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Interference of coexisting copper and aluminum on the ammonium thiosulfate leaching of gold from printed circuit boards of waste mobile phones

Sanghee Jeon [a,*], Carlito Baltazar Tabelin [b], Hirotaka Takahashi [a], Ilhwan Park [a], Mayumi Ito [b], Naoki Hiroyoshi [b]

[a] *Laboratory of Mineral Processing and Resources Recycling, Division of Sustainable Resources Engineering, Graduate School of Engineering, Hokkaido University, Japan*
[b] *Laboratory of Mineral Processing and Resources Recycling, Division of Sustainable Resources Engineering, Faculty of Engineering, Hokkaido University, Japan*

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ABSTRACT

Ammonium thiosulfate solution is an ideal lixiviant to extract gold (Au) from electronic wastes (E-wastes) because it is non-toxic, less corrosive, and more selective than conventional cyanide or halide solutions. It was reported recently, however, that Au leaching efficiency in ammonium thiosulfate medium dramatically decreased at high solid-to-liquid ratios (S/L), even though the amounts of reagents used were in excess. To understand how this occurred, leaching experiments were conducted using printed circuit boards (PCBs) from waste mobile phones, and Au distribution in the leaching residues was examined by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX). Significant amounts of Au were found together with copper (Cu) and aluminum (Al), implying that extracted Au ions were likely re-deposited during leaching onto Cu and Al found in PCBs via cementation (i.e., reductive deposition). A more detailed elucidation of this phenomenon by cementation experiments using pure Cu and/or Al powders indicates that these metals could only recover Au ions alone via cementation at very high amounts, however, this process became more extensive when Cu and Al powders were suspended together in solution even though the amounts of the individual metals were much lower. Electrochemical experiments (chronoamperometry) in ammonium thiosulfate solutions containing Au ions using an Al working electrode also showed that Au ion cementation was dramatically enhanced when Cu powder was present in solution, and the bulk of Au was cemented on Cu powder rather than on the Al electrode. These results suggest that coexistence of Cu and Al interfered with the extraction of Au in ammonium thiosulfate medium at high S/L because of the enhanced re-deposition of extracted Au via galvanic interaction.

1. Introduction

The rapid increase in the number of discarded mobile phones has been especially remarkable in the last few years (Gurung et al., 2013; Li et al., 2017). A report by the United Nations (UN), for example, predicted that by 2020, the generation of waste mobile phones around the world would be about 18 times higher than in 2007 (Tripathi et al., 2012). Printed circuit boards (PCBs) of mobile phones contain a wide variety of materials with diverse compositions including hazardous elements like lead (Pb) and arsenic (As) as well as valuable metals such as gold (Au), copper (Cu), aluminum (Al), iron (Fe), nickel (Ni), and zinc (Zn) (Duan et al., 2016; Hall and Williams, 2007; Park et al., 2017; Petter et al., 2014; Yamane et al., 2011). Over 70% of the total metal price in mobile phones is typically accounted for by Au in PCBs. In a previous study of the authors, it was reported that PCBs of waste mobile phones in Japan could contain up to 0.3 wt% of Au (3000 ppm), which is more than 300-fold higher than typical Au ores (2–10 ppm) (Jeon et al., 2018), so its recovery from these electronic wastes (E-wastes) is not only necessary but also economically viable. Both pyrometallurgical and hydrometallurgical techniques have been applied to recover Au from PCBs. In hydrometallurgy, Au is first leached in suitable aqueous solutions and then recovered by adsorption, precipitation or cementation (Jeon et al., 2017b; Korolev et al., 2018; Yoo et al., 2012). Cyanide and the halides (e.g., aqua regia) are two of the most widely used

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[*] Corresponding author at: Division of Sustainable Resources Engineering, Graduate School of Engineering, Hokkaido University, Kita 13, Nishi 8, Kita-ku, Sapporo 060-8628, Hokkaido, Japan.

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

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extractants of Au largely because of their high extraction efficiency. Although effective, alternative lixiviants have been developed because cyanide is very toxic while the halides are highly corrosive (Ha et al., 2010). Among these alternatives, ammonium thiosulfate is attractive because it is non-toxic, less corrosive, and highly selective for Au (Ha et al., 2010).

Numerous studies have been done to extract Au from ores and E-wastes by ammonium thiosulfate leaching (Grosse et al., 2003; Ha et al., 2010, 2014; Jeffrey & Brunt, 2007; Petter et al., 2014; Senanay, 2004; Tripathi et al., 2012). Using PCBs of waste mobile phones, for example, Tripathi et al. (2012) examined the leaching of Au under various conditions (i.e., thiosulfate and Cu ion concentrations, pH, and solid-to-liquid ratio (S/L)), and they reported that maximum Au extraction (57%) was achieved under the following conditions: 0.1 M of ammonium thiosulfate, 40 mM of Cu(II) ion, pH of 10, agitation speed of 250 rpm, temperature of 25 °C, leaching time of 8 h, and S/L of 10 g/l. Among these parameters, S/L was noted by these authors as one of the most important because Au extraction significantly decreased at S/L > 10 g/l. Unfortunately, Tripathi et al. (2012) did not explain the reasons why this negative effect occurred at high values of S/L. Unless this crucial problem is addressed, scaling-up of ammonium thiosulfate leaching of Au from waste mobile phones would be difficult because large reactors are required to obtain high Au extraction efficiency. A previous study of the authors showed that one possible reason for the low Au extraction at high S/L is the re-deposition of extracted Au via cementation (i.e., reductive deposition) on some of the coexisting metals present in PCBs (Jeon et al., 2017a). The details of this phenomenon, however, remain unclear so it is important to understand how coexisting metals in PCBs affect the dissolution of Au in ammonium thiosulfate solution.

In this study, PCBs of the waste mobile phones were leached in ammonium thiosulfate solution under various conditions and the leaching residues were examined by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX). To interpret the observed results and clarify the mechanism(s) involved in the suppression of Au extraction at high S/L, cementation experiments using pure metal powders were conducted supplemented by electrochemical studies.

2. Materials and methods

2.1. Materials

2.1.1. Printed circuit boards of waste mobile phones

Waste mobile phones were obtained from a recycling shop in Japan. The PCBs were manually collected by hand-dismantling and then crushed in liquid nitrogen by a cutting mill (TPH-02, As One, Japan) to obtain a particle size fraction of less than 5 mm. The crushed sample was further ground with a disk mill (RS 100, Retsch Co., Ltd., Germany) and sieved to obtain a –106 μm size fraction. At this size fraction, preliminary experiments of the authors showed that extraction of Au was almost 100%, so it was selected in this study.

For the chemical composition of PCBs, a special ashing method was used to remove combustibles without Au volatilization (Jeon et al., 2018; Tomita et al., 1983), and the ash was digested using aqua regia (a 1:3 by volume mixture of concentrated nitric and hydrochloric acids) at 90 °C for 2 h (Shen et al., 2018; Yamane et al., 2011). The leachates were filtered through 0.2 μm syringe-driven membrane filters (LMS Co., Ltd., Japan), diluted with deionized (DI) water (18 MΩ·cm, MillQ® Integral Water Purification System, Merck Millipore, USA), and analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES, ICPE-9820, Shimadzu Corporation, Japan) (margin of error = ±2%). As shown in Table 1, the sample used in this study contains Cu and Al as major metallic components as well as Ni, Zn, Fe, Pb, and Au in minor amounts.

2.1.2. Metal powders

For the cementation experiments, pure Cu, Al, Fe, Zn, Pb, and Ni powders (−75 μm, 99.9%, Wako Pure Chemical Industries, Ltd., Japan) were used as reductants of Au.

2.2. Experimental methods

2.2.1. Leaching experiments

Ammonium thiosulfate solutions with pH of around 9.5–10 containing 1 M (M) $Na_2S_2O_3$, 0.5 M NH_3, 0.25 M $(NH_4)_2SO_4$, and 10 mM $CuSO_4$ (Wako Pure Chemical Industries, Ltd., Japan) were used in the leaching experiments (This solution composition was selected based on our preliminary experiments (Supplementary Fig. 1)). The experiments were carried out by mixing known amounts of PCBs (−106 μm) and 10 ml of the ammonium thiosulfate solutions in 50-ml Erlenmeyer flasks. The flasks were shaken at 25 °C in a water bath shaker with constant shaking amplitude and frequency of 40 mm and 120 min^{-1}, respectively. After 24 h, the leachate was collected by filtration and analyzed by ICP-AES. Meanwhile, the solid residues were thoroughly washed with DI water, dried in a vacuum oven at 40 °C for 24 h, and analyzed by SEM-EDX (Superscan SSX-550, Shimadzu Corporation, Japan).

2.2.2. Cementation experiments

Among the metal powders used in this study, Al has the lowest standard redox potential at −1.66 V, so an insulating oxide layer is easily formed on it, which could limit electron transfer from Al powder to Au ions in the solution during the experiments. To elucidate this effect, a separate set of experiments were done in which Al powder was washed to remove the Al-oxide layer using the method of Seng et al. (2017). The washing method involves mixing of the Al powder and a solution containing 2 M sodium chloride and 0.1 M hydrochloric acid in a beaker with a magnetic stirrer at 400 rpm for 15 min, thorough rinsing of the washed Al powder with DI water, and drying in a vacuum oven at 40 °C for 24 h. The rest of the metal powders were used in the cementation experiments without washing or pretreatment.

The ammonium thiosulfate solution containing 100 mg/l of Au ions (Au-ammonium thiosulfate solution) was prepared by dissolving 0.01 g of Au powder with 100 ml of ammonium thiosulfate solution in 300 ml Erlenmeyer flasks shaken in a water bath shaker at 25 °C for 24 h with constant shaking amplitude and frequency of 40 mm and 120 min^{-1}, respectively. For the cementation experiments, predetermined amounts of metal powders (e.g., Cu and Al before/after washing) and 10 ml of Au-ammonium thiosulfate solution were mixed in a 50-ml Erlenmeyer flask at 25 °C (shaking amplitude of 40 mm and frequency of 120 min^{-1}). After cementation for 24 h, the leachate and residue were separated by filtration using 0.2 μm syringe-driven membrane filters. The

Table 1
The composition of waste mobile phone PCBs.

	Metals							Combustibles	Others
	Cu	Al	Fe	Ni	Pb	Zn	Au		
Amount (wt.%)	37.1	19.2	3.7	2.1	0.2	0.1	19.2	31.2	6.1