi, A., Kumar, M., Sau, D.C., Agrawal, A., Chakravarty, S., Mankhand, T.R., 2012. Leaching of gold from the waste mobile phone printed circuit boards (PCBs) with ammonium thiosulphate. *Int. J. Metallurgical Eng.* 1(2), 17-21.
- Tabelin, C.B. and Igarashi, T., Mechanisms of arsenic and lead release from hydrothermally altered rock, 2009. *Journal of Hazardous Materials* (169), 980–990.
- Tabelin, C.B., Veerawattananun, S., Ito, M., Hiroyoshi, N. and Igarashi, T., 2017b. Pyrite oxidation in the presence of hematite and alumina: II. Effects on the cathodic and anodic half-cell reactions. *Science of The Total Environment*, 581, pp.126-135.
- Tabelin, C.B., Sasaki, R., Igarashi, T., Park, I., Tamoto, S., Arima, T., Ito, M. and Hiroyoshi, N., 2017c. Simultaneous leaching of arsenite, arsenate, selenite and selenate, and their migration in tunnel-excavated sedimentary rocks: II. Kinetic and reactive transport modeling. *Chemosphere*, 188, pp.444-454.
- Tomiyama, S., Igarashi, T., Tabelin, C.B., Tangviroon, P. and Ii, H., 2019. Acid mine drainage sources and hydrogeochemistry at the Yatani mine, Yamagata, Japan: A geochemical and isotopic study. *Journal of contaminant hydrology*, 225, p.103502.
- Yoo, K., Kim, H., Development of Ammoniacal Leaching Processes; A Review, 2012. *Journal of the Korean Institute of Resources Recycling* 21(5), 3–17.

Table

Table 1. Material and chemical compositions of the crushed PCBs sample.

	Cu	Al	Fe	Metals			Au	Combustibles	Others
				Ni	Pb	Zn			
Amount (wt.%)	30	1.6	4.7	2.1	1.3	0.9	0.1	34.5	24.8

Table 2. Rate constants and coefficient of determination obtained from pseudo-first-order kinetic model using various cementing agents on Au recovery.

Cementing agents	$cm\ h^{-1}$	R^2
Pb	-3.87×10^{-2}	0.9382
Ni	-5.38×10^{-2}	0.9446
Cu	-1.45×10^{-1}	0.9679
Zn	-1.69×10^{-1}	0.9877

Figures

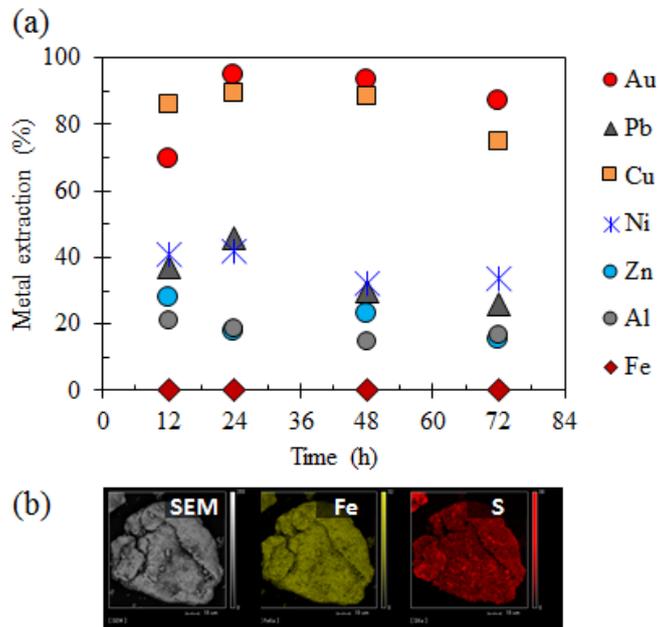


Fig. 1. (a) Extractions of Au, Cu, Ni, Pb, Zn, Al and Fe with time in ammonium thiosulfate solution and (b) SEM photomicrograph of the residue after leaching of PCBs with corresponding elemental maps of Fe and S.

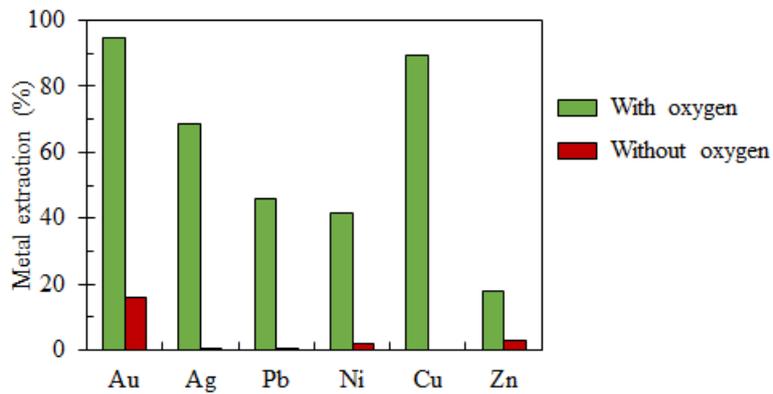


Fig. 2. Extractions of Au, Pb, Ni, Cu, Zn, Fe and Al with and without oxygen.

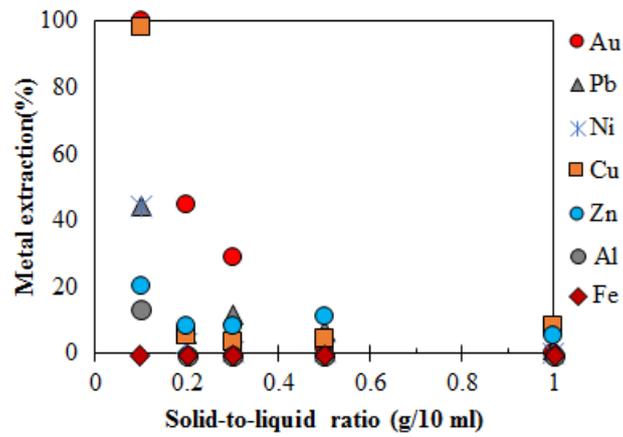


Fig. 3. Extractions of Au, Cu, Ni, Pb, Zn, Al, and Fe with varying solid-to-liquid ratio.

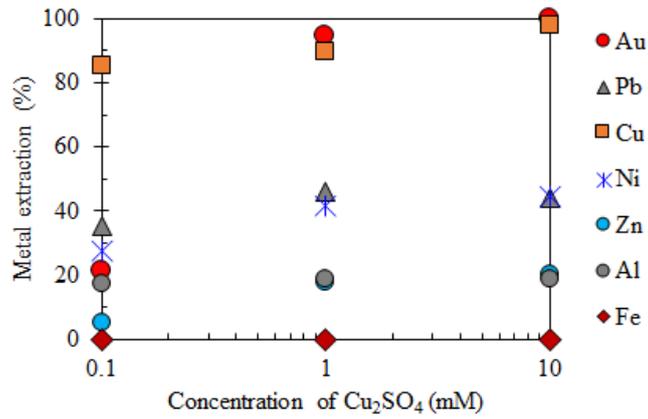


Fig. 4. Extractions of Au, Cu, Ni, Pb, Zn, Al, and Fe with varying concentration of CuSO₄.

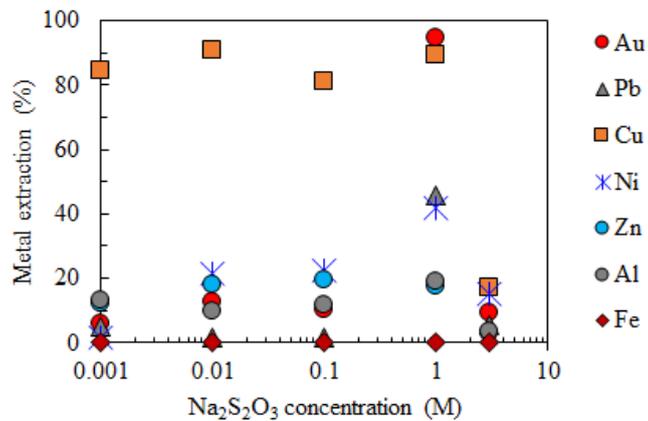


Fig. 5. Extractions of Au, Cu, Ni, Pb, Zn, Al, and Fe with varying concentration of Na₂S₂O₃.

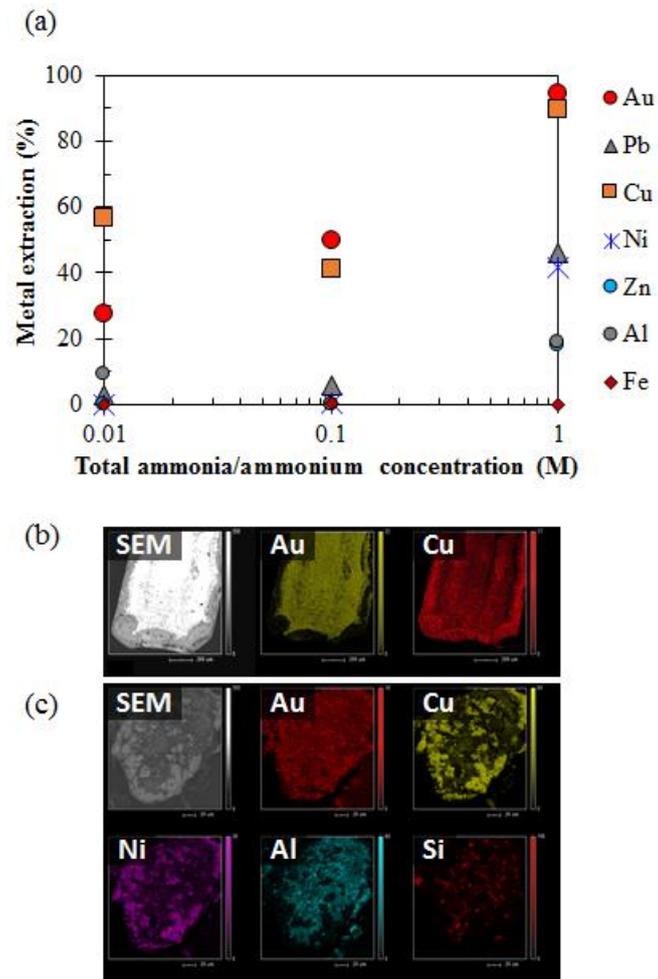


Fig. 6. (a) Extraction of Au, Pb, Cu, Ni, Zn, Al and Fe with varying total concentrations of ammonia/ammonium and (b) SEM photomicrograph of a Cu-bearing component in printed circuit boards with the corresponding elemental maps of Au and Cu prior to the leaching experiment as well as (c) SEM photomicrograph of the leaching residue with the corresponding elemental maps of Au, Cu, Ni, Al, and Si

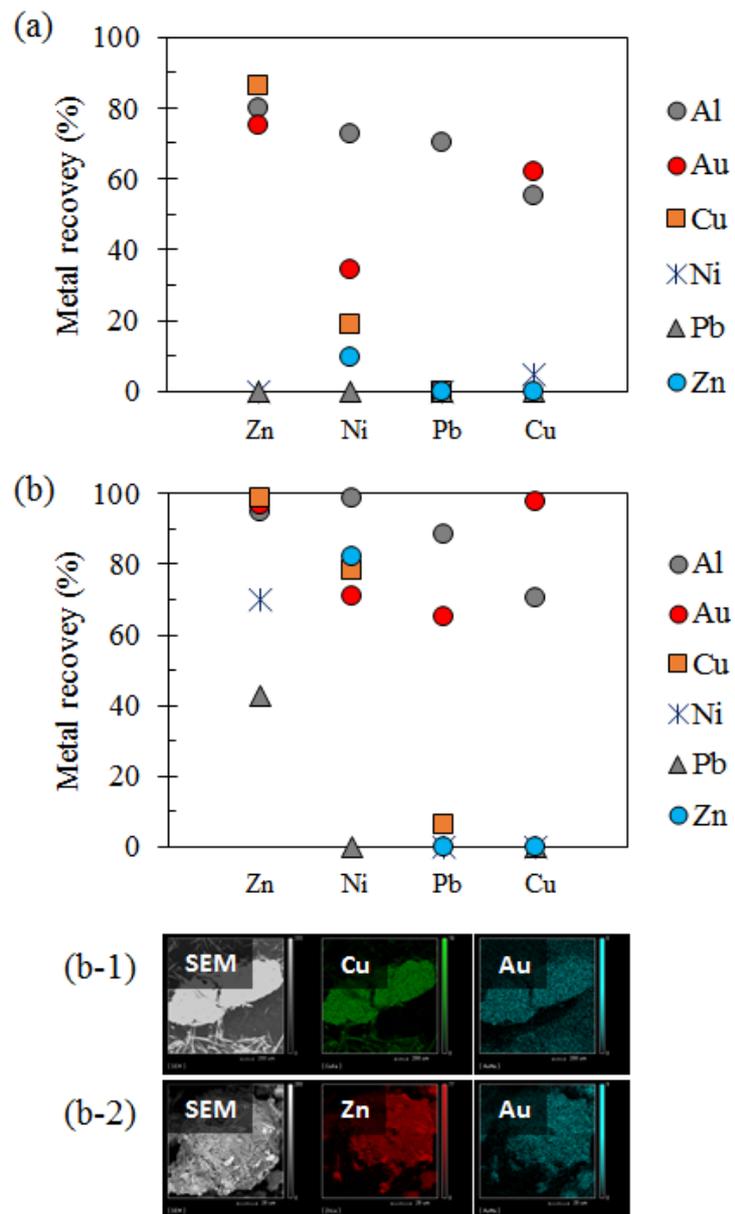


Fig. 7. Recovery of extracted metals from PCBs by Pb, Ni, Cu, Zn and Fe (a) with oxygen and (b) without oxygen as well as SEM photomicrographs of residues after the cementation experiments using (b-1) Cu, and (b-2) Zn with their corresponding elemental maps.

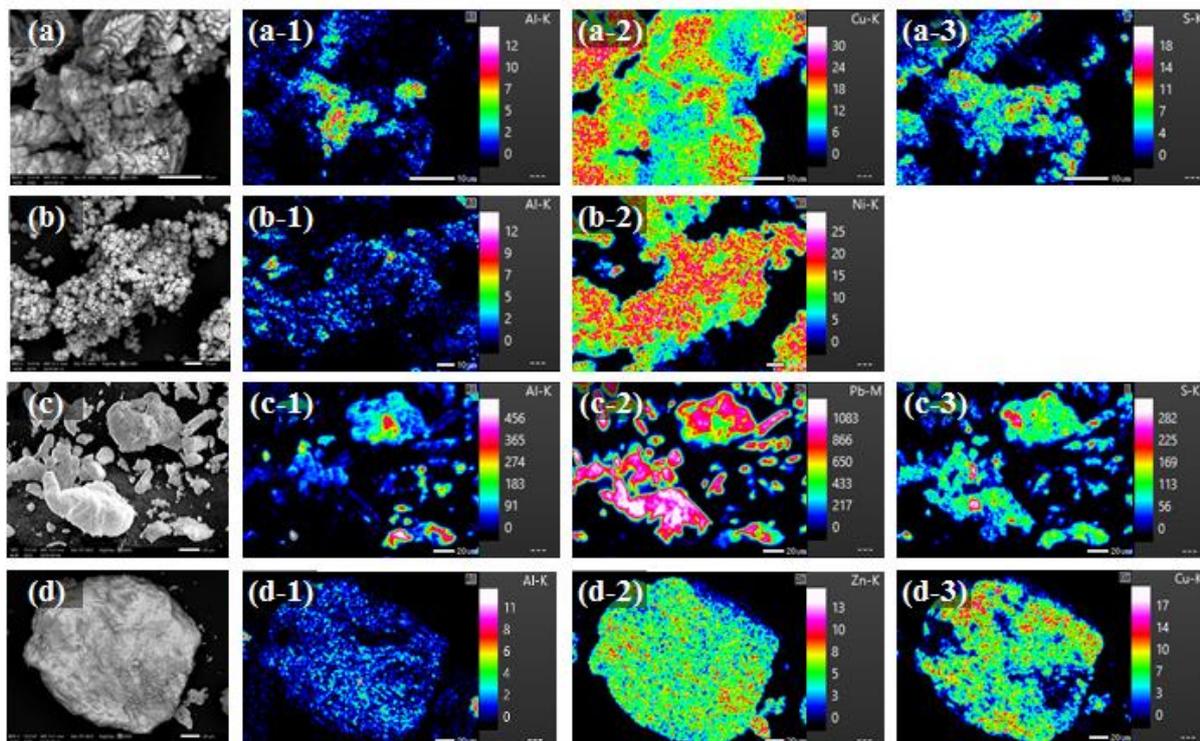


Fig. 8. SEM photomicrographs of the (a) Cu residue and its corresponding elemental maps of (a-1) Al, (a-2) Cu, and (a-3) S, (b) Ni residue and its corresponding elemental maps of (b-1) Al and (b-2) Ni, (c) Pb residue and its corresponding elemental maps of (c-1) Al, (c-2) Pb, and (c-3) S, as well as (d) Zn residue and its corresponding elemental maps of (d-1) Al, (d-2) Zn, and (c-3) Cu,

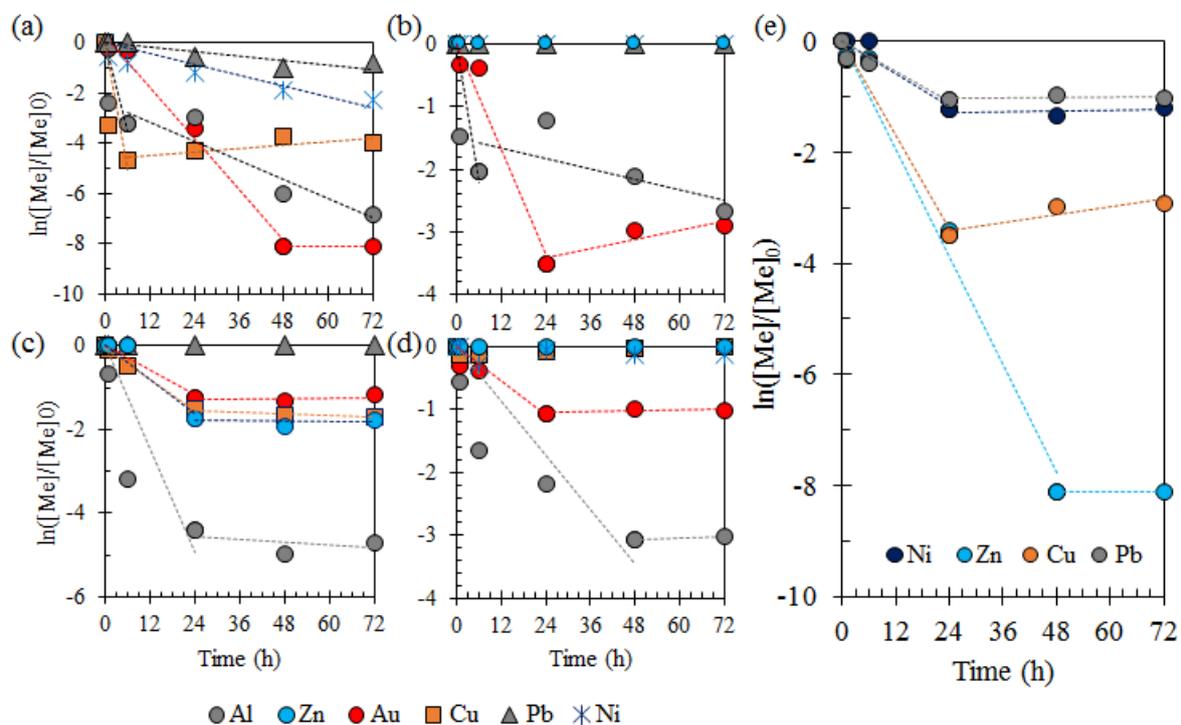


Fig. 9. The effects of cementing agents ((a) Zn, (b) Cu, (c) Ni and (d) Pb) on metal recovery as well as (e) on Au recovery from ammonium thiosulfate pregnant solution with varying time.

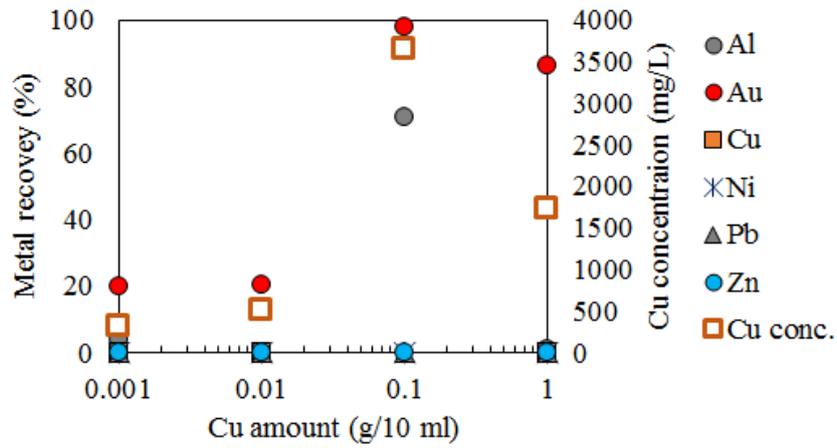


Fig. 10. Recovery of metal ions with varying dosage of Cu in grams

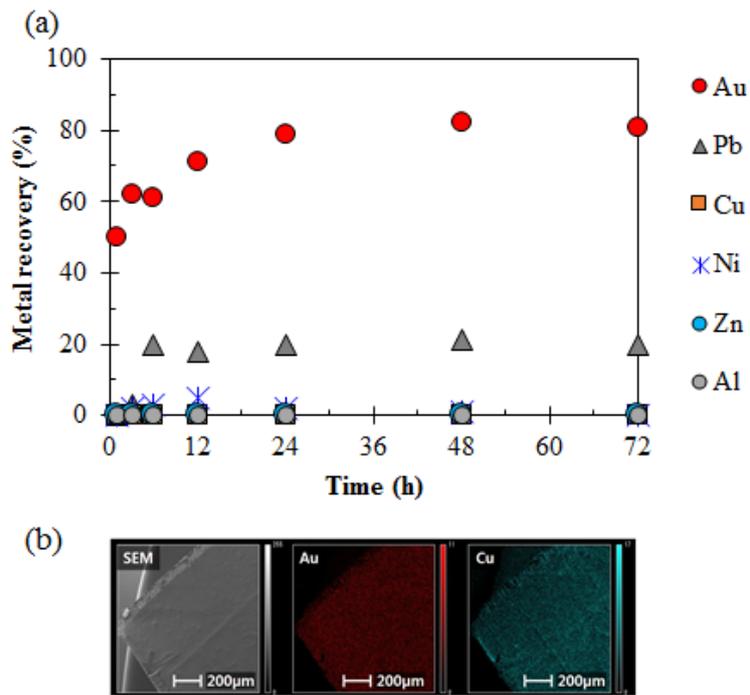


Fig. 11. (a) Recovery of metal ions using Cu plate with time in ammonium thiosulfate pregnant solution and (b) SEM photomicrograph of the Cu plate after cementation experiments with corresponding elemental maps.