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Doctoral Thesis

Development of a new method for gold recovery from waste mobile phones by combining physical separation and hydrometallurgical techniques using ammonium thiosulfate medium

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctorate in Engineering

by
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ABSTRACT

The life-cycle of mobile phones is probably the shortest among electronic devices, which leads to the generation of waste mobile phones annually. Mobile phones are complex devices typically composed of a plastic frame, liquid crystal displays, and a keyboard as well as printed circuit boards (PCBs). PCBs in mobile phones contain a wide variety of materials including not only hazardous elements but also valuable metals like copper (Cu), aluminum (Al), iron (Fe), and gold (Au). The average Au content in PCBs is often several tens or hundreds of times higher than natural ores, so the recycling and recovery of Au from waste mobile phones are needed for resources sustainability and conservation. The recovery of Au from electronic wastes typically requires two stages: (1) hand-dismantling to specifically target valuable components (e.g., PCBs), and (2) metallurgical treatments to extract and refine target metals. For waste mobile phones, hand-dismantling to recover PCBs is difficult and impractical due to their small sizes, so only batteries are removed, and the remainder is treated by metallurgical techniques. Pyrometallurgical treatment, however, requires high initial capital and operational costs, so hydrometallurgical technique is a good alternative in areas without any pyrometallurgical facilities. In hydrometallurgy, Au is first leached in suitable aqueous solutions and then recovered by adsorption, precipitation or cementation. Cyanide and the halides are most widely used but they are either very toxic or highly corrosive. Among the available alternatives, ammonium thiosulfate is attractive because it is non-toxic, less corrosive, and highly selective for Au. Despite these many advantages, its use in recycling is still limited primarily because of two drawbacks: (1) Au extraction is low at high solid-to-liquid ratio (S/L), and (2) acceptable methods to recover extracted Au ions are not yet established. This study investigated the leaching of Au in waste mobile phones and identified the reasons why Au extraction was low at high S/L. Moreover, a pretreatment flowchart was developed to separate interfering metal(s) from the Au-containing fractions and improved the Au leaching efficiency in ammonium thiosulfate medium. Finally, a novel method to recover extracted Au ions in ammonium thiosulfate medium was developed.

Chapter 1 gives the background, importance and objectives of the study.

In Chapter 2, previous studies on electronic wastes recycling by physical and chemical techniques (i.e., leaching) were reviewed.

In Chapter 3, optimum leaching conditions for Au extraction from waste mobile phones was established. The parameters evaluated include S/L (0.1–1g/10ml), concentration of $\text{Na}_2\text{S}_2\text{O}_3$ (0–3 M), CuSO_4 (0–10 mM), $(\text{NH}_4)_2\text{SO}_4$ (2.5–250 mM), and NH_4OH (5–500 mM), leaching time (0–75 h) at 25 °C (pH 9–10). The results showed that Au extraction increased with increasing shaking time, total ammonium, and CuSO_4 concentration. Increasing the concentration of $\text{Na}_2\text{S}_2\text{O}_3$ also enhanced the extraction of Au but only up to about 1 M. Higher than this value, however, the extraction of Au from waste mobile phones decreased. Based on these results, the optimum Au extraction was achieved under the following condition: 1 M of $\text{Na}_2\text{O}_2\text{O}_3$, 10 mM of CuSO_4 , 1 M of total ammonium concentration, 0.1 g sample and 24 h.

Chapter 4 identified the interfering metal(s) that caused cementation/precipitation of extracted Au ions during ammonium thiosulfate leaching. SEM-EDX observations of Au distribution in the leaching residues showed significant amounts of Au together with Cu and Al, implying that extracted Au ions were likely re-deposited during leaching onto these metals found in waste mobile phones via cementation (i.e., reductive deposition). A more detailed elucidation of this phenomenon showed that although Cu or Al alone could recover Au ions via cementation, this process became more extensive when they were suspended together in solution even though the amounts of the individual metals were very low. 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 the 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, so physical separation treatment is needed to separate interfering metals like Cu and/or Al prior to leaching.

Chapter 5 identified the effects of physical separation of interfering metals on Au extraction and a practical physical treatment flowchart was proposed. Several studies that applied both physical separation and hydrometallurgical treatment have been conducted, but most of them focused on hand-dismantled “clean” PCBs and only one particle size fraction. Most importantly, these studies did not evaluate how physical separation affects the leaching efficiency of Au. In this chapter, mineral processing techniques were applied to crushed mobile phones, and the effects of these techniques on Au extraction were evaluated. The proposed flowchart includes the following: (1) pre-concentration (jig separation) of PCBs from coarse crushed products (+2–10 mm), (2) removal of Cu-/Al-containing parts by jig separation after fine crushing the concentrated PCBs, (3) ammonium thiosulfate leaching of Au concentrated products. The fine fractions generated from coarse and fine crushing stages were treated by flotation and hybrid jig separation. The leaching results using ammonium thiosulfate solution showed that Au extraction was improved by about 11-fold after physical pretreatments.

In Chapter 6, the novel method to recover Au ions from ammonium thiosulfate leached solution using the synergistic effects of Al and activated carbon on Au cementation was developed. When only activated carbon or Al was present in a thiosulfate solution containing Au ions, Au recovery was negligible under the following conditions: 0.15 g of activated carbon or Al with 10 ml thiosulfate solution containing 100 mg/l of Au ions at 25 °C for 24 h with 120 rpm. When both 0.15 g of activated carbon and 0.15 g of Al coexisted in the solution, however, Au recovery significantly increased (>99%) via two possible mechanisms. Firstly, nano-scratches on the oxide film of Al were formed by particle-particle collision during shaking. Fine particles of activated carbon attached to the nano-scratches most likely enhanced the transfer of electrons from Al to Au ions, which resulted in Au cementation on activated carbon. Secondly, the thin Al oxide film most probably acted as a dielectric material that accumulated electrons within the oxide film and

donating them to the attached activated carbon on Al where Au ions could be deposited.

Finally, Chapter 7 gives the general conclusions of this study.

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CHAPTER 1

GENERAL INTRODUCTION

1.1 Background

Worldwide demand for electric and electronic equipment (EEE) has been steadily increasing due to rapid advancements in technology, which lead to the higher generation of waste electric and electronic equipment (WEEE). WEEE includes not only industrial electronic wastes (e.g., copy machines and automated teller machines) and home appliances (e.g., refrigerators, television sets, and washing machines) but also small electronic gadgets and devices such as remote controls, game consoles, and mobile phones. Among hand-held gadgets, mobile phones are the most ubiquitous, but their life-cycle is probably the shortest (~2 years), which leads to the significant generation of waste mobile phones annually. Mobile phones are complex devices composed typically of a plastic frame, liquid crystal displays (LCD), and a keyboard as well as printed circuit boards (PCBs) containing integrated circuits and other electronic components. PCBs in mobile phones contain a wide variety of materials including not only hazardous elements (e.g., arsenic, mercury, and cadmium) that could pollute the environment when burned or disposed of in landfills but also valuable metals like copper (Cu), aluminum (Al), iron (Fe), and gold (Au). Recent studies have reported that the average Au content of PCBs is often several tens or hundreds of times higher than natural ores. This means that recycling and recovery of Au from waste mobile phones are needed for resources sustainability and conservation.

To recover the Au from waste mobile phones, both pyrometallurgical and hydrometallurgical techniques have been applied. Pyrometallurgical treatment, however, requires high initial capital and operational costs, so hydrometallurgical technique is a good alternative in areas without any pyrometallurgical facilities. In hydrometallurgy, Au is first leached in suitable aqueous solutions and then recovered by adsorption, precipitation or cementation. Cyanide and the halides (e.g., aqua regia) are two of the most widely used extractants of Au largely because of their high extraction efficiency. Although effective, alternative lixivants have been developed because cyanide is very toxic while the halides are highly corrosive. Among these alternatives, ammonium thiosulfate is attractive because it is non-toxic, less corrosive, and highly selective for Au. Despite these many advantages, its use in recycling is still limited primarily because of two drawbacks: (1) Au extraction is low due primarily to the cementation/precipitation of extracted Au ions by coexisting base metal(s) in waste mobile phones and (2) there is no acceptable method for recovery of Au ions from leached solution to date.

This study investigated the leaching of Au in waste mobile phones and identified the interfering metal(s) during leaching. After that, to minimize the effects of the interfering base metals, pretreatment of the feed materials by separating these base metals from the Au-containing fractions prior to ammonium thiosulfate leaching via physical separation techniques was carried

out and leaching of Au-containing product was conducted to determine the effects of separation of base metals on Au extraction efficiency. Finally, a method of Au ions recovery from leached solution was developed.

1.2 Outline of the dissertation

This dissertation is composed of seven chapters. The key contents of each chapter are outlined as follows:

Chapter 1 gives the general introduction including background, statement of the problem and outline of the dissertation.

Chapter 2 reviews previous studies on recycling techniques of electronic wastes including waste mobile phones.

Chapter 3 describes the leaching of metals from PCBs of end-of-life laptop to optimize the leaching conditions.

Chapter 4 investigated the interfering coexisting metals in ammonium thiosulfate leaching of Au from waste mobile phones by cementation experiments, and mechanisms were detailed by electrochemical experiments.

Chapter 5 presents the effects of physical separation as a pretreatment on Au leaching in ammonium thiosulfate medium by separating interfering metals from Au-containing fractions.

Chapter 6 describes the recovery of Au ions from leached solutions via synergistic effects of activated carbon and Al.

Chapter 7 gives the summary, implications and conclusion of the dissertation.

CHAPTER 2

RECYCLING TECHNIQUES OF ELECTRONIC WASTES: A REVIEW

2.1 Introduction

The recycling market of waste electrical and electronic equipment (WEEEs) is growing up in the world due to short life cycle of electric and electronic equipment. Commonly in United States of America, 80% of the collected domestic WEEEs is not recycled but shipped to another country (Huang et al., 2009) and only 50% of WEEE is recycled in Europe (Maurell-Lopez et al., 2011). In case of Australia, most of the WEEEs go to landfill (David et al., 2006). In China, open burning of WEEEs is commonly used for handling the WEEEs (Huang et al., 2009).

The WEEEs contain Printed Circuit Boards (PCBs) and the PCBs mechanically supports and electrically connects electronic components using conductive tracks and pads and the plate part is composed of Cu sheets laminated onto a non-conductive (plastic resin) substrate. The PCBs contains the integrated circuits (IC) and it contains gold (Au) (Cui et al., 2008; Laere et al., 2007; Lee et al., 2000; Yu et al., 2009). The Au is used due to its electrical conductivity, low contact electrical resistance for inserting connections and outstanding corrosion resistance (Syed, 2012).

Recycling treatment of WEEEs is important to recover valuable components and reduce volume of final disposal and physical separation treatments are applied to concentrate metals containing Au. The process can be classified 1) concentration of PCBs from WEEEs and 2) separation of metals and plastic compounds from crushed PCBs. To recover Au from PCBs or metal concentration products from PCBs, pyrometallurgical and hydrometallurgical treatments are used (Cui et al., 2008; Syed, 2012; Yap et al., 2007; Sohaili et al., 2012; Luda, 2011). This section reviews recent advances in physical pretreatments and pyrometallurgical and hydrometallurgical techniques to recover Au from WEEEs and PCBs.

2.2 Physical techniques

Physical separation treatments have been applied to concentrate valuable components from WEEEs. The processes can be classified; 1) concentration of PCBs from WEEEs and 2) separation of metal and plastic compounds from crushed PCBs. Fig. 2-1 is an example of WEEEs treatment flowsheet in Japanese recycling company (Re-Tem, 2017). Non-metal, ferromagnetic metal, Al, stainless, and Cu-Ag-Au concentrates are obtained by crushing, size classification, magnetic separation, and eddy current separation technique. The PCBs are concentrated in the Cu-Ag-Au concentrates and the concentrate is treated by a Cu smelting furnace and Cu and precious metal including Au are recovered.

The PCBs contain electronic parts and the plate part is composed of Cu sheets laminated onto a non-conductive (plastic resin) substrate. Physical separation treatments are used to separate metals and plastics. Research including crushing, electromagnetic separation, gravity separation,

and flotation were investigated.

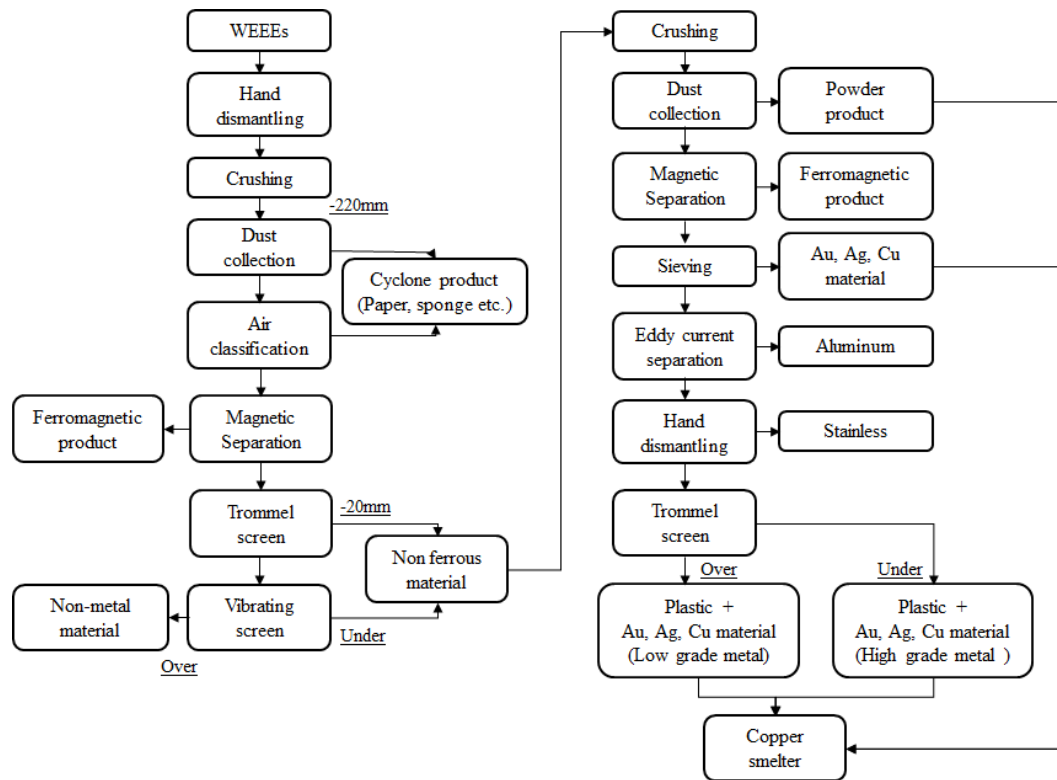


Fig. 2-1. Flowsheet of WEEEs treatment in Japanese recycling company.

2.2.1 Crushing

Wang et al. (2005) investigated crushing performance of PCBs using a jaw crusher, roller crusher, disk crusher, vibrating mill and better crushing performance was obtained by impacting and cutting force types. Li et al. (2007) used a high-speed hammer crusher and completely stripped metal parts were obtained by two-step crushing. Peng et al. (2004) developed a crusher with impacting and shearing forces and high liberation degree was obtained. Yoo et al. (2009) investigated crushing behavior of metal components (Ni, Fe, Cu, Al) in PCBs using a stamp mill utilizing the up and down reciprocating motion of the hammer and concentrated metals by size classification, zigzag classification (gravity separation), two-step magnetic separation. Koyanaka et al. (1995) developed a shape sorting technique using a hummer mill. By using impactation force for ductility of Cu, highest sphericity was obtained, and inclined vibration separator recovered the spherical Cu particles. Oki et al. (2011) developed an active crushing technique to obtain high liberation degree. Selective breakage at phase boundary and selective crushing of weak materials were achieved by a PC controlled operation. Lee et al. (2012) developed an effective apparatus for removing parts from PCBs. This apparatus removes parts from PCBs with four diamond grinders that wear down the solder joints and 15 elements were separated by sizing and magnetic separation.

2.2.2 Electromagnetic separation

Magnetic separation is used for the recovery of ferromagnetic metals and various classification schemes have been introduced for magnetic separations (Veit et al., 2005). Li et al. (2007) applied a corona electrostatic separation for several size fractions crushed by a high-speed hammer crusher and better separation efficiency was obtained for +0.6–1.2 mm fraction, while fine fraction showed low separation efficiency due to electrostatic cohesion.

2.2.3 Gravity separation

Gravity separation can concentrate heavy particles such as metals from light particles in air and water mediums. Lee and coworkers (2012) developed an effective apparatus for removing parts from PCBs and dense medium separation was applied to recover different type of parts. Long et al. (2010) treated PCBs by a vacuum pyrolysis to remove gas and oil contents and the residue was fed to a zigzag air classification and high Cu recovery was obtained. Ito et al. (2013) crushed PCBs by a cutting mill and +2–5mm fraction was treated by a jig. High Cu recovery was obtained as bottom layers. Sarvar et. el (2015) crushed PCBs by a hammer mill and coarse fraction (+1.68 mm) was treated by a jig and high Cu recovery was obtained. Habib et al. (2013) crushed PCBs by a cutting mill and -1.5mm fraction was treated by a dry vertical vibration separator and high metallic grade was obtained. Yuemin et al. (2006) crushed PCBs by roll and hammer crusher and coarse fraction (+0.074–2.0 mm) was treated by a electrostatic separator and fine fraction (–0.074mm) was treated by a centrifugal separator (falcon concentrator).

2.2.4 Flotation

PCBs contain plastic resin and metals and separation of these components is possible by flotation using wettability differences. Ogunniyi et al. (2009) applied collector less flotation for –0.075mm fraction and Au and Pd were concentrated in tailing. Kumar et al. (2013) treated –0.15mm fraction by collector less flotation and high metal grade was obtained. Sarvar et el. (2015) crushed PCBs by a hammer mill and coarse (+1.68 mm) and fine fraction (–0.59 mm) were treated by jig and flotation.

Table 2-1 The studies of physical separation from PCBs.

	Sample type	Results	Note	Ref.
Crushing	PCBs scrap	-	Hammer type impact mill (rotating speed 70.2 m/s), inclined vibrating plate	(Koyanaka et al., 1995)
	WPCBs	-	Crusher with impacting and shearing forces	(Peng et al., 2004)
	PCBs	-	Jaw crusher, roller crusher, disk crusher, vibration grinding	(Hui et al., 2005)
	PCBs	-	Hammer crusher (Two step crushing)	(Li et al., 2007)

	PCBs	-	Stamp mill	(Yoo et al., 2009)
	PCBs	-	Active crushing technique using hammer crusher	(Oki et al., 2011)
	Video-cassette-records PCBs	-	Self-designed disassembling apparatus, sieving, magnetic separation, dens media separation (± 9.5 mm)	(Lee et al., 2012)
	PCBs	-	Cutting mill (-1.5 mm)	(Habib et al., 2013)
	Computer PCBs	-	Hammer mill	(Sarvar et al., 2015)
Electro magnetic	PCBs	Ni, Fe recovery 94 %	Two-step magnetic separation	(Yoo et al., 2009)
	PCBs	Better separation at 0.6-1.2mm size fraction	Corona electrostatic separation for several size fractions	(Li et al., 2007)
	Video-cassette-records PCBs	15 elements	Self-designed disassembling apparatus, magnetic separation, dens media separation (± 9.5 mm)	(Lee et al., 2012)
Gravity	PCBs	Integration efficiency 77%	Falcon concentration (-0.074 mm)	(Yue-min et al., 2006)
	Video-cassette-records PCBs	15 elements	Self-designed disassembling apparatus, sieving, magnetic separation, dens media separation (± 9.5 mm)	(Lee et al., 2012)
	Waste PCBs	Cu recovery 99%	Vertical zigzag airflow (-4 mm (after vacuum pyrolysis))	(Long et al., 2010)
	PCBs	Metal grade 95%	Dry vertical vibration separation (-1.5 mm)	(Habib et al., 2013)
	PC-PCBs	Cu recovery > 90%	Jig separation (2–5 mm)	(Ito et al., 2013)
	Computer PCBs	Metal content 98%	Jig separation (0.59 to 1.68 mm)	(Sarvar et al., 2015)
	PCBs	Au, Pd	Reverse flotation (-75 μ m)	(Ogunniyi et al., 2009)
Flotation	DVD players PCBs	75% metal. Recovery / 88% grade	Reverse flotation (-150 μ m)	(Kumar et al., 2013)
	PC-PCBs	85% metal recovery / 75 % grade	Flotation (-0.59 mm)	(Sarvar et al., 2015)

2.3 Metallurgical techniques

2.3.1 Pyrometallurgy

Since three decades, pyrometallurgy treatment has become a traditional method to recover metals from W EEs (Syed, 2012). Despite difference in the plants, leading recycling companies, such

as Boliden, Dowa, Umicore and X-Strata, employ pyrometallurgical treatment in their recycling systems (Yu et al., 2009). Umicore can recycle 17 metals including 7 precious metals. The plant is divided into 2 major operation methods: Precious Metals Operations (PMO) and Base metals operations (BMO). PMO is composed of smelter, leaching, electro-winning and precious metals refining. BMO is composed of the blast furnace, Pb refinery. The Boliden Ltd. Ronnskar smelter in Sweden uses a Kaldo technique. Kaldo technique uses the plastic in WEEEs to smelt the metals. The Kaldo Furnace produces a mixed Cu alloy that is sent to the Cu conversation operation for metal recovery such as Au (Yu et al., 2009). And Mitsubishi material in Japan also do the pyrometallurgical treatment using incineration and smelting to recover precious metals (Mitsubishi, 2016). A pyrometallurgical conventional process involves pretreatment of WEEEs including dismantling, shredding, and incineration and smelting. Incineration is followed by electric arc furnace treatment using Cu as the collector metal. And another treatment of WEEEs is the melting, together with a Cu anode slime containing lead and silver, and addition of sodium carbonate as flux (Schmidbaur, 1999). Slimes collected from Cu electrorefining are further refined to recover precious metals including Au (Tuncuk et al., 2012).

This part will introduce about pyrometallurgical treatment including cupellation process, roasting, calcination, incineration, supercritical fluid extraction process from PCBs existed in WEEEs.

Incineration involves the pyrolysis (inert atmosphere) and combustion (oxidizing atmosphere) of organic substances contained in WEEEs (Maurell-Lopez et al., 2011). Pyrolysis decomposes the organic part of the WEEEs. It can separate the organic, metallic and glass fractions of PCBs much easier and recycling of each fraction more viable. If the temperature is high enough, the pyrolysis process will melt the solder in PCBs (Schmidbaur, 1999). For separating organics, a temperature of 500 °C to 800 °C is needed (Maurell-Lopez et al., 2011). Combustion is a thermal decomposition such as pyrolysis but includes oxidation and temperature range is higher than pyrolysis (Juma et al., 2006). In a thermal gravimetric investigation, the thermal decomposition occurs as a heavy weight loss. The oxidation reaction is accompanied with an additional weight loss. It is clear that the oxidation reaction is post combustion of the solid residue, because compared to pyrolysis there is no ash product (Maurell-Lopez et al., 2011).

The melting point of Au is 1063 °C. At temperature of 1200 °C or higher Au cannot oxidized by oxygen. In this temperature range all base metals are easily oxidized by oxygen. This process is so called cupellation process (Schmidbaur, 1999). Using cupellation process, recovery studies of the precious metals from WPCBs were done (Long et al., 2010). Conventionally furnaces with a horizontal hearth were used as cupellation furnaces. Nowadays cupellation furnaces are replaced by top-blown rotary converters (TBRC) due to relatively low energy consumption (Maurell-Lopez et al., 2011; Schmidbaur et al., 1999) and studies recovering precious metals from used PCBs were also done by suing TBRC (Maurell-Lopez et al., 2011).

In conventional pyrometallurgy treatment, EEEs containing brominated flame retardants are incinerated and the formation of pernicious compounds (e.g., halogenated dibenzodioxins and dibenzofurans) from the flame retardants are occurred. Supercritical fluid extraction with CO₂ is a process to extract brominated flame retardants (Yu et al., 2009). Table 2-2 shows the studies on Au recovery using pyrometallurgy treatment from used PCBs.

Table 2-2 The studies of recovery Au using pyrometallurgy treatment from used PCBs.

	Year	Sample type	Results	Note	Ref.
Pyrometallurgy (Incineration Calcination, TBRC, Supercritical fluid extraction, Smelting, Roasting)	2014	E-waste	Au 97%	Roasting (750 °C) After roasting, Aqua regia leaching, solvent extraction	(Kavitha, 2014)
	2007	PCBs (Computer)	70 wt.% residue, 23 wt.% oil, and 5 wt.% gas	Pyrolysis (800 °C) The pyrolysis gases consisted of CO ₂ and CO	(Hall et al., 2007)
		PCBs (Television)	60 wt.% residue, 29 wt.% oil, and 7 wt.% gas		
		PCBs (Mobile phone)	82 wt.% residue, 15 wt.% oil, and 2 wt.% gas	Following pyrolysis, electrical components and glass fibre could be easily removed from the remains of PCBs	
	2010	WPCBs	74.7 wt.% residues, 15 wt.% oils, and 10 wt.% gases	Vacuum pyrolysis (550 °C)	(Long et al., 2010)
	2010	PCBs	70 wt.% residue, 28 wt.% oil, and 3 wt.% gas	Centrifugal separation (240 °C / 140 rpm / 6 min) + vacuum pyrolysis (600 °C / 30 min)	(Zhou et al., 2010)
	2012	PCBs	Organic brominated compounds are decomposed (more than 99.9%).	Combustion (1200 °C / 0.75 s) Combustion efficiency depends on temperature	(Ni et al., 2012)
	2010	WPCBs	Glass fiber could be obtained from the non-metal components	Calcination (600° C / 10 min) / muffle furnace	(Long et al., 2010)
	2011	WEEEs	Unknown	Top-blown rotary converters (1250 °C / 10 rpm) Rate of feed infection: 120 kg/h	(Maurell-Lopez et al., 2011)
	2010	PCBs	66 wt.% residue, 30 wt.% oil, and 4 wt.% gas	Supercritical methanol (380 °C / 30 min)	(Xiu et al., 2010)
	2005	PC PCBs	Au 99% from matte	Smelting Particle size 200 mm 950 °C	(Araki et al., 2005)
	2006	PC PCBs	Au > 90%	Smelting Particle size 250 µm	(Nishida et al.,

				1500 °C	2006)
				Smelting	(Takanori
2009	PC PCBs	-		Particle size 250 µm	et al.,
				1500 °C	2009)
				Smelting	(Shibiaya
2012	WPCBs	Au 60%		Particle size –100 µm	ma et al.,
				1000 °C	2012)

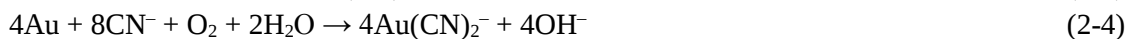
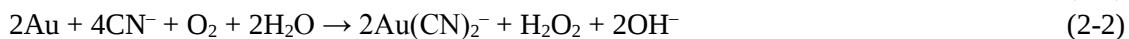
2.3.2 Hydrometallurgical treatment

Hydrometallurgical treatment is a method to extract metals from solid matters using aqueous solutions and it includes the leaching of metals as well as purification of leachate and recovery of metals from solutions (Tuncuk et al., 2012). Hydrometallurgical treatment of PCBs started in 1970s aiming Ag and Au recovery (Akcil et al., 2015). Cyanide and aqua regia leaching are conventional methods for recovering Au from used EEEs because of high efficiency. Due to environmental issues, non-cyanide leaching using thiourea and thiosulfate has been also investigated for dissolving Au from used EEEs (Akcil et al., 2015; Gurung et al., 2013; Ha et al., 2010; Havlik et al., 2014; Sheng et al., 2007; Quinet et al., 2005).

Generally, adsorption using activated carbon has been used for separation and purification of Au from leached solution as well as zinc precipitation is conventional methods, widely used for direct recovery of Au from clarified leached solution (Marsden, 1991). This part will introduce about hydrometallurgical treatment including leaching, purification and recovery process from PCBs existed in WEEEs.

2.3.2.1 Cyanide leaching

Cyanide compound like sodium cyanide is dissociate in aqueous solutions to form cyanide ions (Eq. (2-1)). In the solution containing cyanide ions, Au is oxidized by dissolved oxygen to form Au(I) cyanide complex, $\text{Au}(\text{CN})_2^-$, and hydrogen peroxide, H_2O_2 (Eq. (2-2)). Formed hydrogen peroxide also act as an oxidant to dissolve Au in Eq. (2-3). The overall reaction for Au dissolution in cyanide solutions is expressed as Eq. (2-4). Dorin and Woods reported that a maximum dissolution of Au occurs at pH 10–10.5 (Kulandaisamy et al., 2003).



Coexisting metal ions such as Cu^{2+} in the solution inhibit the recovery of Au from cyanide solutions. To remove coexisting metal ions, ion exchange or adsorption using activated carbon has been used.

Adsorption using activated carbon and cementation using Zn have been used to recover Au from cyanide solutions. Adsorption of Au from cyanide solution using activated carbon was patented by Mcquiston and Chapman (1951). Since that, carbon-in-pulp (CIP), carbon-in-leach (CIL) and carbon-in-column (CIC) methods have been developed for Au recovery in commercial operations (White et al., 1905).

Precipitation or cementation of Au occurred by a result of charge-transfer reactions (Eqs. (2-5) and (2-6)) (Syed, 2012; Yannopoulos, 1991). In case of Zn, it normally is used for cementation due to efficiency. Mg, Fe and Al can also be used for cementation, but the cementation rate is slow (Yannopoulos, 1991).



2.3.2.2 Halide leaching

Halide leaching uses chloride, bromide, and iodide ions to form water soluble complexes with Au^+ and Au^{3+} (Syed, 2009). Aqua regia, a mixture of hydrochloric acid (HCl) and nitric acid (HNO_3) at volume ratio of 3 HCl : 1 HNO_3 (Donmez et al., 2001; Park et al., 2009) (Eq. (2-7)).



With oxidant like chlorine gas, Cl_2 , Hydrochloric acid is also used to dissolve Au. The reaction is expressed as



In bromine solution, Au is oxidized by bromine and stabilized by bromide as the Au bromide complex in bromine/bromide as follow (Melashvili et al., 2014):



Au-iodine complex is most stable form in halogen complexes with Au. Stability of Au complex in halide (AuX_2) is as bellows; $\text{I}^- > \text{Br}^- > \text{Cl}^-$ (Wang et al., 2013). The reactions of Au dissolution in iodine-iodide solution are shown as Eqs. (2-10) and (2-11) (Wang et al., 2013).

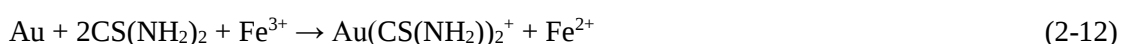


Many studies are conducted for the purification, separation and recovery of Au in halide leaching of W EEEs. In ion-exchange, a weak-base cation exchanger can be used to separate Au

from chloride solutions and bromide solutions (Marsden, 1992). Sodium borohydride is used to precipitate Au from chloride leach solution (Marsden, 1992). The electrolytic recovery of Au from chloride solutions are applied commercially for Au refining (Lekka et al., 2015; Marsden, 1992). The ability of activated carbon to adsorb Au complexes is high (Marsden, 1992; White et al., 1905).

2.3.2.3. Thiourea leaching

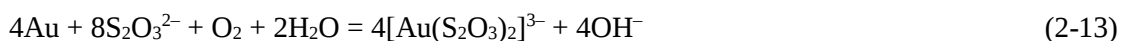
Au is dissolved in acidic thiourea solutions containing ferric ions as oxidant (Hilson et al., 2006; Pyper et al., 1981). The reaction is expressed as:



Thiourea leaching should be done under acidic conditions (pH 1–2), since it is unstable under alkaline conditions. Strong cation-exchange resins are effective in extracting the Au(I)-thiourea complex. Higher Au recovery is obtained with cationic resins than with activated carbon (Yannopoulos, 1991). Al metal has been used to recover Au from thiourea leached solution (with 99.5% efficiency) (Marsden, 1992). Iron powder was also considered as a precipitant of Au from thiourea solutions. However, loading efficiency is low (Yannopoulos, 1991).

2.3.2.4 Thiosulfate leaching

The pH of the thiosulfate leaching process is generally maintained between 9 and 10. The mechanism of the ammonium thiosulfate leaching, ammonia-thiosulfate-Cu system, is complex and both ammonia and thiosulfate are needed as ligands. In alkaline solution of thiosulfate, Au is oxidized by dissolved oxygen to form Au thiosulfate complex, as follows;

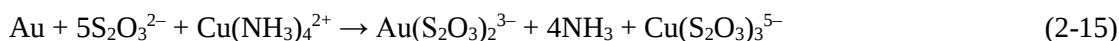


Once formed, the thiosulfate complex, $\text{Au}(\text{S}_2\text{O}_3)^-$ and $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$ is stable (Aylmore et al., 2001). When ammonia is absent, Au is passivated by the sulfur coatings formed as a result of decomposition of thiosulfate on the Au surface (Chen et al., 1996; Jiang et al., 1993). Ammonia inhibits Au passivation by being preferentially absorbed on Au surfaces over thiosulfate thus bringing Au into solution as an ammine complex (Chen et al., 1996; Jiang et al., 1993). The ammine complex is varying to thiosulfate complex by Eq. (2-14).

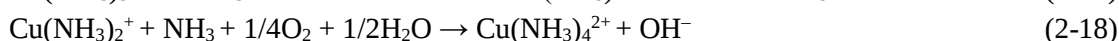


Cu(II) catalyzes Au dissolution in ammonia-thiosulfate solutions (Aylmore et al., 2001; Tyurin et al., 1960): Presence of Cu ions in solution can be speed up the rate of Au dissolution by 18 to 20 times comparing to absence of Cu ions. In the presence of ammonia, Cu^{2+} is stabilized as

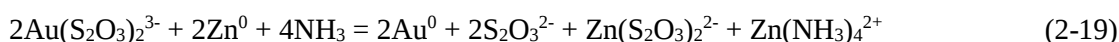
ammonia complex like $\text{Cu}(\text{NH}_3)_4^{2+}$ and this complex acts as an oxidant for Au dissolution as follow:



Oxygen convert Cu(I) to Cu(II) for further Au leaching (Byerley et al., 1973) (Eqs. (17) and (18)).



Ion exchange, adsorption activated carbon, precipitation and electrowinning can be used to recover Au from thiosulfate solution (Eq. (2-19)). The reaction of Au recovery by Zn cementation in ammonium thiosulfate solution can be represented in the following reactions (White et al., 1905):



Au in Cu-ammonia thiosulfate solutions can also be precipitated by the addition of metallic Cu, Zn, Fe, Al (Jiexue et al., 1983; Panayoto et al., 1994; Perez et al., 1987). At thiosulfate, however, because of the oxidation and reduction reactions of $\text{S}_2\text{O}_3^{2-}$ which occur at the anode and cathode, electrowinning is difficult to apply for recovery of Au (White et al., 1905).

Table 2-3 is the list of researches of different leaching methods for Au extraction from used PCBs and table 2-4 shows the studies of recovery Au after leaching from used PCBs. Table 2-5 and 2-6 summarize the advantage and disadvantage of leaching and recovery methods described above.

Table 2-3 The studies of leaching Au from used PCBs.

Method	Sample type	Results	Comment	Ref.
Cyanide	Mobile phone PCBs	Au > 90%	After oxidative sulfuric and oxidative chloride leaching / 25 °C	(Quinet et al., 2005)
	PCBs	Au 48%	Hammer mill / Column leaching / particle size 3.33 to 0.43 mm / 15 days	(Montero et al., 2012)
	Mobile phone PCBs	Au 70%	2 h	(Petter et al., 2014)
Halide	PCBs	Highest Extraction.	After pyrolysis Aqua regia	(Madenoglu, 2005)
	PC PCBs	Rapid dissolution	Aqua regia / 90 °C	(Sheng et al., 2007)
	PCBs	Au 97%	Aqua regia pulp density 1 g/20 ml / 3 h	(Park et al., 2009)

Thiourea	Scrap integrated circuits	Au 100%	Aqua regia / 1 h / 27 °C / Pulp density 0.01 g/200 ml	(Lee et al., 2010)
	Waste PCBs	Au 95%	Iodine (1~1.2% iodine con., 1~2% H ₂ O ₂ Con., Solid: Liquid = 1:10) / 25 °C / 4 h	(Xu et al., 2010)
	Waste PCBs	Au 95%	Sodium hypochlorite (NaClO 6 M, NaOH 8 M, Solid: Liquid=1:6) / 40 min	(Li et al., 2011)
	Mobile phone PCBs		Did not give a sufficiency high yield	(Quinet et al., 2005)
	Scrap integrated circuits	Au 99%	After pretreatment (Roasting, magnetic separation) Under 50 mesh / 70 g/L thiourea / 13 g/L ferric sulfate pulp density 1% / 150 rpm / 20 °C / 7 h	(Lee et al., 2010)
	Waste mobile phone	Au 90%	100 mesh / 24 g/L thiourea / 0.6% Fe ³⁺ / 25 °C / 2 h	(Li et al., 2012)
	Waste PCBs	Au 90%	53-75 µm/ 0.5 M thiourea / 0.05 M of sulfuric acid / 45 °C / 6 h	(Gurung et al., 2013)
	PCBs	Au 90%	20 g/L of thiourea / 6 g/L of ferric ion / 0.1 M of sulfuric acid / 25 °C / 1 h	(Birloaga et al., 2016)
	PCBs	Au > 95%	After magnetic separation /Ammonium thiosulfate (20 mM copper / 0.2 M thiosulfate / 0.4 M ammonia) Pulp density 5 g/L / 48 h / 40 °C	(Oh et al., 2003)
	Scrap sample	Au 98%	Ammonium thiosulfate (20 mM copper / 0.12 M thiosulfate / 0.2 M ammonia) / 2 h/ 25 °C	(Ha et al., 2010)
Thiosulfate	Waste mobile phones	Au 90%	Ammonium thiosulfate (20 mM copper / 0.12 M thiosulfate / 0.2 M ammonia) / 10 h / 25 °C	(Ha et al., 2010)
	Waste material	Au 98%	Ammonium thiosulfate / 48 h	(Ficeriov'a et al., 2011)
	Mobile phones PCBs	Au 58%	Ammonium thiosulfate (40 mM copper. 0.1 M ammonium thiosulfate) / 25 °C / 8 h	(Tripathi et al., 2012)
	Mobile phone PCBs	Au 70%	After cutting mill /Ammonium thiosulfate (20 mM copper / 0.2 M thiosulfate) / 20 °C / 2 h	(Camelino et al., 2015)

Table 2-4 The studies of recovery Au from used PCB.

Method	Results	Comment	Ref.
Solvent extraction	Au 97%	Waste PCBs / Aqua regia leaching / Toluene	(Park et al., 2009)
	Unknown	Wasted electronic parts / KI/I ₂ and NaCl/hypochlorite leaching /	(Camelino et al., 2015)
Ion exchange	Au 95%	Mobile phone PCBs scraps / Chlorine leaching	(Kim et al., 2011)

Adsorption	/ Amberlite XAD-7HP resin (46.03 mg/g) /	
	Au 98%	PCBs / Aqua regia leaching / Amberlite IRC 718 (Park et al., 2000)
	Unknown	PCBs / Hydrofluoric acid, nitric acid / Dowex 1X8 (Werner et al., 1981)
	Au 99%	WEEEs / Hydrochloric acid solution / 5 g/L Carbon nanotube / 48 h (Peng et al., 2014)
	Au 99%	PCBs / $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ solution / Paper cellulose (Adsorption gel from filter paper by treating sulfuric acid) / 24 h (Pangenit et al., 2012)
	Au 99%	Waste PCBs / HCl-thiourea solution / Banana peel carbon / 30 min / pH 2.5 (Pangenit et al., 2012)
	Au > 99%	Waste LED / Aqua regia 80 °C / Column adsorption / 25 °C / 24 h (Murakami et al., 2015)
	Au > 99%	Waste PCBs / thiourea leaching / Sodium borohydrate (SBH(NaBH_4)) / 15 min (Behnamfard et al., 2013)
Precipitation	Unknown	Waste Computer PCBs / Aqua regia leaching / potassium metabisulfite ($\text{K}_2\text{S}_2\text{O}_4$) (Sinioros et al., 2015)
	Au > 99%	Waste LED / Aqua regia 80 °C / Sodium borohydrate (SBH(NaBH_4)) (Murakami et al., 2015)
	Au 96%	Scrap of PCBs / chlorine:hypochlorite of 2:1 / sodium metabisulfite (You et al., 2014)
	Au 99%	Mobile phone PCBs / Ammonium thiosulfate leaching (Kasper et al., 2015)
Electrowinning	Low efficiency	PCBs / aqua regia leaching (Lekka et al., 2015)

Table 2-7 Summarize of advantage and disadvantage of each leaching reagent

Method	Advantage	Disadvantage
Cyanide	High efficiency, Low cost	High toxicity
Halide	High efficiency, High rate, High chemical stability	High cost, High corrosive condition Low developmental stage
Thiourea	High selective at precious metal, High rate	High cost, High consumption Potential carcinogen, Low chemical stability
Thiosulfate	Low toxicity High chemical stability	Low rate (Slow), High consumption

Table 2-6 Summarize of advantage and disadvantage of recovery methods.

Method	Advantage	Disadvantage
Solvent extraction	High rate (faster than adsorption and ion exchange) High loading	Slow stripping (2-4 h) Need the pretreatment (Solid/Liquid separation) Solvent remains at aqueous phase
Ion-exchange	High rate and efficiency Lower temperature and pressure	Less selectivity Small particle size High cost

Adsorption	No pretreatment of pregnant liquor High efficiency	Carbon can easily influence by calcium and magnesium salts. High cost (more expensive than precipitation) Au loss at fine carbon
Precipitation	Low cost High efficiency	Need additional process to recovery pure Au
Electrowinning	No need to add new chemicals or metals Selective for Au Relatively higher purity	Low rate

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CHAPTER 3

AMMONIUM THIOSULFATE LEACHING OF GOLD FOR OPTIMIZING THE LEACHING CONDITION

3.1 Introduction

Printed circuit boards (PCBs) are essential parts of many modern electric and electronic equipment and they contain significant amounts of gold (Au), and its contents of PCBs are more than 10 times higher than those of natural Cu ores. One method to recover Au from waste PCBs is to use pyrometallurgical Cu smelting facilities, where PCBs are treated together with Cu concentrates and Au is recovered from the anode slime of the electro-refining process. This is an efficient method to recover Au from waste PCBs but is not possible where there are no Cu smelting facilities. Large scale facilities are required in the pyrometallurgical Cu smelting process, and it is difficult to justify their construction for waste PCB treatment alone. Without smelting facilities, hydrometallurgical processes are potentially more attractive for Au recovery from waste PCBs because they require only small-scale plants and the operation is simple. The most common hydrometallurgical process for Au recovery is cyanide leaching, however, an alternative technique is required because cyanide is toxic. The leaching experiment was conducted to determine the maximum Au extraction under the conducted conditions in this section using end-of-life laptop PCBs. This part investigates Au leaching from PCBs of end-of-life laptops using thiosulfate ammonium and Au recovering from pregnant solutions.

3.2 Materials and methods

3.2.1 Printed circuit boards of waste mobile phones

Printed circuit boards (PCBs) obtained from end-of-life laptops were crushed by a cutting mill (VH16, Seishin Enterprise Co., Ltd., Japan), freeze crusher (TPH-02, As One, Japan), and disk mill (RS 100, Retsch Co., Ltd., Germany) to obtain particles with D_{50} and D_{80} of 85 and 224 μm , respectively. The elemental composition of the crushed product determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) (ICPE-9820, Shimadzu Corporation, Japan) after microwave digestion in aqua regia is shown in Table 3-1.

Table 3-1. 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

3.2.2 Leaching experiments

Deionized water 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 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) were used to prepare the solutions. Leaching experiments were carried out in 50ml

Erlenmeyer flasks containing 0.1 g of crushed PCBs and 10 ml of ammonium thiosulfate solution. The flasks were shaken in a thermostat water bath (shaking rate = 120 rpm, amplitude = 40 mm, temperature = 25 °C). After the predetermined shaking duration, the suspension was filtered through 0.22 μm membrane filters (Sartorius AG, Germany) and the metal ion concentration was measured by ICP-AES. The effects of leaching time, cupric ion concentration, sodium thiosulfate concentration, total ammonia concentration, and different gas environments on the metal extraction from the crushed PCBs were investigated. Standard leaching was for 24 h, with 1 mM CuSO_4 , 1 M $\text{Na}_2\text{S}_2\text{O}_3$, 0.5 M NH_4OH , 0.25 M $(\text{NH}_4)_2\text{SO}_4$, and air as the gas phase. Au was recovered from pregnant solutions by Cu cementation. The cementation experiments were carried out in 50 ml Erlenmeyer flasks containing about 1g of Cu boards (1 cm $\times$ 1 cm $\times$ 0.4 mm) and 10 ml of pregnant solution. The flasks were shaken in a thermostat water bath (shaking rate 120 min⁻¹, amplitude 40 mm, temperature 25 °C). After the shaking, the suspension was filtered through a 0.22 μm membrane filter and the metal ion concentrations were measured by ICP-AES.

3.3 Results and discussion

3.3.1 Effects of leaching time

Fig. 3-1 shows the changes in the metal extraction with time. The extraction of Fe and Al, which do not form complexes with thiosulfate and ammonia, were less than 20 % and the results are not shown here. The maximum extraction of Au, Ag, Pb, Ni, Cu, and Zn were obtained between 12 and 24 h, so the reaction time was fixed at 24 h in succeeding experiments.

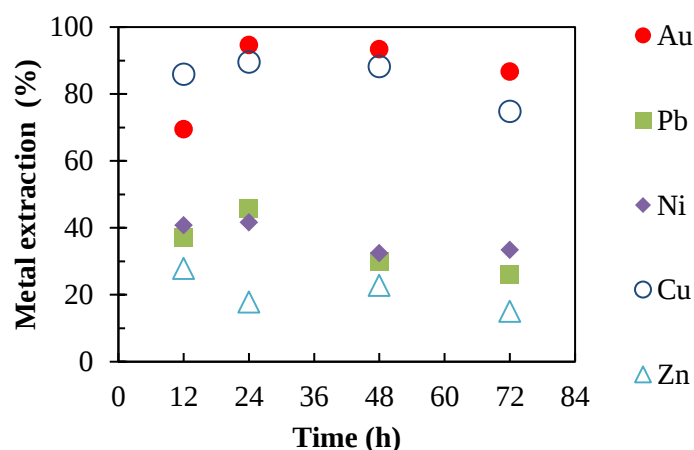


Fig. 3-1. Changes in metal extraction with leaching time.

3.3.2 Effects of CuSO_4 concentration

Fig. 3-2 shows the effect of the CuSO_4 concentration on the metal extraction from crushed PCBs. Metal extraction increased with increasing CuSO_4 concentration. As shown in Eq. 3-1, cupric ions interact with ammonia to form cupric-ammonia complexes, which are able to solubilize elemental metals via oxidative dissolution (Eq. 3-2).

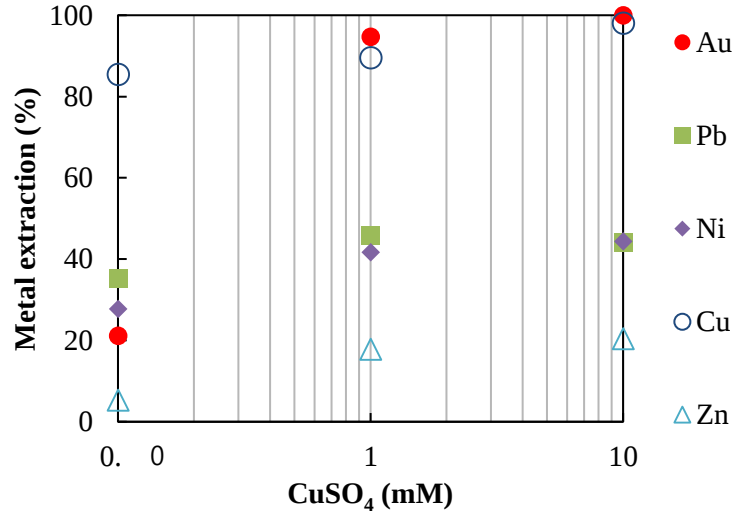
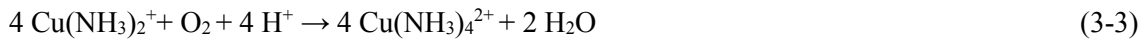


Fig. 3-2. The effect of CuSO₄ concentration on metal extraction from the crushed PCBs.

3.3.3 Effects of oxygen

Fig. 3-3 shows the effect of O₂ on the metal extraction from crushed PCBs. Higher metal extraction was obtained in air than in pure N₂, which could be attributed to the presence of O₂. From Eq.2, Cu(NH₃)₄²⁺ is consumed and reduced to Cu(NH₃)₂⁺ during the reaction and can only be regenerated in the presence of an oxidant like oxygen in the air. The regeneration of Cu(NH₃)₄²⁺ by O₂ can be explained as follows:



Once regenerated, Cu(NH₃)₄²⁺ could again act as oxidant for further metal extraction (Eq.3-2). These results indicate that oxygen is essential in the continuous oxidative leaching of metals like Au.

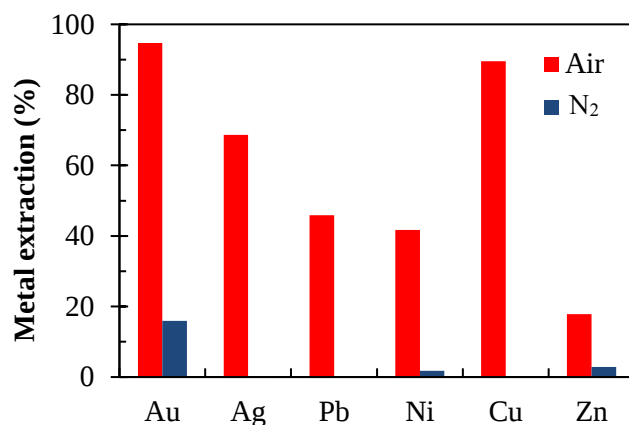


Fig. 3-3. Metal extraction with and without dissolved oxygen in the leaching solution.

3.3.4 Effects of Na₂S₂O₃ concentration

Fig. 3-4 shows the effect of the Na₂S₂O₃ concentration on metal extraction from the crushed PCBs. When the Na₂S₂O₃ concentration was below 1 M, Cu and Zn extraction were unaffected by the Na₂S₂O₃ concentration and the Au, Ag, Pb, and Ni extraction increased with increasing Na₂S₂O₃ concentration. This suggests that Au, Ag, Pb, and Ni are dissolved as thiosulphate-metal complexes. The extraction of all metals with 3 M Na₂S₂O₃ was lower than that with 1 M Na₂S₂O₃. This may be due to the reduction of Cu(NH₃)₄²⁺ with the large amounts of Na₂S₂O₃, resulting in decreases in Cu(NH₃)₄²⁺ which acts as an oxidant for the metal dissolution.

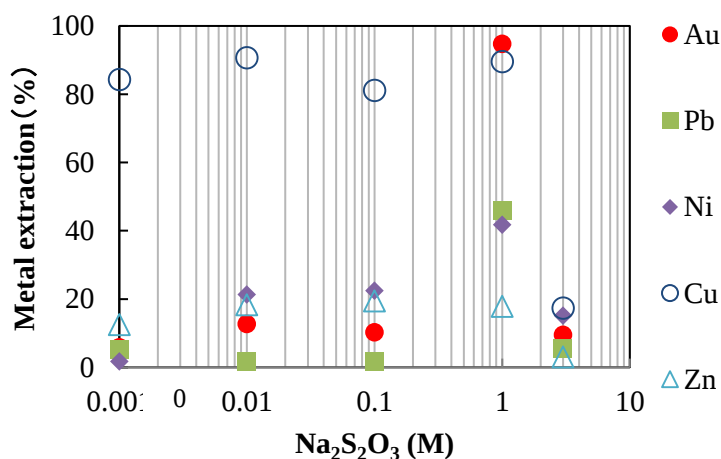


Fig. 3-4. The effect of Na₂S₂O₃ concentration on metal extraction from the crushed PCBs.

3.3.5 Effects of total ammonia concentration

Fig. 3-5 shows the effect of the total ammonia concentration on the metal extraction from the crushed PCBs. In this series of experiments, the molar ratio of NH₄OH and (NH₄)₂SO₄ was kept

at 2:1 and the total ammonia concentration (the sum of the concentrations of ammonia species (NH_3 and NH_4^+)) was varied. Metal ions like Cu, Zn, and Ni have a strong affinity to ammonia and they form soluble metal ammonia complexes. Because of this, the highest extraction of these metals was obtained at the highest concentration of ammonia (1 M). The ability of Au, Ag, and Pb to form metal complexes with NH_3 is very low, and it may be expected that the extraction of these metals is not affected by the total ammonia concentration. The results, however, show that the extraction of Au, Ag, and Pb was significantly affected by the total ammonia concentration and that the maximum extraction was obtained with the highest concentration of ammonia. Possible reasons for this are (a) decreases in oxidant ($\text{Cu}(\text{NH}_3)_4^{2+}$) available for metal dissolution due to the lack of ammonia, (b) a part of the Au, Ag, and Pb is present as alloys with Cu and Zn, (c) reductive deposition of Au and Ag ions on Cu and Zn.

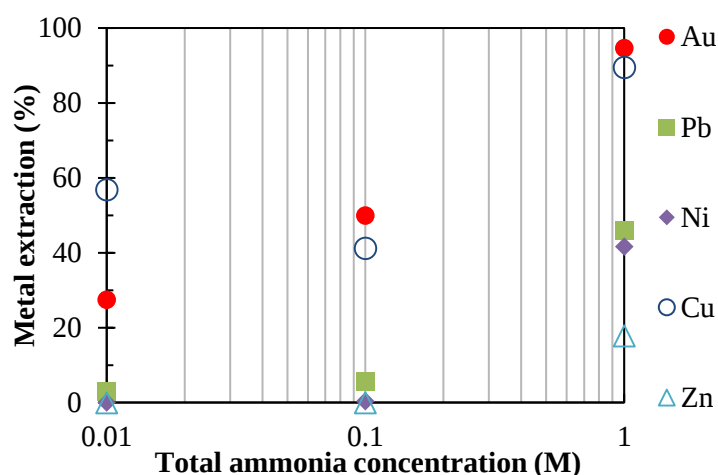


Fig. 3-5. The effect of total ammonia concentration on metal extraction from crushed PCBs.

The obtained results show that the leaching of metals from PCBs by ammonium thiosulfate is possible and that more than 98% of Au and Cu can be leached under suitable conditions. The maximum amount of Au extracted was 99% 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 and a treatment time of 24 h.

3.4 Summary

Ammonium thiosulfate leaching of metals from waste mobile phone PCBs was carried out under the various parameters (i.e., leaching time, CuSO_4 , $\text{Na}_2\text{S}_2\text{O}_3$, and total ammonia concentration, and with/without oxygen). The maximum extraction was obtained at 24 h. Metal extraction increased with increasing CuSO_4 concentration, and maximum extraction was obtained in 10 mM of CuSO_4 concentration. Higher metal extraction was obtained in air than in pure N_2 . Metal extraction increased with increasing $\text{Na}_2\text{S}_2\text{O}_3$ concentration, but extraction of 3 M $\text{Na}_2\text{S}_2\text{O}_3$ was lower than that with 1 M $\text{Na}_2\text{S}_2\text{O}_3$.

CHAPTER 4

IDENTIFICATION OF INTERFERENCE METALS ON AMMONIUM THIOSULFATE LEACHING OF GOLD FROM WASTE MOBILE PHONES

4.1 Introduction

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; Senanayake, 2004; Tripathi et al., 2012). Using PCBs of waste mobile phones, for example, Tripathi and coworkers (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 and coworkers (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 section PCBs of the waste mobile phone 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.

4.2 Materials and methods

4.2.1 Materials

4.2.1.1 Printed circuit boards of waste mobile phones

Waste mobile phones were obtained from a 2nd hand shop in Japan. The PCBs were manually collected by hand-dismantling and then crushed by a cutting mill (TPH-02, As One, Japan) in

liquid nitrogen to obtain a particle size fraction of less than 5 μm . The crushed sample was further ground with a disk mill (RS 100, Retsch Co., Ltd., Germany), and sieved to obtain a $-106\ \mu\text{m}$ 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 (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 M Ω ·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 = $\pm 2\%$). As shown in Table 4-1, 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.

Table 4-1. The composition of waste mobile phone PCBs.

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

4.2.1.2 Metal powders

For the cementation experiments, pure Cu, Al, Fe, Zn, Pb, and Ni powders ($-75\ \mu\text{m}$, 99.9%, Wako Pure Chemical Industries, Ltd., Japan) were used as reductants of Au.

4.2.2 Experimental methods

4.2.2.1 Leaching experiments

Ammonium thiosulfate solutions with pH of around 9.5-10 containing 1 molar (M) $\text{Na}_2\text{S}_2\text{O}_3$, 0.5 M NH_3 , 0.25 M $(\text{NH}_4)_2\text{SO}_4$ 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 in CHAPTER 3). The experiments were carried out by mixing known amounts of PCBs ($-106\ \mu\text{m}$) 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, solid residues were thoroughly washed with DI water, dried in a vacuum oven at 40 °C for 24 h, and analyzed by SEM-EDX (SSX-550, Shimadzu Corporation, Japan).

4.2.2.2 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 where Al powder was washed to remove the Al-oxide layer using the method of Seng et al. (2017). The washing method involves mixing the Al powder with a solution containing 2 M sodium chloride and 0.1 M hydrochloric acid at 400 rpm for 15 min, thorough rinsing of the washed Al powder with DI water, and drying in a vacuum oven at $40\text{ }^{\circ}\text{C}$ for 24 h. The rest of the metal powders was 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 $25\text{ }^{\circ}\text{C}$ 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 before/after washing) and 10 ml of Au-ammonia thiosulfate solution were mixed in 50-ml Erlenmeyer flask at $25\text{ }^{\circ}\text{C}$ (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 a $0.2\text{ }\mu\text{m}$ syringe-driven membrane filters. The residues were washed thoroughly with DI water, dried in a vacuum oven, and analyzed by SEM-EDX and X-ray powder diffraction (XRD, MultiFlex, Rigaku Corporation, Japan) while the filtrates were analyzed by ICP-AES.

4.2.2.3 Electrochemical experiments

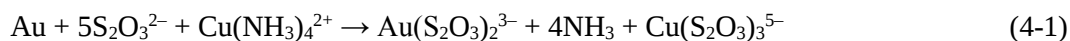
Chronoamperometry, an electrochemical technique that measures the electrons generated by redox reactions with time (Park et al., 2018), was carried out to understand the mechanism(s) involved in Au ion cementation in the presence of Al and/or Cu. These experiments were conducted using a computer-controlled electrochemical measurement unit (SI 1280B, Solatron Instruments, UK), and a conventional three-electrode system composed of Al as the working electrode, Ag/AgCl in saturated KCl solution as the reference electrode, and a platinum plate as the counter electrode. Before each measurement, the working electrode was exposed using Si-carbide papers (#240, #600, #1000 and #1500) and polished with alumina (Al_2O_3) pastes (5 and $1\text{ }\mu\text{m}$) on a smooth glass plate (Tabelin et al., 2017; Park et al., 2018). The electrode was then sonicated in DI water for 5 min to remove residual alumina particles and then washed thoroughly with DI water. Prior to the measurements, the electrolyte solution containing Au ions (0.1 M Na_2SO_4 containing 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$, 0.05 M NH_3 , 0.025 M $(\text{NH}_4)_2\text{SO}_4$, and 10 mg/l of Au ions) was poured into a jacketed glass cell and its temperature was equilibrated to $25\text{ }^{\circ}\text{C}$ by a water recirculation system. To minimize the interference from dissolved oxygen (DO), it was removed by purging the electrolyte solution with ultra-pure nitrogen gas (99.999%) for 45 min. For the

chronoamperometry measurements to investigate Au ion cementation, the working electrode was allowed to equilibrate at the open circuit potential (OCP) and then polarized at -1.5 V vs. Ag/AgCl for 1 h (This value was selected based on our preliminary experiments). Gold concentration before and after the electrochemical experiments were quantified by ICP-AES while the Al electrode and residual Cu powder were examined by SEM-EDX.

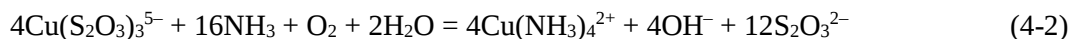
4.3 Results and discussion

4.3.1 Leaching of gold from PCBs of waste mobile phones in ammonium thiosulfate solution

The dissolution of Au in ammonium thiosulfate solution is described as follows (Chu et al., 2003; Ha et al., 2014):



Ammonia/ammonium alkaline buffer maintains the solution pH between 9 and 10 to prevent the decomposition of thiosulfate ions. In this medium, Au is oxidized by $\text{Cu}(\text{NH}_3)_4^{2+}$ and extracted as Au-thiosulfate complex, $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$. The thiosulfate complex of Cu(I), $\text{Cu}(\text{S}_2\text{O}_3)_3^{5-}$, generated in Eq. (4-1) is then oxidized by DO, which regenerates Cu(II) ammonia complex, $\text{Cu}(\text{NH}_3)_4^{2+}$, as follows:



Cu(II) ammonia complex is a strong oxidant that catalyzes the dissolution rate of Au by about 18-fold (Aylmore and Muir, 2001). Fig. 4-1(a) shows the effects of leaching time on metal extraction from PCBs of waste mobile phones at S/L of 0.1 g/10 ml. Metal extraction increased with time and reached apparent equilibrium after ca. 24 h. The effects of S/L on Au extraction from PCBs are illustrated in Fig. 4-1(b), and the results showed that Au extraction decreased with increasing S/L; that is, Au extraction was as high as 66% at the lowest S/L (0.1 g/10 ml) but plummeted to only 1.7% at the highest S/L (1 g/10 ml). Similar to Au, extraction of other metal ions (i.e., Cu, Pb, Zn, Ni, Al, and Fe) also decreased with increasing S/L.

One reason for the low extraction of Au is the possible lack of chemical reagents at high S/L. Although the chemistry of Au leaching in ammonium thiosulfate medium is complicated because of the coexistence of two complexing ligands (ammonia and thiosulfate), the Cu(II)/Cu(I) redox couple, and possible oxidative decomposition of thiosulfate to tetrathionate and other sulfur compounds (Aylmore and Muir, 2001), the stoichiometry of this process is well-established, so Au in 1 g of PCBs and the reagents required to dissolve this amount were calculated using Eqs. (4-1) and (4-2). Equation (4-1) suggests that 5 moles of $\text{S}_2\text{O}_3^{2-}$ is required to dissolve 1 mole of Au. The solution used in the leaching experiments contains 1 mole of $\text{S}_2\text{O}_3^{2-}$, which could

theoretically extract 0.4 g of Au in 10 ml of solution. The amounts of extracted Au were 0.002 mg at S/L of 0.1 g/10 ml and 0.02 mg at S/L of 1 g/10 ml, which were both much lower than that calculated values from stoichiometric considerations. This indicates that the lack of $\text{S}_2\text{O}_3^{2-}$ was not the main cause of low Au extraction efficiency at high S/L. Another possible reason for the low Au extraction is the lack of NH_3 in solution (Eq. (4-2)). NH_3 is required to convert Cu(I) to Cu(II) complex, which is an important catalyst during Au dissolution. As shown in Eqs. (4-1) and (4-2), about 0.0002 M of Cu(I) is generated when all of Au is extracted from 1 g of PCBs, and if all of this Cu(I) complex is converted to Cu(II) complex, 0.0032 M of NH_3 is consumed. In our experiments, 0.5 M of NH_3 was used, which was more than enough not only to extract all of the coexisting base metals found in the sample but also to form the catalyst necessary to dissolve Au. This means that the reagents used in our experiments were more than enough to extract Au in PCBs and was not the primary reason for the observed low extraction efficiency at high S/L.

Another possible reason for the low Au extraction at high S/L is the re-deposition of extracted Au ions onto coexisting base metals in the sample via cementation. Figs. 4-1(c) and (d) show SEM photomicrographs of the sample before and after the leaching experiments, respectively. Compared with Au on PCBs prior to leaching (Fig. 4-1(c)), the morphologies of Au in the leaching residue were quite different (Fig. 4-1(d)). Elemental maps of a representative particle illustrate that Au was present together with Cu and Al (Fig. 4-1(e)–(g)) and imply that extracted Au ions were likely re-deposited onto these metals during the leaching experiments. To verify this deduction and identify which base metals were responsible for the re-deposition of extracted Au ions, the coexistence of Au with different base metals in the leaching residue was semi-quantitatively analyzed by SEM-EDX. An example of how this analysis was done is illustrated in Fig. 4-2(a). First, relatively large particles are randomly selected for the analysis, and their compositions were individually analyzed by SEM-EDX. For the photomicrograph shown in the Fig. 4-2(a), for instance, Au was detected in seven particles (particles 1, 3, 5, 8, 9, 11, and 12), which will be denoted as “Au-containing particles”. Among the seven Au-containing particles, Cu was detected in six of them (particles 1, 3, 5, 9, 11, and 12), so the detection probability (termed as “Au appearance ratio”) of Cu in Au-containing particles was roughly 0.86 (6/7). Using this procedure, the Au appearance ratio in Au-containing particles could be determined for the other coexisting metals as 0.86 (6/7) for Al, and 0.29 (2/7) for Fe. Fig. 4-2(b) shows the Au appearance ratio in Au-containing particles composed of the different base metals in the leaching residues and determined by randomly analyzing 100 Au-containing particles. Detection probabilities were high (0.98) for both Cu and Al but very low (less than 0.04) for Fe, Pb, Zn, and Ni, indicating that Au was preferentially re-deposited on Cu and/or Al particles in crushed PCBs during the leaching experiments. To evaluate this phenomenon in more detail, Au cementation experiments using Cu and Al powders were conducted and the results are discussed in the next section.

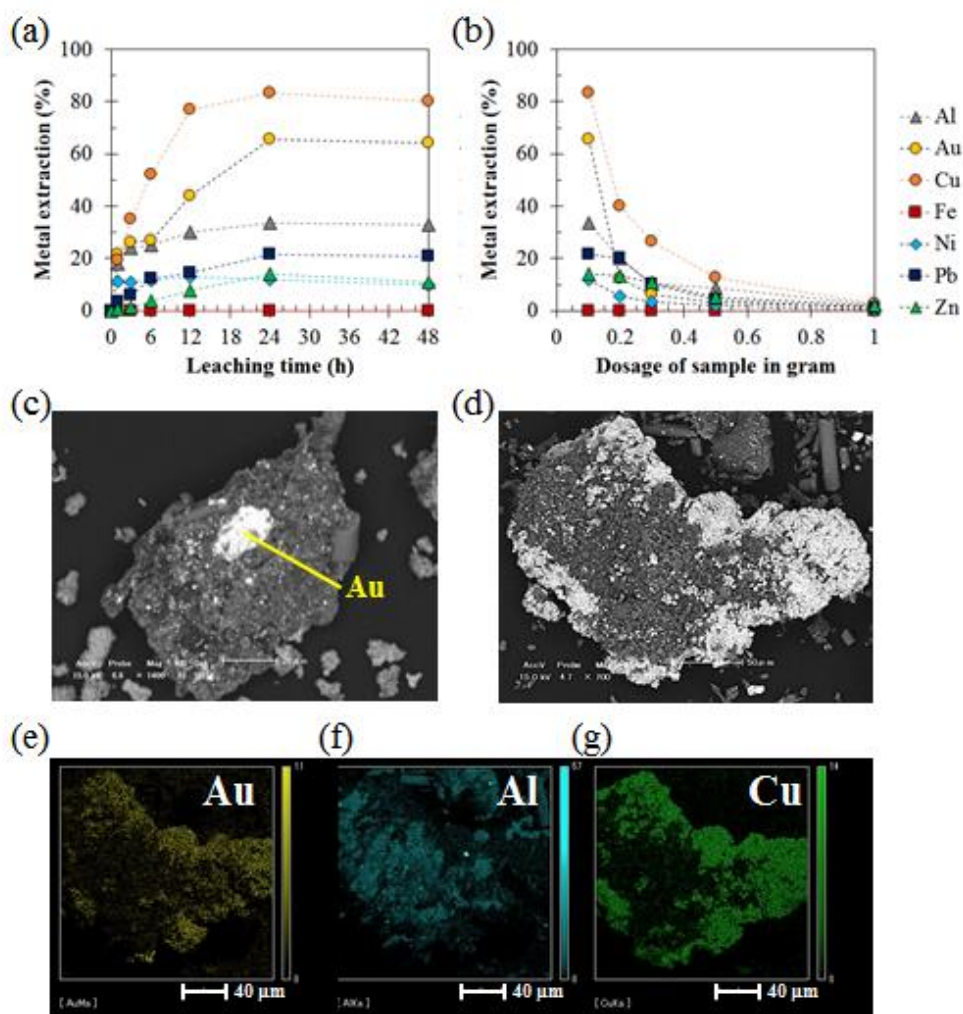


Fig. 4-1. Effects of (a) time and (b) solid-to-liquid ratio (S/L) on the leaching of metals from waste mobile phones PCBs in ammonium thiosulfate solution, and SEM photomicrograph of a representative PCB particle (c) before leaching, (d) after leaching with the corresponding elemental maps of (e) Au, (f) Al, and (g) Cu.

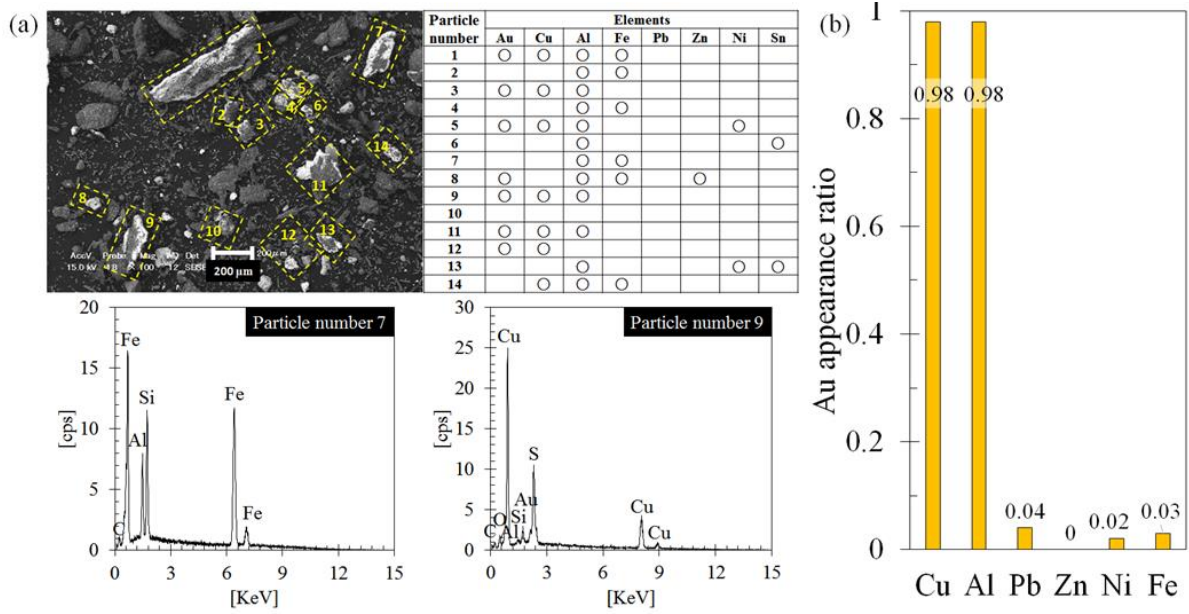


Fig. 4-2. (a) SEM photomicrograph with EDX results of particles as well as (b) Au appearance ratio of each base metals (i.e., Cu, Al, Pb, Zn, Ni, and Fe) (Note: “Circle” in the table means that the metal was detected).

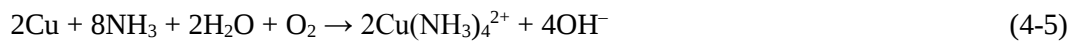
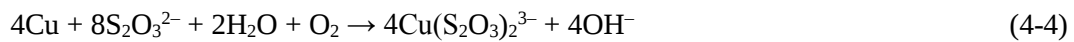
4.3.2 Gold cementation experiments using copper and aluminum powders

4.3.2.1 Effects of copper on gold ion cementation

The effects of Cu on Au ion cementation in ammonium thiosulfate solution were investigated by mixing various amounts of Cu powder and solutions containing 100 mg/l of Au ions. Figure 4-3(a) shows the relationship between Cu powder dosage and Au cementation ratio (R_{Au}) as well as Cu extraction. R_{Au} is defined as:

$$R_{Au} = \frac{[Au]_I - [Au]_F}{[Au]_I} \quad (4-3)$$

where $[Au]_I$ and $[Au]_F$ are the initial and final concentrations of Au ions, respectively. As shown in Fig. 4-3(a), the leaching behaviors of Au and Cu could be divided into three regions depending on the Cu dosage. When the Cu dosage was less than 0.1 g/10 ml (Region I), R_{Au} was zero while most of the Cu powder added was dissolved, indicating that cementation of Au ions did not occur in this region because of Cu dissolution in ammonium thiosulfate solution according to Eqs. (4-4) and (4-5).



In Region II, the concentration of dissolved Cu decreased with increasing Cu powder dosage, but the R_{Au} remained zero. To explain this apparent contradiction, the residue obtained at a Cu powder dosage of 0.5 g/10 ml was analyzed by SEM-EDX, and the results showed that oxygen and sulfur were present together with Cu (Fig. 4-3(b-1)). XRD analysis of this residue (Fig. 4-3(b-2)) revealed that it is mainly composed of $((Cu(NH_3)_4)(Cu(S_2O_3)_2)_2)$ and $Cu_4(SO_4)(OH)_6 \cdot H_2O$ rather than elemental Cu. These results indicate that the bulk of Cu powder added in the solution was most likely completely dissolved and the extracted Cu ions were then precipitated, so the concentration of Cu ions was low but Au ion cementation was negligible.

In Region III (Cu powder dosage > 0.5 g /10 ml), R_{Au} started to increase, reaching a value of 1 at a Cu dosage of 1g/10 ml. SEM-EDX results show that Au was present on the surface of metallic Cu particles (Fig. 4-3(c-1)), indicating that Au re-deposition could occur on Cu as explained in Eq. (4-6) (Arima et al., 2002).



These results also suggest that a large amount of metallic Cu (> 0.5 g/10 ml) is required for the recovery of Au ions in ammonium thiosulfate solutions via cementation. Although conditions of the cementation experiments of Arima et al. (2002) were different, these authors also reported that a large amount of Cu powder was required to recover Au ions in ammonium thiosulfate system via cementation compared with other base metals because of its dissolution and precipitation.

In the leaching experiments using PCBs of waste mobile phones, the maximum S/L was 1 g/10 ml and because the sample contains about 37% of Cu, this translates to an S/L of 0.37 g Cu/10 ml. This means that Cu in PCBs was lower than the S/L of 0.5 g/10 ml needed for Au re-deposition, so the presence of Cu alone in PCBs was insufficient to explain the extensive Au re-deposition observed during the leaching experiments.

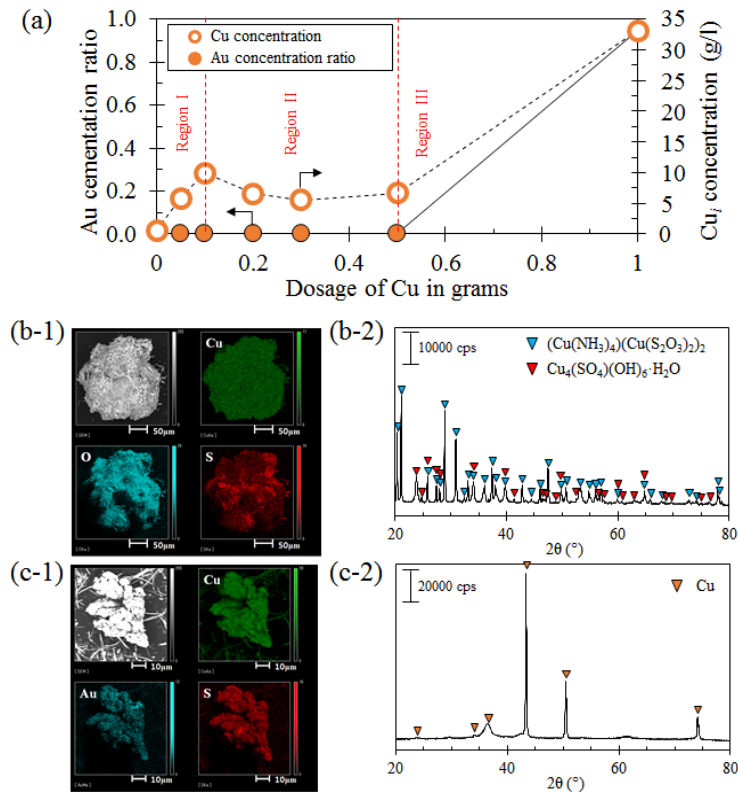


Fig. 4-3. (a) Cementation experiments of Au ions with varying dosage of Cu, (b-1) SEM image with corresponding elemental mapping images as well as (b-2) XRD pattern of the leaching residue at 0.5g/10ml, and (c-1) SEM image with corresponding elemental mapping images as well as (c-2) XRD pattern of leaching residue at 1g/10ml.

4.3.2.2 Effects of aluminum on gold ion cementation

The effects of Al on Au ion cementation in ammonium thiosulfate solution were investigated by mixing various dosages of Al powder in 10 ml solutions containing 100 mg/l of Au ions. The results illustrated in Fig. 4-4(a), however, showed that R_{Au} was negligible when Al dosage was less than 0.2 g /10 ml (Region I). Moreover, R_{Au} only slightly increased to 0.2 even after adding 1 g of Al in 10 ml solution. SEM-EDX observations of Al powders after the cementation experiments showed that Au ion cementation on Al was localized around areas resembling scratches, which were probably formed by particle-particle collisions during the experiments (Fig. 4-4(b)). These observations are consistent with previous studies on Au cementation in ammonium thiosulfate solution using Al powder. The low recovery of Au ions has also been attributed by other authors to the rapid formation of an insulating Al-oxide layer on metallic Al, which limited electron transfer from this metal to Au ions in solution (Arima et al., 2002; Foley et al., 2005; Karavasteva, 2010).

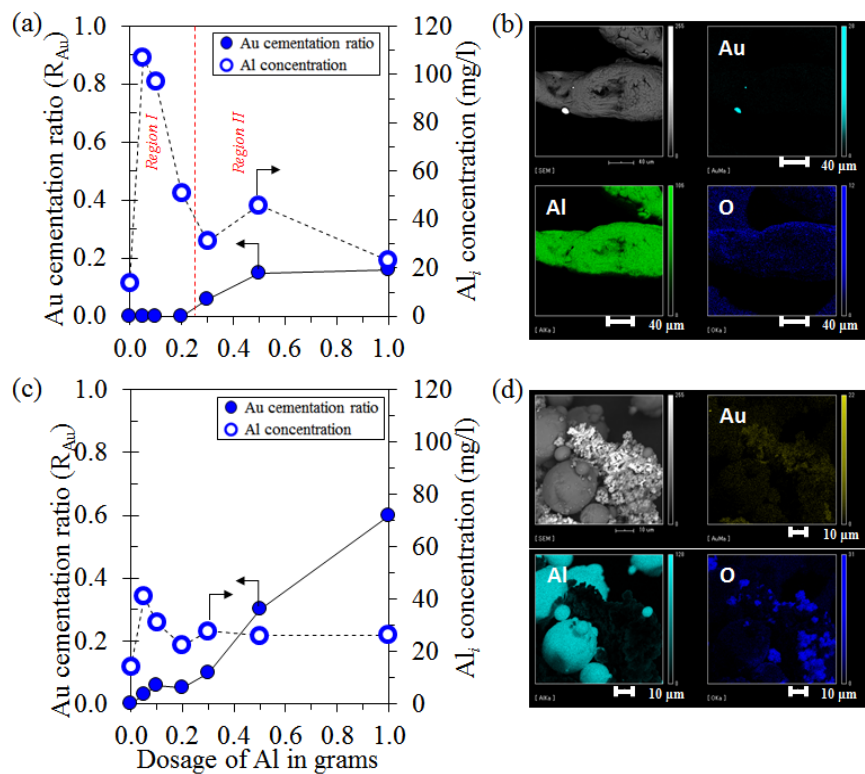


Fig. 4-4. (a) Cementation experiments of Au ions with varying dosage of Al without washing, and (b) SEM image with corresponding elemental mapping results of its leaching residue at 1g/10ml as well as (c) cementation experiments of Au ions with varying dosage of Al with washing and (d) SEM image with corresponding elemental mapping results of leaching residues at 1g/10ml.

To elucidate the effects of the Al-oxide layer on Au cementation, an identical experiment was carried out using Al powder that was washed to remove this Al-oxide layer. The results of Au cementation experiments using 1 g/10 ml of washed Al powder showed higher R_{Au} (0.7) compared with that of the unwashed Al powder (Fig. 4-4(c)), indicating that the oxide layer on Al powder suppressed Au cementation. SEM-EDX observations of the residue after the cementation experiments using washed Al powder showed that Au was more extensive (Fig. 4-4(d)).

The crushed PCBs of waste mobile phones used in this study contains 19% of Al (Table 4-1), which means that less than 0.2 g of Al was present in the ammonium thiosulfate leaching experiments of PCBs at the maximum S/L of 1 g/10 ml. This low Al amount coupled with the low efficiency of Al powder as a reductant of Au ions imply that Al only, similar to Cu, could not account for the low Au extraction observed in the leaching experiments at high S/L.

4.3.2.3 Synergistic effects of copper and aluminum on gold ion cementation

Fig. 4-5 compares the results of Au cementation experiments using Cu or Al powders only with

those of Cu and Al mixtures. The mixing ratio of Cu and Al was fixed at 1:1, and the total amount of Cu-Al mixture added to the thiosulfate solution containing Au ions was varied. Gold cementation ratio (R_{Au}) significantly increased when both Cu and Al were present compared with those in single metal systems (Figs. 4-5(a) and (b)). These results indicate that the coexistence of Cu and Al enhances Au ion cementation. Figs. 4-5(c) and (d) show Al and Cu extractions during the Au ion cementation experiments, respectively. Al extraction when Cu was present was higher while Cu extraction when Al was present was lower, which means that Cu enhances the oxidative dissolution of Al while Al galvanically protects Cu. In other words, the synergistic effects of Al and Cu on Au ion cementation could be attributed to the galvanic interaction between these two metals in solution.

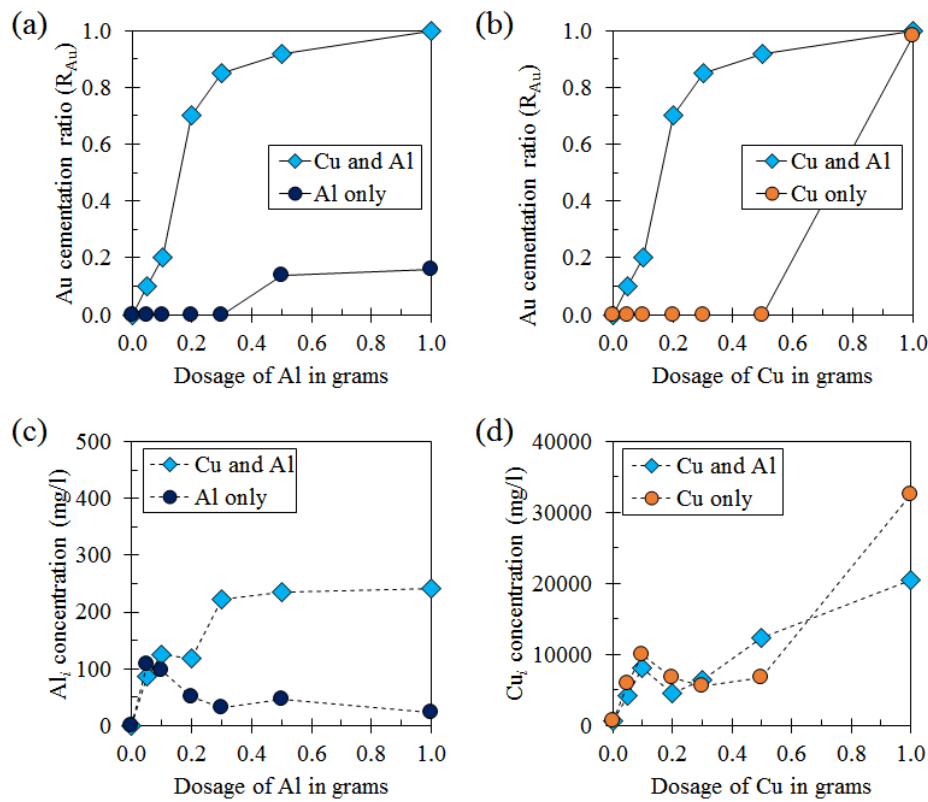


Fig. 4-5. Cementation experiments of Au ions using (a) Al only with those of Cu and Al mixtures, and (b) Cu only with those of Cu and Al mixtures, as well as their (c), extracted Al and (d) Cu concentrations (Note: Al_i and Cu_i denote the Al and Cu in ion states, respectively).

Fig. 4-6(a) displays a representative photomicrograph of the leaching residue at 1 g/10 ml (Cu-Al mixture), and the results of point analysis (Fig. 4-6(b)) suggest that there is a strong statistically significant negative correlation between Al and Au, while a moderate statistically significant positive correlation exists between Cu and Au. These results indicate that Au is preferentially deposited on Cu rather than Al supporting our earlier deduction of the importance of galvanic interaction between Cu and Al for the enhancement of Au ion cementation. The standard redox

potential of $\text{Cu}(\text{NH}_3)_4^{2+}/\text{Cu}$ redox pair is +0.026 V, that is higher than the Al^{3+}/Al redox couple (–1.66 V), so when a particle of Cu is in contact with that of Al, a galvanic cell composed of an Al anode and a Cu cathode is formed. Although Al is easily covered with an Al-oxide coating, this layer is typically very thin, so electrons could still pass through it via quantum tunneling effects (Fig. 4-7(a)) (Fisher and Giaever, 1961; Hunter and Fowle, 1956). In addition, this Al-oxide film is quite fragile, so micro-scratches are easily formed due to particle-particle collisions during shaking (Khanna et al., 2006), which makes the direct contact between Al and Cu possible (Fig. 4-7(b)). These two mechanisms could allow the transfer of electrons from Al to Cu and finally to Au ions, which are deposited on the Cu surface as metallic Au. Formation of an Al-Cu galvanic cell could also explain the higher extraction of Al and galvanic protection of Cu illustrated in Fig. 4-5.

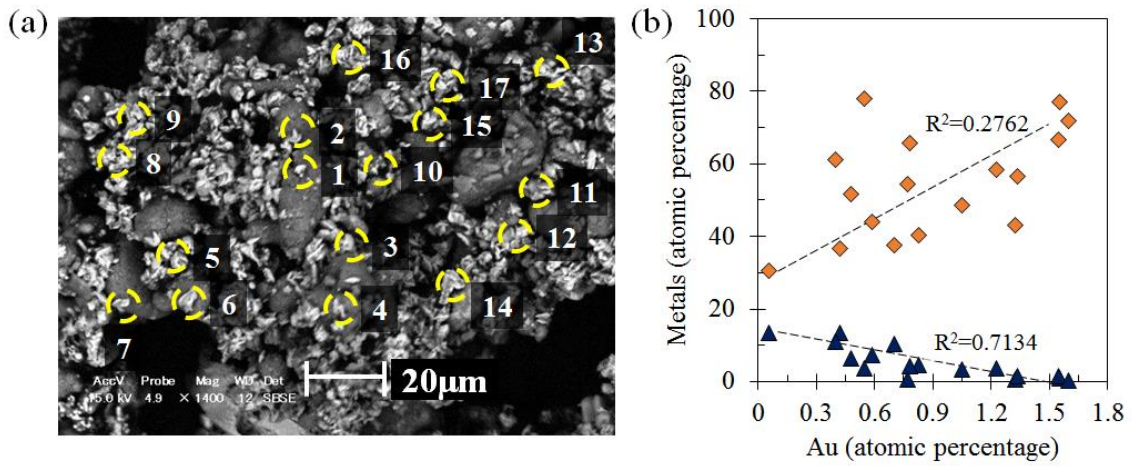


Fig. 4-6. (a) SEM photomicrograph of the residue of Au cementation experiments at 0.5 g of Cu and 0.5 g of Al mixture, and (b) correlation between Au atomic percentages and Cu as well as Al atomic percentages by point analysis using SEM-EDX.

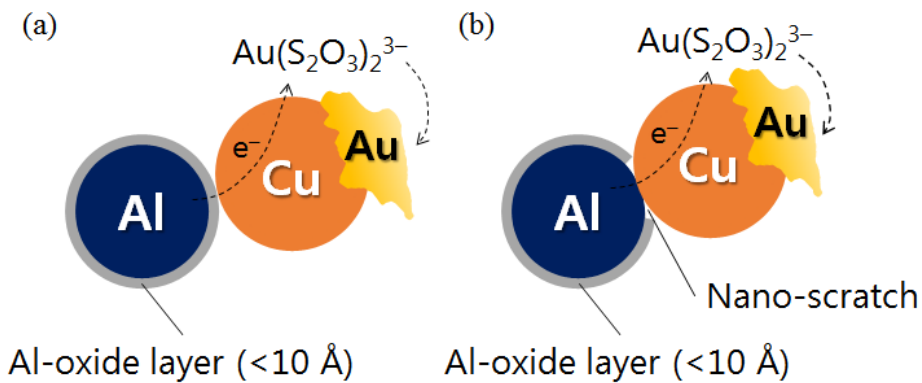


Fig. 4-7. Schematic diagram of mechanisms: (a) Au deposition because of the quantum tunneling effect and (b) nano-scratches on Al particles)

4.3.3 Galvanic interactions between copper and aluminum in gold-containing ammonium thiosulfate solution

In this section, electrochemical experiments were conducted to understand how Cu enhanced the cementation of Au when Al was present. Fig. 4-8(a) shows the results of chronoamperometry using an Al working electrode in 120 ml of a solution containing 0.1 M Na₂S₂O₃, 0.05 M NH₃, 0.025 M (NH₄)₂SO₄, and 10 mg/l of Au ions. After polishing, the Al working electrode was oxidized in the air for 14 days to form the oxide layer prior to the measurements. Case-I and Case-II denote the chronoamperometry measurements without and with 0.1 g of Cu powder, respectively. In Case-II, 0.1 g of Cu powder was added to the electrolyte after 300 s, which was suspended immediately due to the continuous magnetic stirring (300 rpm). Without Cu powder (Case-I), the cathodic current density became more negative with time. A possible reaction corresponding to this trend is the gradual reduction of Au ions to metallic Au on the surface of the electrode (Fig. 4-8(a-1)). The concentration of Au ions decreased from 10 mg/l to 8 mg/l during the experiments (Fig. 4-8(b)), indicating that 2 mg/l of Au was deposited on the electrode (Eq. (4-7)). Aside from Au ion reduction, additional electrons could come from the decomposition of water to hydrogen gas ($-1.4 \text{ V}_{\text{Ag/AgCl}}$) as well as the reduction of thiosulfate to sulfite ($-0.8 \text{ V}_{\text{Ag/AgCl}}$) as illustrated by Eqs. (4-8) and (4-9) (Molleman and Dreisinger, 2002):



In the presence of Cu powder (Case-II), a larger cathodic current density than that of Case-I was observed. Gold concentration in the electrolyte solution also decreased from 10 mg/l to 2 mg/l after the experiment (Fig. 4-8(b)). These results indicate that the higher cathodic current density of Case-II was likely because of not only the decomposition of water or thiosulfate but also the enhanced cementation of Au ions by Cu. Figures 4-8(a-2) and (a-3) illustrate the SEM-EDX observations of the Al electrode and Cu powder after the electrochemical experiments (Case-II), respectively. The results showed that Au was deposited on both the Al electrode and the surface of metallic Cu, which was identical to those observed in the leaching experiments of waste mobile phone PCBs.

Based on these results, the coexistence of Cu and Al is the main reason why Au extraction during ammonia thiosulfate leaching of PCBs was very low at high S/L, which could be explained by the formation of Al-Cu galvanic cells that enhanced the re-deposition of extracted Au. These results also imply that Au extraction from PCBs using ammonium thiosulfate medium could be improved by removing Cu and/or Al prior to the leaching process.

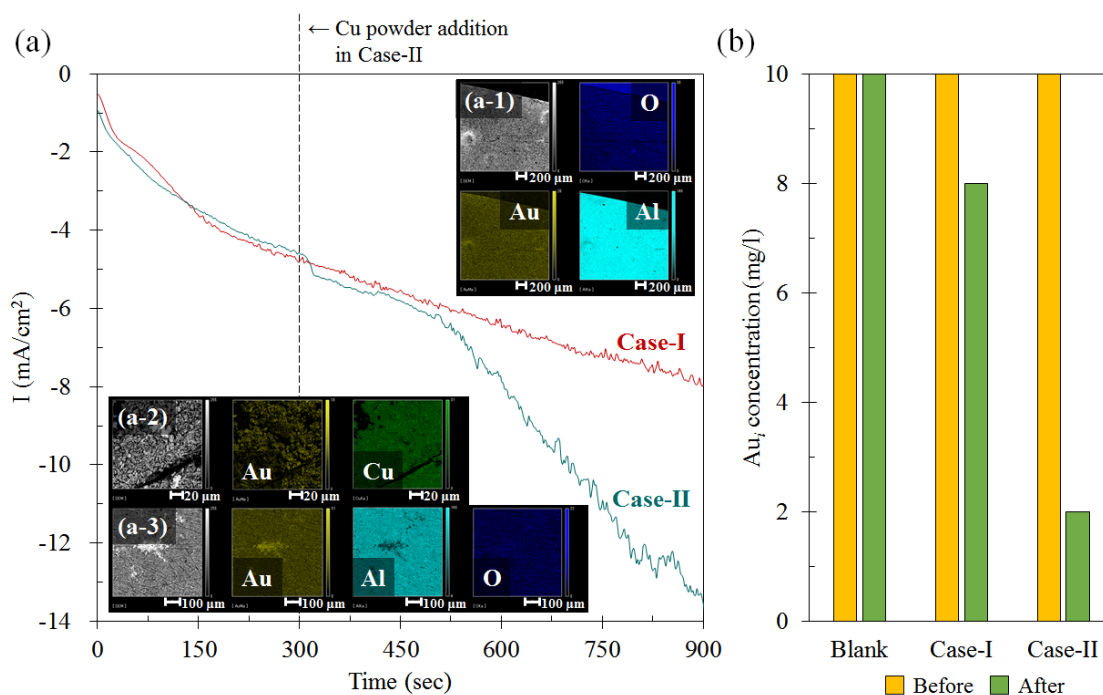


Fig. 4-8. (a) Chronoamperometry measurements without Cu powder (Case-I) and with 0.1 g of Cu powder (Case-II), and SEM photomicrograph with corresponding elemental maps of (a-1) Al electrode in Case-I, (a-2) Cu residue and (a-3) Al electrode in Case-II, and (b) Au concentration before and after electrochemical experiments.

4.4 Summary

This section evaluated the factors and processes responsible for the low extraction of Au from waste mobile phone PCBs in ammonium thiosulfate solution. Furthermore, the mechanisms involved in this phenomenon were investigated using cementation experiments, SEM-EDX, and electrochemical studies. Although Au was mainly observed with Cu and Al in the residues after the leaching of PCBs in ammonium thiosulfate solution, cementation experiments using pure Cu or Al alone were not sufficient to explain the very low Au extraction efficiency at high S/L. Extensive re-deposition of extracted Au occurred when both Cu and Al were present in the ammonium thiosulfate solutions, a synergistic effect that could be explained by two mechanisms: (1) mechanical removal of Al-oxide layer on Al by Cu via particle-particle collisions, which enhanced Au cementation on Al, and (2) galvanic interaction via the formation of Al-Cu galvanic cells. Based on the findings of this study, the overall extraction efficiency of Au from E-wastes could be improved even at high S/L by removing the Cu- and/or Al-containing components prior to ammonium thiosulfate leaching.

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CHAPTER 5

EFFECTS OF PHYSICAL SEPARATION AS A PRETREATMENT ON AMMONIUM THIOSULFATE LEACHING OF GOLD FOR REMOVING EITHER COPPER OR ALUMINUM FROM WASTE MOBILE PHONES

5.1 Introduction

The recycling of WEEE typically requires three stages: (1) hand-dismantling to specifically target big valuable components (e.g., electric motors and PCBs), (2) separating and concentrating valuable components from non-valuable materials in the end-products by physical separation techniques, and (3) metallurgical treatments (e.g., hydrometallurgy and pyrometallurgy) to extract and refine target metals (Cui and Forssberg, 2003; Yoo et al., 2010). For waste mobile phones, hand-dismantling to recover PCBs is difficult and impractical due to their small sizes, so only batteries are removed, and the remainder are treated by either pyrometallurgical or hydrometallurgical technique depending on the country (Jeplan, Inc., 2007). In Japan and Korea, for example, pyrometallurgical approach is preferred because of the large number of smelting facilities in these countries. Pyrometallurgical treatment, however, requires high initial capital and operational costs, so hydrometallurgical technique is a good alternative in areas without any pyrometallurgical facilities (Jeon et al., 2015, 2017). In hydrometallurgical techniques that target Au, leaching is the first stage with the primary goal of extracting Au using various types of lixiviants (e.g., halide, thiourea, and ammonium thiosulfate) (Jeon et al., 2017). Among these solutions, ammonium thiosulfate is attractive because it is non-toxic, less corrosive and has high selectivity for Au (Ha et al., 2010). Despite these many advantages, its use in recycling is still limited primarily because of the low Au extraction efficiency at high solid-to-liquid ratios (Jeon et al., 2016). A previous study of the authors reported that Au extracted into solution was rapidly converted back to metallic Au via reductive precipitation on Cu that is contact with Al particles, both of which are found in PCBs (Jeon et al., 2017). One way to limit this phenomenon is to pretreat the feed materials by separating these base metals from the Au-containing fractions prior to ammonium thiosulfate leaching.

For the separation of Au-containing parts and Al/Cu particles, several physical separation techniques could be applied. During the crushing of feed materials, the bulk of non-valuable parts is liberated at a coarse size. Crushing to a size much coarser than the optimum is economical because it produces large middlings in the subsequent concentration/separation process while most of the unnecessary parts could be discarded (Tsunekawa et al., 2007; Wills and Napier-Munn, 2006). The middlings could then be re-crushed and treated to produce the final concentrates. Because this strategy discards most of the coarse non-valuable parts early, unnecessary comminution of liberated gangue is avoided. That considerably reduces grinding costs and energy consumption. In recycling certain circumstance, lower energy and recycling cost (i.e., economic process) are required (Tsunekawa et al., 2007; Wills and Napier-Munn, 2006). As mentioned

earlier, waste mobile phones are made up of various type of materials including plastics, glasses, and PCBs, and a bulk of metals is concentrated in PCBs. In the case of plastics and glasses (i.e., non-valuables), they are easy to break down while PCBs (i.e., valuables) are hard to be crushed owing to the ductility of the metallic parts in PCBs. Because of this, in this study, (1) pre-concentration of PCBs from coarse crushing products by 1st crushing was conducted and then (2) removal of Cu-/Al-containing parts from re-crushed PCBs by 2nd crushing, and (3) ammonium thiosulfate leaching of Au concentrated products were conducted.

Jig separation is widespread technology in mineral processing because of its high separation precision and cost-effectiveness (Hori et al., 2009a; Tsunekawa et al., 2005), and advanced jig separation methods have been developing for recycling. In the case of hybrid jig that combines flotation and jig, it could be treated with a larger size than applied in flotation as well as the smaller size that applied in jig via specific gravity as well as different surface property (Hori et al., 2009b). Flotation also could be utilized for recycling. For example, Jeon et al. (2018) separated gold and other base metals from shredder light fraction of E-waste by flotation. Several studies that applied both physical separation techniques and hydrometallurgical treatment have been conducted, but most of them focused on hand-dismantled “clean” PCBs, not the entire waste mobile phones. These previous studies also applied physical separation to only one particle size fraction generated after crushing. Most importantly, these previous studies did not evaluate how physical separation affects the leaching efficiency of target metal(s) (Havik et al., 2014; Kasper et al., 2011; Silvas et al., 2015). To the best of our knowledge, this is the first paper to evaluate the applicability of physical separation techniques by separating Au-containing parts and Cu/Al-containing parts in varying size fractions of crushed waste mobile phones to improve the Au extraction efficiency.

In this section, jig separation and flotation were applied to separate plastic and metallic parts in coarse and fine fractions, respectively. Aside from coarse and fine fractions, a kind of “intermediate” fraction is also generated during crushing. The jig separation of intermediate-sized fractions is possible; however, the separation efficiency of finer components is relatively lower than coarse size because this technique is ideal for relatively large particles. Thus, the hybrid jig (Hori et al., 2009b) was applied for the intermediate-sized fraction. With this technique, separation efficiency is expected to increase because the specific gravity of hydrophobic light plastics with attached air bubbles is smaller compared with those components without attached air bubble. To recover Fe alloys, magnetic separation, which is widely used in recycling because of the predominance of steel in WEEEs, was used. Finally, ammonium thiosulfate leaching of the concentrated Au-containing product was conducted to determine the effects of physical separation techniques on Au extraction efficiency.

5.2 Materials and methods

5.2.1 Waste mobile phones

Various types of waste mobile phones were obtained from a 2nd hand mobile phone shop in Japan. Prior to crushing, their batteries were manually removed to avoid incidents like ignition, explosions, and chemical burns. The waste mobile phones were then crushed by a cutting mill (VH16, Seishin Enterprise Co., Ltd., Japan) with either 10 or 5.6 mm of the bottom screen.

5.2.2 Analyses of the chemical compositions of crushed sample and physical separation products

The chemical compositions of the bulk crushed waste mobile phones and those separated into several size fractions by screening were determined by ashing and aqua regia digestion. Samples were ground with a disk mill (RS 100, Retsch Co., Ltd., Germany) followed by ashing in an electronic furnace (Ishizuka Denki Seisakusho, Japan) using a special method developed by Tomita et al. (1983) that prevents the volatilization of Au during thermal treatment. This was followed by digestion of the ash using aqua regia, a 1:3 by volume mixture of concentrated nitric and hydrochloric acids, for 2 hours at 90 °C to dissolve all of the metals (Jeon et al., 2018; Yamane et al., 2011). The leachates were then filtered through 0.2 µm syringe-driven membrane filters (LMS Co., Ltd., Japan), diluted with deionized (DI) water (18 MΩ·cm, Milli-Q[®] 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 %).

5.2.3 Treatment flowchart

Fig. 5-1 shows a treatment scheme applying both physical separation and hydrometallurgical techniques. Waste mobile phones were coarsely crushed (1st crushing stage) by a cutting mill with a 10 mm bottom screen and the crushed products were sieved using a 2 mm. The +2–10 mm fraction was treated by jig separation to separate plastics (i.e., frame and keyboard) and PCBs. The concentrated PCBs was re-crushed (2nd crushing stage) by a cutting mill with a 5.6 mm bottom screen to liberate Au-containing parts from the PCBs. Subsequently, magnetic separation was carried out to separate magnetic from the non-magnetic products and then the non-magnetic products were treated by a 2nd jig separation (+2–5.6 mm: jig separation, +0.5–2 mm: hybrid jig separation) to separate Au-containing parts from other metals like Al and Cu liberated from PCBs. The fine fraction from the 1st crushing stage was treated by flotation to separate plastics from other metallic parts. The froth products containing plastics were treated by sink-float separation to separate heavy plastics containing Au and light plastics, and the concentrated Au-bearing fractions were leached in ammonium thiosulfate solution.

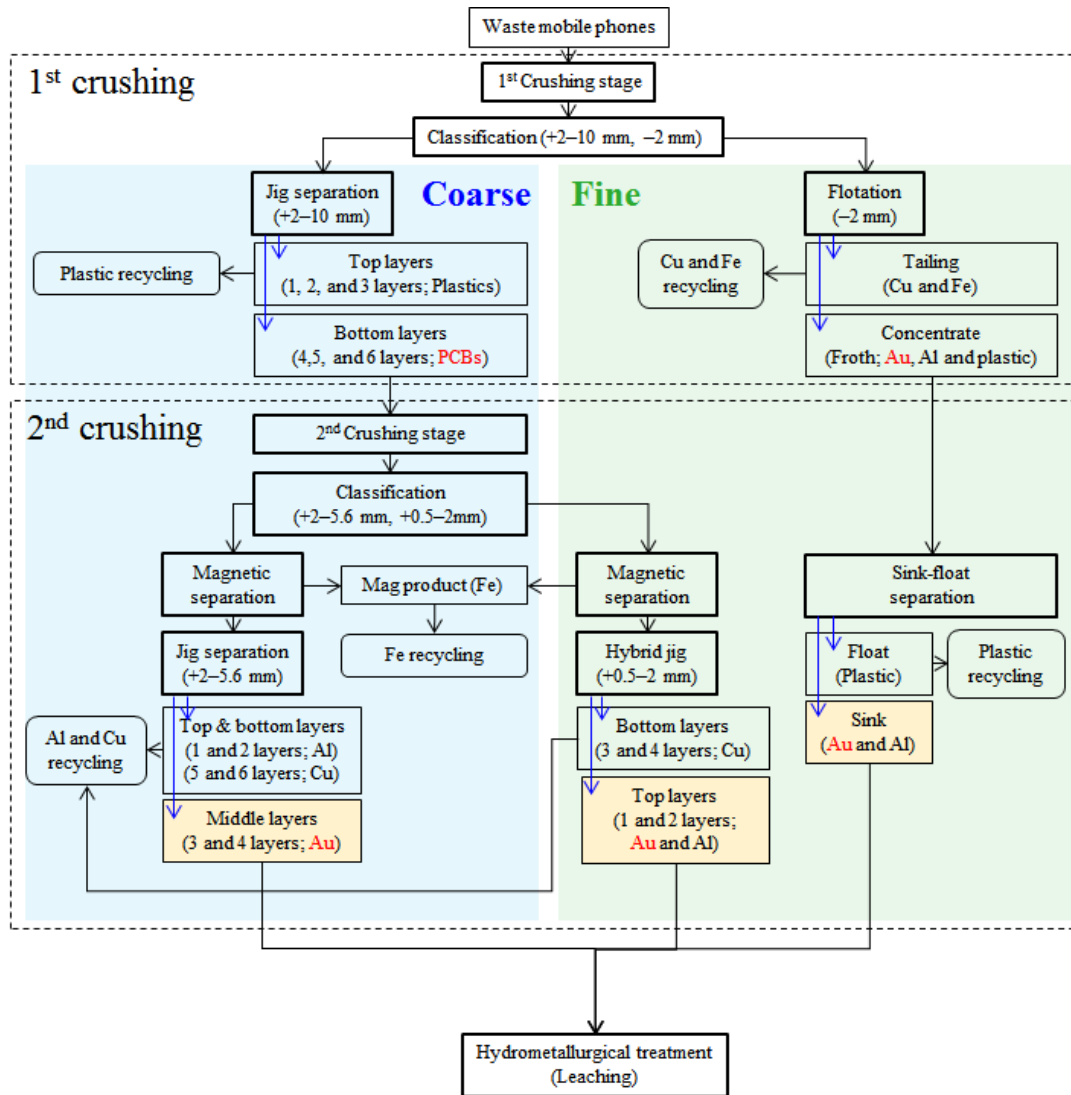


Fig. 5-1. Whole scheme for waste mobile phone recycling.

5.2.4 Jig separation

Jig separation experiments were carried out using a small batch-type jig (Fig. 5-2(a)). The separation chamber has dimensions of 135 x 145 x 320 mm (length x width x depth). A tube was connected to a pump to supply air to the air chamber via a hole in the flange. The sample was placed in the separation chamber, and jig separation was carried out using a displacement of 2 cm, frequency of water pulsation of 30 cycles/min, and separation time of 5 min. Aerosol OT (AOT, 15 mg/l), a wetting agent, was added to prevent changes in the apparent specific gravity (S.G.) of particles because of attached bubbles on their surfaces (Ito et al., 2016). After jig separation, the products were divided into 6 layers from top to bottom, and their compositions were quantified by ashing, aqua regia digestion, and ICP-AES as outlined previously. Moreover, the average S.G. of each layer was determined using an ultra pycnometer (Yuasa Ionics Co., Ltd., Japan).

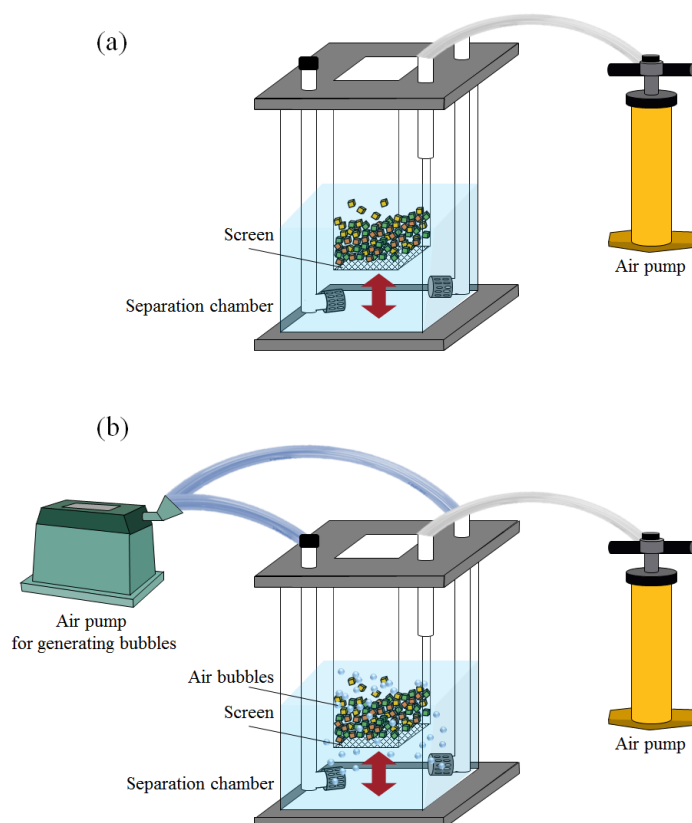


Fig. 5-2. Schematic diagram of (a) jig and (b) hybrid jig

5.2.5 Hybrid jig separation

The hybrid jig separation experiments were conducted using a batch-type hybrid jig similar to the batch-type jig but with the same modifications (Fig. 5-2(b)). Bubbles were generated by introducing air into ceramic filters below the separation chamber using an electric air pump (GEX, NewLUNG GX700N-2). The electric air pump was set at a constant flow rate of 3,000 cm³/min. Hybrid jig separation was carried out using a displacement of 2 cm, a frequency of water pulsation of 30 cycles/min, and separation time of 5 min. After which, the products were divided into 4 layers due to the insufficient amount of sample, and their compositions were measured by ICP-AES after ashing and aqua regia digestion. The average S.G. of each layer was also determined using an ultra pycnometer.

5.2.6 Magnetic separation

Dry magnetic separation was carried out using a hand magnet (0.3 T, Eriez Magnetics Japan, Japan). In this process, magnetic and non-magnetic fractions were separated, and each fraction was analyzed by ashing, aqua regia digestion, and ICP-AES.

5.2.7 Flotation

Flotation experiments were conducted with 20 g of the fine fraction (-2 mm) generated in the 1st crushing stage. This sample and 400 ml of water were mixed in an agitator-type batch flotation cell (FT-1000, Heiko, Japan), and flotation was done at an impeller speed of 1000 rpm, air flow rate of 0.75 l/min, 40.5 $\mu\text{l/l}$ of MIBC as a frother, and kerosene as a collector. Plastic particles in crushed waste mobile phones are inherently hydrophobic similar to coal, so kerosene was selected as a collector to enhance the hydrophobicity of plastic particles (Jeon et al., 2018). To recover most of the hydrophobic materials, the froth was first recovered without kerosene addition. After which, 2 $\mu\text{l}/400\text{ ml}$ of kerosene was added in the flotation cell to recover more materials, and this procedure was repeated until 15 $\mu\text{l}/400\text{ ml}$ of total kerosene was added (Tsunekawa et al., 1998). The froth and tailing products were analyzed by SEM-EDX (SSX-550, Shimadzu Corporation, Japan), and their compositions were determined by ashing and ICP-AES after aqua regia digestion of the ash.

5.2.8 Sink-float separation

Sink-float separation (S.G.: 2.1) was carried out using sodium polytungstate solution (SPT, $\text{Na}_6\text{O}_{39}\text{W}_{12}$) (Wako Pure Chemical Industries, Ltd., Japan). The samples were placed in separatory funnels at 25 °C, shaken for 3 min, and then left to stand still to allow for the separation of particles. Float and sink products were recovered, and the chemical compositions of each product were determined by ashing and ICP-AES after aqua regia digestion of the ash.

5.2.9 Ammonium thiosulfate leaching

The Au-bearing concentrates obtained after physical pretreatments were mixed and leached to extract Au. Ammonium thiosulfate leaching experiments were conducted by mixing 1 g of sample (feed or mixture of physical pretreatment products) and 10 ml of a solution containing 1 M $\text{Na}_2(\text{S}_2\text{O}_3)$, 0.5 M NH_4OH , 0.25 M $(\text{NH}_4)_2\text{SO}_4$ and 10 mM CuSO_4 in 50 ml Erlenmeyer flasks. This solution composition was selected based on our experiments in Chapter 3. The suspensions were shaken in a thermostat-controlled water bath shaker with shaking amplitude of 40 mm and frequency of 120 min^{-1} at 25 °C. After 24 h, the leachates were collected by filtration through 0.2 μm membrane filters and then analyzed by ICP-AES.

5.3 Results and discussion

5.3.1 Chemical compositions of crushed waste mobile phones and each size fraction after classification

Table 5-1 shows the compositions of waste mobile phones after crushing and each size fraction after classification. The waste mobile phones used in this study contain 58% of combustibles and

39% of metals, including 17% of Cu, 16% of Fe, 2% of Al, and 0.2% of Au. The remainder (about 3%) is mainly composed of various types of glasses and ceramics. After the 1st crushing stage and screening operations, 55% of the yield was obtained as a coarse fraction (+2–10 mm) while the rest (45%) reported to the fine fraction (–2 mm). The distribution ratio of a metallic fraction after classification was 49% in the coarse fraction (+2–10 mm) and 28% in the fine fraction (–2 mm) while for combustibles, 66% were collected in the fine fraction. These results indicate that combustibles were easily crushed by the cutting mill while metals are harder to crush due to their malleability. The fine fraction (–2 mm) generated from the 1st crushing stage also contains 14% Cu, 12% Fe, and 1.5% Al. The coarse fraction was treated by jig separation (1st jig separation) to concentrate PCBs, which was re-crushed to liberate the Au-containing components (Fig. 5-1), and then sieved to obtain +2–5.6 mm (yield: 45%) and +0.5–2 mm (yield: 55%) size fractions. The +2–5.6 mm fraction is composed of 25% Cu, 38% Fe, 3% Al, and 28% combustibles. In comparison, the fraction (+0.5–2 mm) is composed of 38% Cu, 18% Fe, 1.7% Al, and 40% combustibles.

Table 5-1. The composition of waste mobile phone after crushing and each size fraction after classification.

	Waste mobile phone	+2–10 mm	+2–5.6 mm	+0.5–2 mm*	–2 mm**
Cu	17	20	25	38	14
Fe	16	21	38	18	12
Al	1.5	1.5	3	3	1.5
Ni	3	3	2.2	0.1	0.1
Zn	0.8	1	1.2	1.4	0.1
Pb	0.1	1.8	1.8	0.3	0.1
Au	0.2	0.2	0.3	0.1	0.2
Combustibles	58	50	28	40	66
Others	3.4	1.5	0.5	0.4	6

*Fine fraction generated by the 2nd crushing stage

**Fine fraction generated by the 1st crushing stage

5.3.2 1st jig separation of coarse fraction (+2–10 mm) obtained from 1st crushing stage

The +2–10 mm fraction from the 1st crushing stage was treated by jig separation to concentrate PCBs because these contain the bulk of metals including Cu and Au. Figure 5-3 shows the results of the jig separation, where recovery of PCBs was obtained by the hand-picking method. The average S.G. of the 1st layer (top layer) was the lowest at 1.2, which increased with increasing distance from the top, indicating that the products were separated by differences in S.G. The measured S.G. of PCBs was about 3.6, so they were concentrated in the bottom layers while the other combustibles (plastic frame and keyboard) were concentrated in the upper layers, indicating that the various parts of crushed waste mobile phones could be separated. The distribution ratio

of PCBs in the 4th, 5th, and 6th layers were high (i.e., over 96% recovery of PCBs), and combustibles recovery in the 1st, 2nd, and 3rd layers was greater than 99% (Fig. 5-3(a)), indicating that sufficient liberation of PCBs from the other parts of mobile phones was achieved after the 1st crushing stage described previously. Moreover, successful separation of PCBs from other plastic body parts was obtained by jig separation.

Figure 5-3(b) shows the metal recovery in each layer, and the results illustrate that recovery of Au, Cu, and Al in the bottom layers (4-6 layers) were around 99%, 99%, and 89%, respectively. PCBs typically have a laminated sheet structure composed of alternating Cu or Al and resin (Fig. 5-4) and contain electronic components like ICs or CPUs, where most of Au is found (Fig. 5-5). Because of this, the liberation of the Au-containing parts and Cu/Al sheets requires additional crushing of the bottom layer products of jig separation (2nd crushing stage, -5.6 mm).

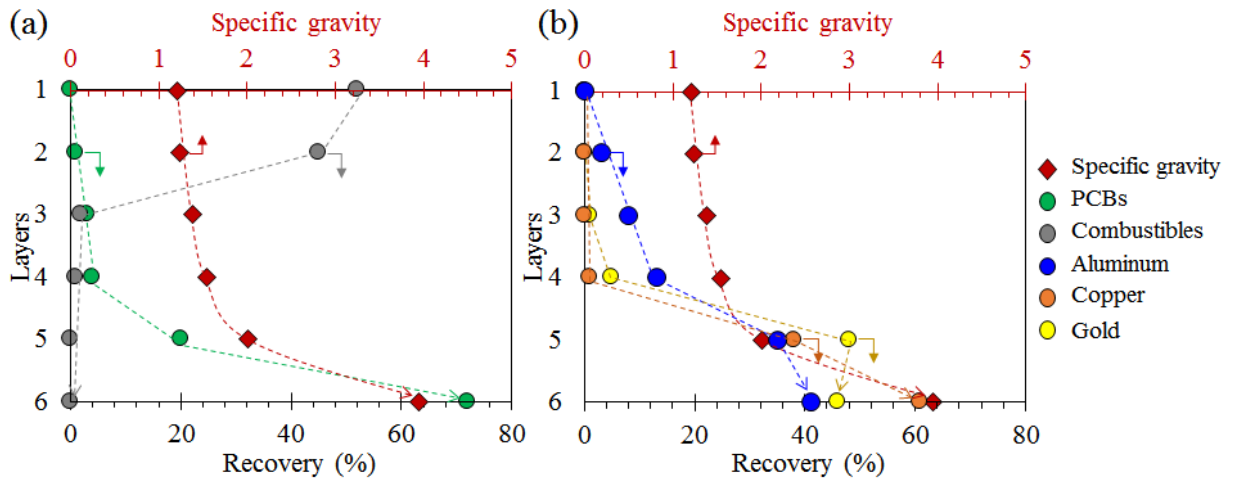


Fig. 5-3. The 1st Jig separation of +2–10 mm fraction generated from 1st crushing: (a) specific gravity and recovery of PCBs and combustibles in each layer, and (b) specific gravity and recovery of Al, Cu, and Au in each layer.

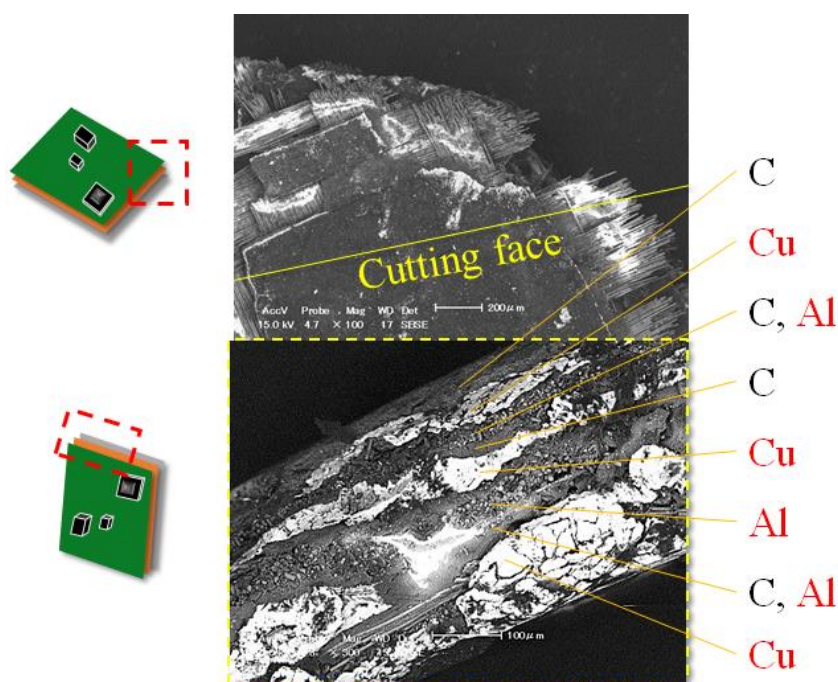


Fig. 5-4. Photomicrograph of front and side-sectional view of PCBs with EDX analysis

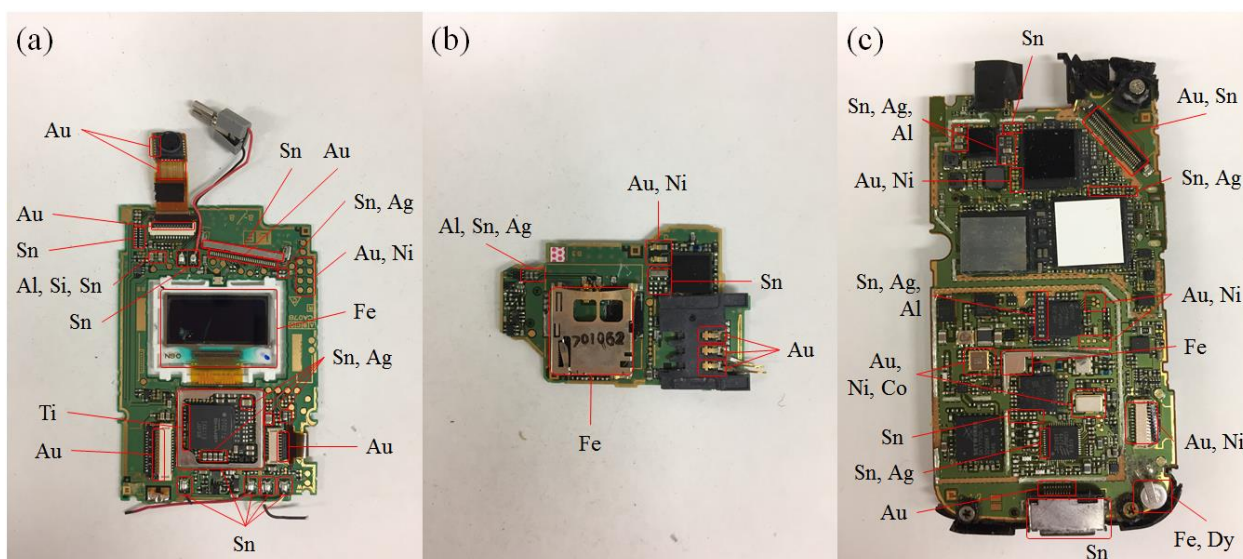


Fig. 5-5. Photograph of waste mobile phone PCBs with SEM-EDX analysis in terms of chemical elements distribution: (a) main part and (b) sub part of liquid crystal display (LCD) PCBs as well as in (c) main frame.

5.3.3 Separation of gold-containing parts from other substances by magnetic and jig separation (+2 –5.6 mm, generated from 2nd crushing of 1st jig separation products)

The concentrated PCBs obtained from the 1st jig separation (4–6 layers) were further crushed for

liberating Au-containing components from Al and Cu sheets followed by sieving to less than 5.6 mm in size. Subsequently, appropriate physical separation of each size fraction (+2–5.6 and –2 mm) was conducted. Magnetic separation was utilized to remove magnetic particles prior to the 2nd jig separation, otherwise, Fe-components could affect the S.G. of materials to be separated, resulting in lower separation efficiency of Au relative to Cu and/or Al (Fig. 5-6). The results showed that Fe-containing components were easily removed with a hand-magnet (0.3 T) (Table 5-2). About 0.3% of Au was recovered with the magnetic fraction because some Au is plated on Fe-containing parts (Fig. 5-7). The non-magnetic fraction was then treated by jig separation.

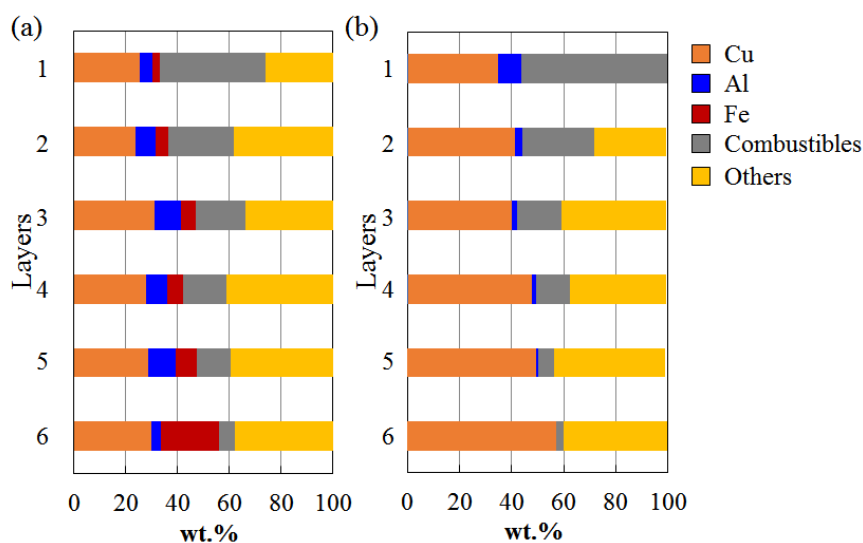


Fig. 5-6. Jig separation (a) without and (b) with magnetic separation.

Table 5-2. The composition of mag-product of magnetic separation (+2–5.6 mm).

	Au	Cu	Al	Fe	Ni	Pb	Zn	Others
Wt.%	0.3	4.4	2.2	77.8	6.1	0.1	0.2	8.9

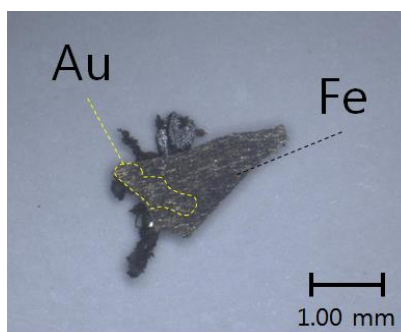


Fig. 5-7. Gold-plating on iron component

Figure 5-8 shows the results of jig separation of +2–5.6 mm fraction, which imply that Au was concentrated in the middle layers (3rd and 4th layers: 54% recovery) (Fig. 5-8(b)). The S.G. of pure

Au is about 19.3, so in theory, it should be recovered in the bottom layers after gravity separation. The results, however, show that Au was concentrated in the middle layers (Fig. 5-8(b)), which could be attributed to how Au is distributed in PCBs. Gold in PCBs is mainly present in three components: (1) electronic parts like ICs and CPUs, (2) Au-plated metals, and (3) Au-plated plastics. (Fig. 5-9(a) and (b)). This means that the S.G. of Au-containing parts are lower than that of pure Au and could explain why Au was concentrated in the middle layers during jig separation.

The recovery of combustible components in the 1st and 2nd layers was 84%, suggesting that light plastics were liberated from PCBs, and then concentrated in the upper layers (Fig. 5-8(a)). Cu recovery in the light S.G. layers showed the lowest values, which increased with increasing S.G. of the layers (Fig. 5-8(c)). Aluminum (S.G.=2.6) recovery in the 1st (31% recovery, 9% grade) and 2nd (20% recovery, 3% grade) layers were the highest, suggesting that a portion of Al was liberated from PCBs (S.G.: 3.6) and recovered as light products. Fig. 5-8(d) shows that Al recovery in the light S.G. layers was high, and it decreased with increasing S.G. of the layer.

Fig. 5-8(e) shows the separation efficiency (S_E) of Au relative to Cu or Al. The S_E was calculated by Eq. (5-1) as follows (Aravamudhan et al., 1984):

$$S_E = (R_{Au} + R_{BM}) - 100\% \quad (5-1)$$

where S_E represents the separation efficiency, R_{Au} refers to the recovery of Au in the target layer, and R_{BM} denotes the sum of the recovery of Cu or Al in other layers except the target layer. For example, when both Au and Cu recovery are 50%, S_E is 0%, indicating that separation was negligible, while 100% of Au recovery with 0% of Cu recovery means that S_E is 100% (i.e., perfect separation). When 0% of Au recovery with 100% of Cu recovery was obtained, the S_E could be shown minus value (i.e., -100%). The S_E results showed that both Cu and Al could be separated from Au-containing parts as the latter is able to recover in the middle layers (3rd and 4th layers), which means that upper (1st and 2nd layers) and bottom layers (5th and 6th layers) could be removed prior to leaching. The recovered middle layers (3rd and 4th layers) were leached in ammonium thiosulfate to extract Au.

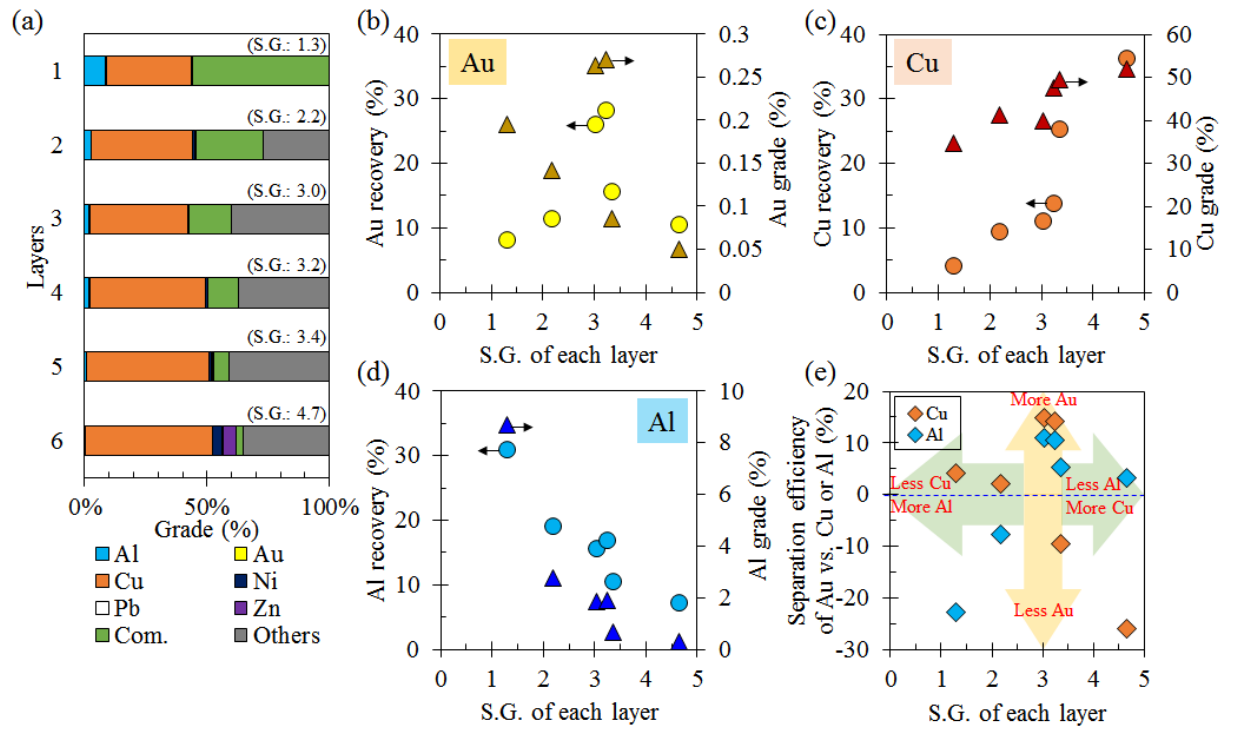


Fig. 5-8. The 2nd Jig separation of +2–5.6 mm fraction generated from 2nd crushing: (a) grade of each element in each layer, and interrelationship between specific gravity and either recovery or grade of (b) Au, (c) Cu, (d) Al, and (e) separation efficiency of each layer.

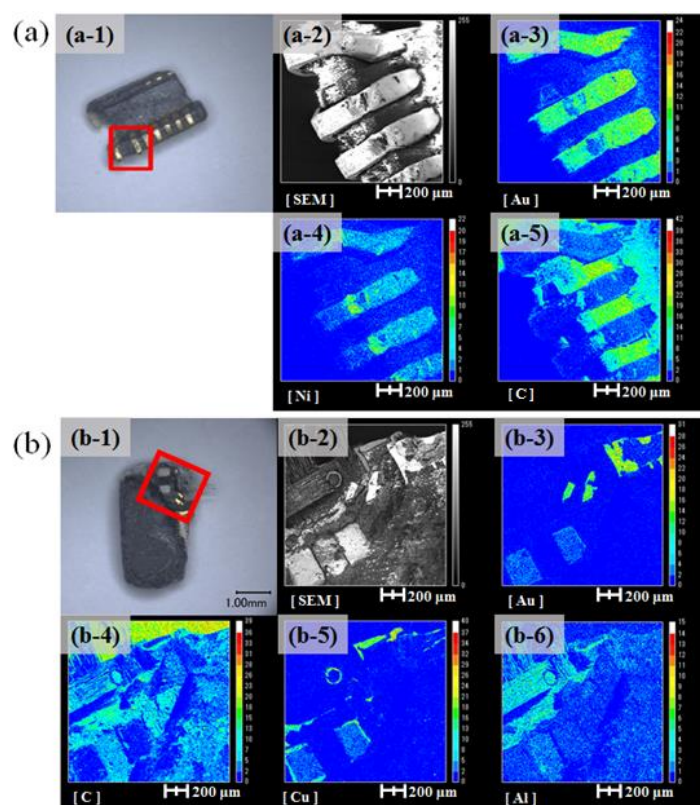


Fig. 5-9. Photomicrographs of representative (a) crushed electronic parts with corresponding elemental maps including (a-3) Au, (a-4) Ni, and (a-5) plastic (c), and (b) crushed PCBs parts with corresponding elemental maps including (b-3) Au, (b-4) plastic (c), (b-5) Cu, and (b-6) Al.

5.3.4 Fine fraction treatments

The fine fraction (-2 mm) generated from the 1st and 2nd crushing stages also contains substantial amounts of Au as well as other base metals as shown in Table 1, so further separation is needed. The fine fraction generated by the 1st crushing stage is mostly composed of plastics ($\sim 66\%$). In comparison, those from the 2nd crushing stage is mostly composed of metals ($\sim 61\%$). Because of their different properties, they were treated with different techniques. Fine fraction from the 1st crushing operation was treated by flotation using the difference of wettability while those generated from the 2nd crushing stage was treated using differences of S.G. of plastics and metals by hybrid jig separation (Fig. 5-2).

5.3.4.1 Separation of gold and other substances by flotation and sink-float separation (-2 mm, generated from 1st crushing stage)

Figure 5-10(a) shows the cumulative recovery of each component with varying dosage of kerosene. The results showed that the recovery of combustibles in froth increased with increasing kerosene dosage and the recovery of combustibles was over 99% after adding 10 μ l of kerosene.

The recovery of Au (81%) and Al (76%) in froth products also increased with increasing kerosene addition. In contrast, the recovery of other metals including Cu and Fe was less than 30%. Figure 5-10(b) describes the cumulative recovery of each component with yield. When strongly hydrophobic and weakly hydrophobic particles exist in the feed, strongly hydrophobic particles are recovered lower kerosene dosage. The blue dashed line in Fig. 5-10(b) shows the ideal recovery of hydrophobic particles and the red dashed line shows the weakly hydrophobic particles. It was observed that the recovery of combustibles, Au, and Al had similar trends with the ideal hydrophobic recovery (blue dashed line in Fig. 5-10(b)), suggesting that Au and Al were unliberated from the hydrophobic plastic parts. To identify how the bulk of Au and Al were obtained in the froth products, the SEM-EDX analysis was conducted. The SEM-EDX results of a representative particle in froth product showed that Au was plated on plastics with Al (Fig. 5-10(c)). Moreover, Au is not only found with plastics on PCBs (e.g., ICs or CPUs), but also plated in casings or connectors of waste mobile phones (Fig. 5-11). Plastics are easier to crush than metals, so they easily become finely sized (~ 2 mm). Because of this, when waste mobile phones are crushed, Au-plated plastics are broken easily and end up in the fine particle size fraction. Au-plated plastics are typically acrylonitrile butadiene styrene (ABS), which is typically more hydrophobic than other plastics (Jeon et al., 2018), so it could be floated up during flotation. These results indicate that flotation could be used to recover Au in fine fractions of crushed waste mobile phones. Most of the base metallic components (e.g., Cu and Fe) were concentrated in the tailing products (less than 30% of recovery in froth). Figure 5-10(d) shows the interrelationship between Cu or Al recovery and Au recovery in the froth, and Fig. 5-10(e) shows the separation efficiency of Au relative to Cu or Al. The results showed that 80% of Au was recovered as froth while about 55% of S_E of Au and Cu was obtained but S_E of Au and Al was low since Au was plated on plastics with Al.

The measured S.G. of Au-plated plastics recovered by hand-picking was 2.5–2.7 while those without Au plating was lower at 1.5–1.9. After flotation, the froth product was further purified by sink-float separation using the dense medium (S.G.: 2.1) to separate plastic without Au plating from those with Au plating. A grade of 99% combustible was obtained in the float with a negligible amount of Au (Fig. 5-12(b)), while the sink product contained most of the Au-plated plastics (c-1 in Fig. 5-12(c)). These results indicate that concentration and volume reduction prior to the leaching process is possible by sink-float separation. This sink product was leached in ammonium thiosulfate to extract Au.

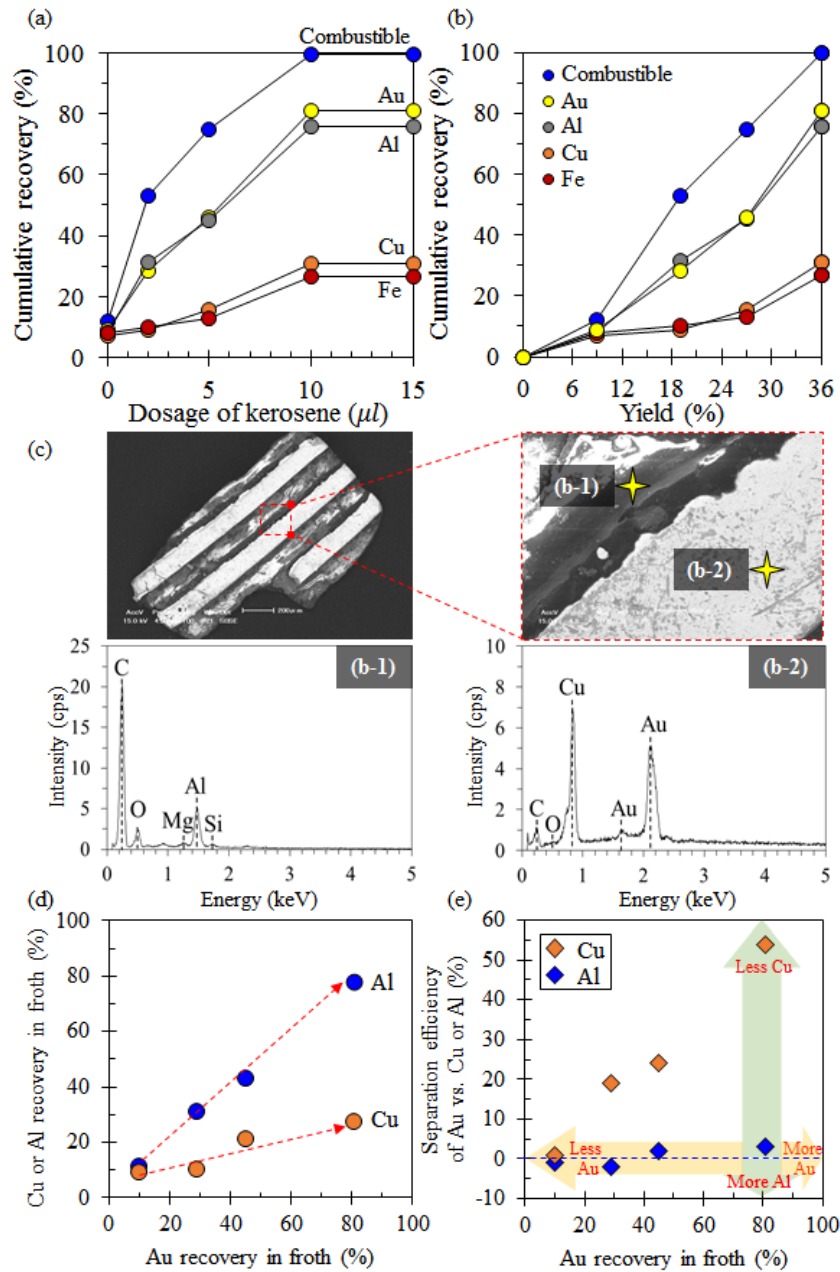


Fig. 5-10. Flotation of -2 mm fraction generated from 1st crushing: cumulative recovery of each components (a) with varying dosage of kerosene, (b) with yield, (c) photomicrograph of a representative particle in froth as well as magnified image with corresponding EDX spectra of either (b-1) or (b-2) point, and (d) interrelationship between Cu or Al recovery and Au recovery in froth, and (e) separation efficiency of Au relative to Cu or Al (Note: red arrows denote increasing addition of kerosene).

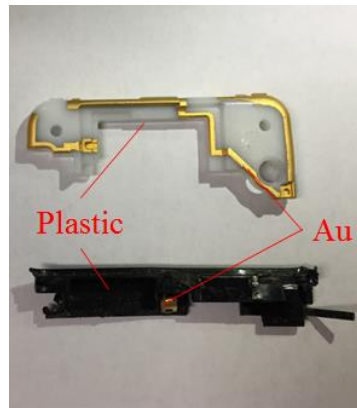


Fig. 5-11. Gold plating on casing and connector of waste mobile phone.

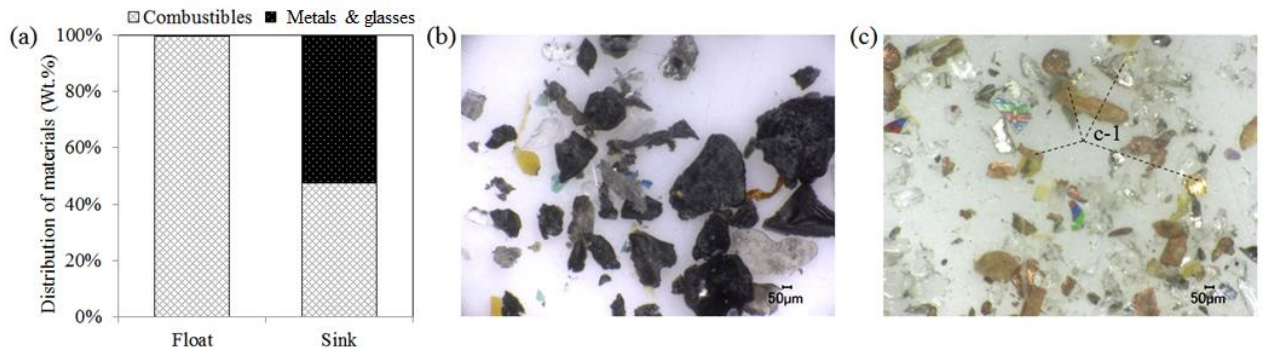


Fig. 5-12. (a) Sink-float separation of froth products, and photomicrographs of (b) float, as well as (c) sink fraction.

5.3.4.2 Separation of gold from other substances by magnetic and hybrid jig separation (+0.5–2 mm, generated from 2nd crushing stage of 1st jig separation products).

The fine fraction (–2 mm) generated by the 2nd crushing stage was treated by magnetic separation to remove the magnetic fractions prior to hybrid jig separation. The results showed that Fe-containing components were easily removed by a 0.3 T hand-magnet (Table. 5-3), and a small portion of Au was collected with the magnetic products because some Fe-components were Au-plated. The non-magnetic fraction was further treated by hybrid jig separation (+0.5–2 mm).

Table 5-3. The composition of mag-product of magnetic separation (–2 mm generated from 2nd crushing of 1st jig product).

	Au	Cu	Al	Fe	Ni	Pb	Zn	Others
Wt.%	0.4	18	1.7	56	4.4	0.2	1.7	18

Although a conventional jig (without bubbles) can also be applied, our preliminary results showed that Au components were mostly recovered in middle layers (2nd and 3rd), Al-bearing components were recovered in the upper layers (1st and 2nd), and those containing Cu were

concentrated in bottom layers (3rd and 4th). Unfortunately, the 2nd layer contains not only Au but also a considerable amount of Al, and the 3rd layer also contains a significant amount of Cu with Au, which would dramatically decrease the separation efficiency of Au from either Cu or Al (Fig. 5-13). To improve the separation efficiency, hybrid jig separation was also utilized for this size fraction. Figure 5-14(a) shows the grade of each element in each layer after hybrid jig separation. The bulk of combustibles, Al, and Au were concentrated in the upper layers while Cu was concentrated in the bottom layers, suggesting that Au associated with plastics floated up due to the decrease in specific gravity as a result of bubble attachment. S_E of Au vs. Cu and Al in the lightest S.G. layer was 23% and 10%, respectively. The upper layer product of hybrid jig separation was leached with ammonium thiosulfate to extract Au.

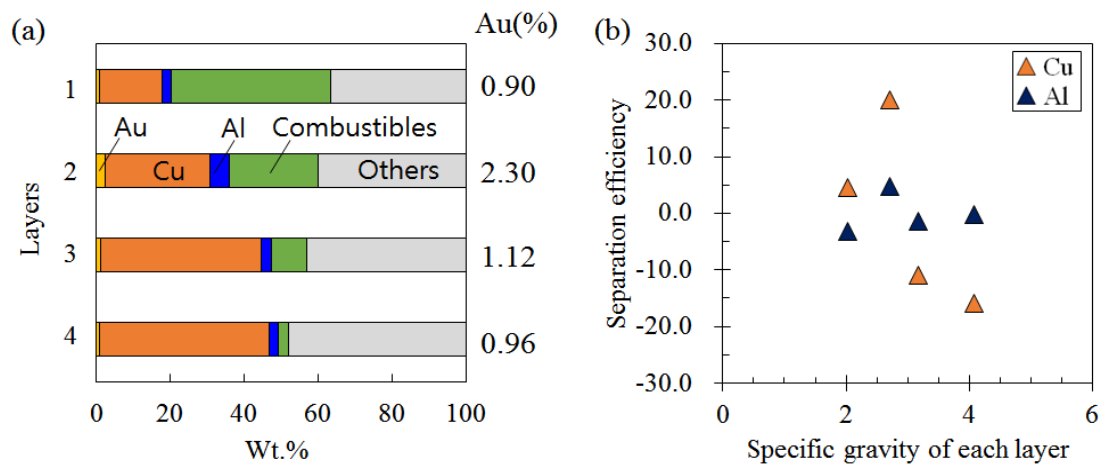


Fig. 5-13. Jig separation (without air bubbles) of fine fraction (-2 mm, generated from 2nd crushing of 1st jig product) (a) elemental composition and (b) interrelationship between specific gravity of each layer and separation efficiency.

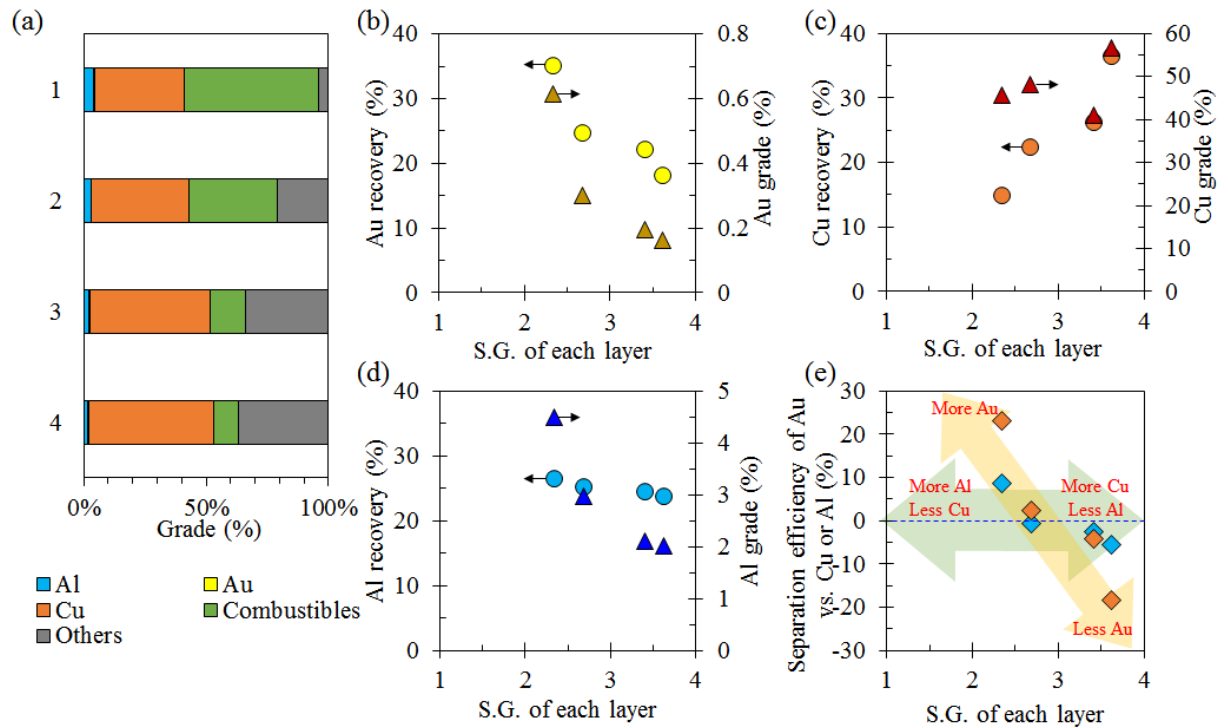


Fig. 5-14. Hybrid jig separation of +0.5–2 mm fraction generated from 2nd crushing: (a) grade of each elements in each layer, and interrelationship between specific gravity and either recovery or grade of (b) Au, (c) Cu, (d) Al, and (e) separation efficiency of each layer.

5.3.5 Ammonium thiosulfate leaching to identify the effects of physical separation

To elucidate the effects of Cu and Al removal on Au extraction, ammonium thiosulfate leaching of Au concentrated fractions (a mixture of 3rd and 4th layers after 2nd jig separation, 1st and 2nd jig separation after hybrid jig separation, and sink product of sink-float separation) was carried out. The leaching results showed that the Au extraction dramatically increased from 1.2 mg/l to 18 mg/l (about 15-fold) while the Au leaching efficiency increased from 5.5% to 16.6% (about 3-fold) (Fig. 5-15(a)). To compare the Au leaching efficiency of products showing different amount of Al and Cu, leaching was carried out as follows: (1) Froth product of flotation, (2) 3rd and 4th layers of 2nd jig separation product, (3) +2–5.6 mm fraction from 2nd crushing of 1st jig product, (4) –2 mm fraction from 1st crushing, (5) 1st and 2nd layers of hybrid jig separation product, (6) –2 mm fraction from 2nd crushing of 1st jig product, (7) whole waste mobile phone. Figs. 5-15(b) and (c) show the correlation of Au leaching efficiency with the amounts of either Al or Cu, and the results showed that the leaching efficiency decreased as Al or Cu amounts increased, indicating that Au leaching efficiency improved due to the removal of Al and Cu.

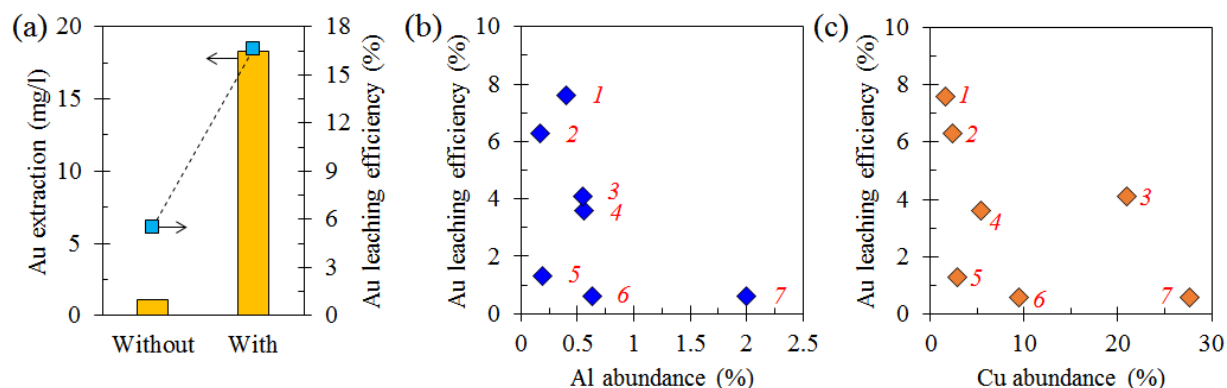


Fig. 5-15. (a) Ammonium thiosulfate leaching of Au with and without physical separation, and correlation between Au leaching efficiency and either (b) Al or (c) Cu amounts of each fraction (Note: 1. Froth product of flotation; 2. 3rd and 4th layers of 2nd jig separation product; 3. +2–5.6 mm fraction from 2nd crushing of 1st jig product; 4. –2 mm fraction from 1st crushing; 5. 1st and 2nd layers of hybrid jig separation product; 6. –2 mm fraction from 2nd crushing of 1st jig product; 7. Whole waste mobile phone).

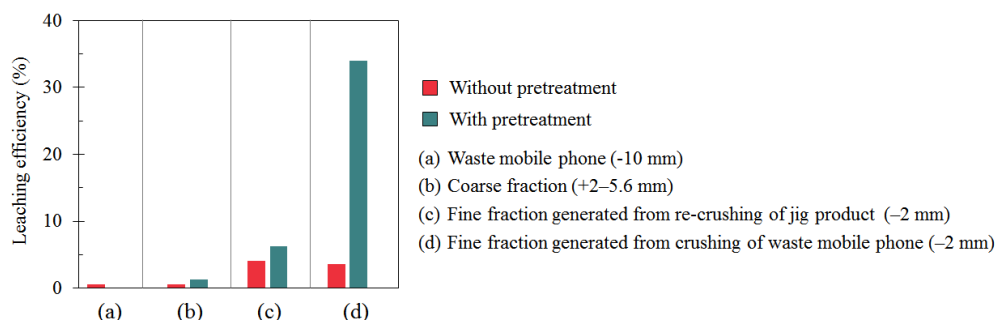


Fig. 5-16. Au leaching efficiency with/without each physical separation pretreatments

5.4 Summary

This section investigated the separation of Au components from either Cu or Al fraction in crushed waste mobile phones by physical separation techniques (i.e., jig separation, magnetic separation, hybrid jig separation, sink-float separation, and flotation). Moreover, the effects of these separation techniques on Au extraction efficiency were evaluated by ammonium thiosulfate leaching. The findings of this study are summarized as follows:

1. Coarse crushing by a cutting mill with 10 mm bottom screen could liberate PCBs from other parts like plastic frame and keyboards, and PCBs were concentrated in the bottom layers by jig separation.
2. Concentrated PCBs were re-crushed (+2–5.6 mm) and treated by jig separation following magnetic separation, which concentrated Au-containing plastics in the middle layers, Al-

containing plastics in the upper layers, and Cu in bottom layers.

3. Fine fractions (–2 mm) generated by the 1st crushing stage were treated by flotation and the froth product was treated by sink-float separation. Au-containing plastics were recovered as froth due to the strong hydrophobic property imparted by kerosene weakly hydrophobic plastics. Fine fractions (+0.5–2 mm) generated by the 2nd crushing stage were treated by magnetic separation and hybrid jig separation to separate Au-containing plastics and metals. Attached bubbles decreased the apparent S.G. of Au-containing plastics and improved the S_E .
4. The Au extraction efficiency increased after physical separation treatments. Leaching efficiency decreased with increasing amounts of Al or Cu in the feed, indicating that Au leaching efficiency improved due to the removal of Al and Cu. Based on the findings of this study, Au extraction could be enhanced by separation of Au-containing components from Cu- and/or Al-containing parts via physical separation techniques prior to ammonium thiosulfate leaching of E-wastes (e.g., waste mobile phones) as well as other similar Au-containing wastes.
5. A physical separation treatment scheme composed of a two-stage crushing coupled with several physical separation techniques based on the size and composition is proposed for crushed waste mobile phones.

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CHAPTER 6

RECOVERY OF GOLD IONS FROM LEACHED SOLUTION IN AMMONIUM THIOSULFATE SYSTEM VIA SYNERGISTIC EFFECT OF ACTIVATED CARBON WITH ALUMINUM

6.1 Introduction

Hydrometallurgical technique has been effectively applied for the treatment of gold (Au)-bearing materials including primary (e.g., Au ore) and secondary resources (e.g., electronic waste) (Ha et al., 2010; Jeon et al., 2018; Langhans et al., 1992), and it consists of two major stages: leaching and recovery. Leaching is the first stage of the hydrometallurgy where the target metal (i.g., Au) is soluble and non-target metals are insoluble, converts target metal into ion phases via lixivants, such as cyanide, halide, thiourea, and thiosulfate. Among the aforementioned lixivants, thiosulfate is the one of the most considerable attractive since it is non-toxic, low-corrosive as well as highly selective for Au (Arima et al., 2002; Karavasteva, 2010). Despite those advantages, its application in real-scale plant is limited by a drawback that there is no acceptable method for recovery of Au ions from leached solution to date. Adsorption using activated carbon (McDougall et al., 1980), and cementation (i.e., reductive-deposition) using base metals such as zinc (Hsu and Tran, 1996; Miller et al., 1990; Vilchis-Carbajal et al., 2000), copper (Cu) (Nguyet et al., 1997; Syed, 2012), and Al (Syed, 2012; Wang et al., 2007) are most typical Au recovery methods in cyanide and halides, but the recovery effects of both former and latter are negligible in thiosulfate medium. Gallagher et al. (1990) reported that among the various leachates that could form Au complex, the adsorption effectiveness of Au thiosulfate complex on activated carbon is most inefficient ($\text{SCN}^- > \text{SC}(\text{NH}_2)_2 > \text{CN}^- > \text{S}_2\text{O}_3^{2-}$). Similarly, Jiexue and Quian (1989) recorded about 30% of Au recovery on activated carbon in thiosulfate system because of its low affinity for Au thiosulfate ions ($\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$), and Navarro et al. (2006) also reported only 13% recovery of Au thiosulfate ions on activated carbon under the following conditions: 10 mg/l Au, 0.8 M NH_4OH , 0.2M $\text{S}_2\text{O}_3^{2-}$, pH 10.5, Temperature 25 °C, time 8 h. Because of this limitation, cementation of Au ions by metal powders might be considered as an alternative technique in thiosulfate system. Cementation is the electrochemical precipitation (i.e., reductive deposition) that transform the Au ions to metallic Au using other base metals acting as reductant. Zinc powder could be basically applied for recovering Au in thiosulfate solution because of its lower standard redox potential (Zn^{2+}/Zn : -0.76 V) than that of Au thiosulfate complex ($\text{Au}(\text{S}_2\text{O}_3)_2^{3-}/\text{Au}$: 0.17 V), but previous research reported that high consumption of zinc by cupric ion in thiosulfate ($\text{Cu}(\text{S}_2\text{O}_3)_2^{2-}$) is required (Alymore and Muir, 2001; Berezowsky and Sefton, 1979). In the case of Cu, it requires even larger amount than zinc about 4-fold since it could dissolve in thiosulfate solution by forming the Cu thiosulfate complex (Arima et al., 2002; Guerra et al., 1999; Jeon et al., 2018). Aluminum might be considered as a good candidate for recovering Au if only standard redox potential is considered (Al^{3+}/Al : -1.66 V), but this low value is resulting in the rapid formation of Al oxide layer on its surface, which could suppress the electron transfer from Al to Au thiosulfate complex,

hence Au recovery efficiency decreased (Jeon et al., 2018; Karavasteva et al., 2010; Panao et al., 2018). For this reason, development of alternative method to efficiently recover Au from ammonium thiosulfate system is required.

A previous study of the authors showed a result that Au extraction suppressed during thiosulfate leaching of printed circuit boards (PCBs) due primarily to the re-deposition of extracted Au by coexistence of Cu with Al in PCBs via galvanic effect (Jeon et al., 2018a, 2018b). Based on this result, we could purpose a new idea: that is, efficient Au recover can be expected when Al as a reductant and other material that is cheaper than Cu as well as manageable at the post-recovery stage such as activated carbon are coexisted in thiosulfate system. To the best of our knowledge, this is the first idea that tackles the synergistic effects of Al and activated carbon on Au recovery in thiosulfate system. For the purpose, Au recovery was conducted using sole either activated carbon or Al as well as activated carbon and Al mixture in ammonium thiosulfate system.

6.2 Materials and methods

6.2.1 Aluminum and activated carbon

For the Au recovery experiments, powder type of Al ($-75\ \mu\text{m}$, 99.99%, Wako Pure Chemical Industries, Ltd., Japan) and activated carbon ($-45\ \mu\text{m}$, 99.99%, Wako Pure Chemical Industries, Ltd., Japan) were used.

6.2.2 Recovery of gold ions from ammonium thiosulfate solution

Ammonium thiosulfate solutions with pH around 9.5–10 containing 1 M $\text{Na}_2\text{S}_2\text{O}_3$, 0.5 M NH_3 , 0.25 M $(\text{NH}_4)_2\text{SO}_4$ and 10 mM CuSO_4 (Wako Pure Chemical Industries, Ltd., Japan) with 100 mg/l of Au ions were used in the Au recovery experiments. The solution containing 100 mg/l of Au ions was prepared by dissolving 0.01 g of Au powder (99.999%, Wako Pure Chemical Industries, Ltd., Japan) in 100 ml of the ammonium thiosulfate solution using 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 Au recovery experiments, 0.15 g of Al and/or 0.15 g of activated carbon powders with 10 ml of Au-ammonia thiosulfate solution were mixed in 50-ml Erlenmeyer flask at 25 °C (shaking amplitude of 40 mm and frequency of 120 min^{-1}). After 24 h, the leachate and residue were separated by filtration using a 0.2 μm syringe-driven membrane filters (LMS Co., Ltd., Japan). The residues were washed thoroughly with deionized water (18 $\text{M}\Omega\cdot\text{cm}$, Mill Q[®] Integral water purification system, Merck Millipore, USA), dried in a vacuum oven at 40 °C, and analyzed by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX, SSX-550, Shimadzu Corporation, Japan) while the filtrates were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES, ICPE-9820, Shimadzu Corporation, Japan)

(margin of error = $\pm 2\%$).

6.3 Results and discussion

Figure 6-1(a) shows the Au recovery results using either activated carbon or Al, as well as mixture of both. Au recovery ratio (Au_R) was calculated according to the following equation:

$$Au_R = \frac{[Au_B] - [Au_A]}{[Au_B]} \quad (6-1)$$

where Au_R denotes the Au recovery ratio, Au_B and Au_A denote the Au concentration before and after Au recovery experiments, respectively. As many previous studies have shown, the Au recovery in thiosulfate solution by both sole activated carbon and sole Al powder is negligible because of low affinity to Au thiosulfate complex as well as insulating oxide film on Al (Jeon et al., 2018; Syed, 2012). In the case of Al and activated carbon mixture, however, Au recovery significantly increased and over 99% of Au recovery was obtained. Residue obtained after recovering Au ions using activated carbon and Al mixture was examined in more detail by SEM-EDX analysis. Figure 6-1(b) shows SEM photomicrograph of the representative particles as well as corresponding EDX spectra of each point (b-1, b-2, and b-3). The b-1 and b-2 points are the surface of Al and activated carbon, respectively, and EDX spectra shows that Al and oxygen peaks were observed in b-1 point, which is surface of the Al particle, while carbon, oxygen, and adsorbed sodium as well as sulfur peaks were observed in b-2 point, which is the surface of the activated carbon particle. In the case of b-3 point, Al and Au peaks were observed, indicating that bright surface on Al is Au. A noteworthy thing is that not only Al and Au peaks but also carbon peak was observed at b-3 point, and this carbon peak shows everywhere where Au peaks were observed, indicating that Au does not present directly on Al (Au-Al) but indirectly on Al via activated carbon (Au-activated carbon-Al). Based on these results, mechanism involved in the recovery of Au via Al with activated carbon is attributed as follows; Al has high affinity for oxygen, so the surface is always covered with oxide film. Although this oxide film is very thin ($\sim 10\text{\AA}$), it wears resistant, thereby behaving as an electrical insulator (Diggle et al., 1968; Poinern et al., 2011). During shaking, however, (1) nano-scratch of oxide film on Al could be generated, very fine activated carbon particles (less than $5\text{ }\mu\text{m}$) that wandered off from original activated carbon powder could stuck into this crack, and Au thiosulfate complex ($\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$) is finally precipitated on the surface via activated carbon as shown in Fig. 6-2(a). (2) The thin oxide layer on Al possesses dielectric property of the Al capacitor that could store potential energy in the electric field (Diggle et al., 1968). In this case, when the Al in contact with activated carbon, electrons that were stored in thin oxide film could transfer to Au thiosulfate complex and Au was recovered on activated carbon attached to Al particle (Fig. 6-2(b)). Potential mechanisms are those two, but most of the Au is in presence of cracks on Al as shown in Fig. 6-1(c), indicating that the first mechanism (i.e., because of nano-cracks on Al particle) might be the main cause in Au recovery by activated carbon and Al. This simple and highly effective Au recovery method could

be widely applicable to the industrial process that utilizing the ammonium thiosulfate medium. Moreover, not only recovery of Au ions from ammonium thiosulfate system but also recovery of hazardous elements from waste water in varying systems might be possible via the present methods.

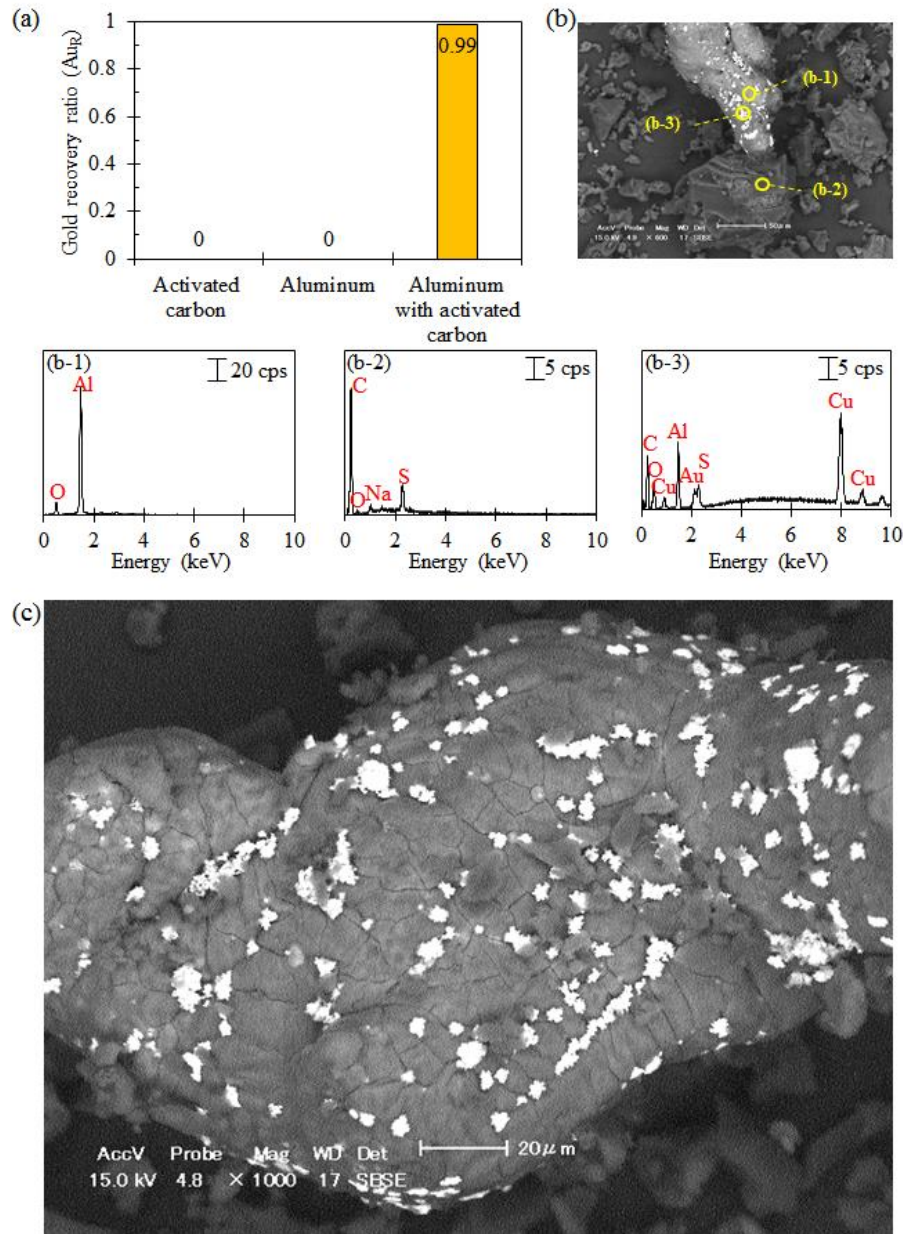


Fig. 6-1. (a) Au recovery results using either sole activated carbon or sole aluminum, and

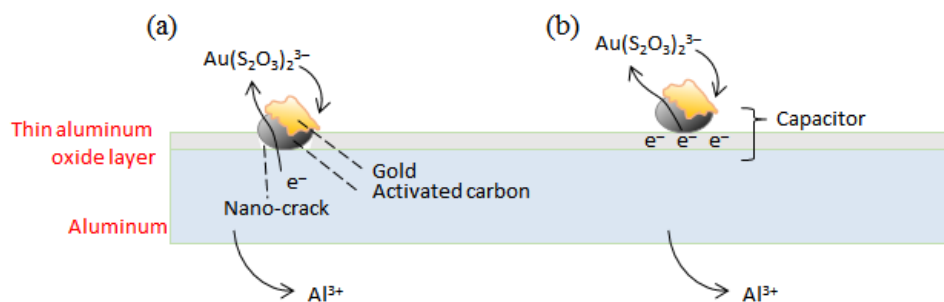


Fig. 6-2. Schematic diagram of the Au recovery mechanisms by nano-cracks on aluminum particle.

6.4 Summary

This study investigated the Au recovery in ammonium thiosulfate system using synergistic effect of activated carbon and Al. When either sole activated carbon or sole Al was presented in ammonium thiosulfate system, Au recovery was negligible. When both Al and activated carbon present together, however, Au recovery significantly increased and about over 99% of Au recovery was obtained via nano-scratches as well as dielectric property of the thin Al oxide film on Al.

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CHAPTER 7

GENERAL CONCLUSION

Worldwide demand for electric and electronic equipment (EEE) has been steadily increasing due to rapid advancements in technology, which lead to the higher generation of waste electric and electronic equipment (WEEE). WEEE includes not only industrial electronic wastes (e.g., copy machines and automated teller machines) and home appliances (e.g., refrigerators, television sets, and washing machines) but also small electronic gadgets and devices such as remote controls, game consoles, and mobile phones. Among hand-held gadgets, mobile phones are the most ubiquitous, but their life-cycle is probably the shortest (ca. 2 years), which leads to the significant generation of waste mobile phones annually. Mobile phones are complex devices composed typically of a plastic frame, liquid crystal displays (LCD), and a keyboard as well as printed circuit boards (PCBs) containing integrated circuits and other electronic components. PCBs in mobile phones contain a wide variety of materials including not only hazardous elements (e.g., arsenic, mercury, and cadmium) that could pollute the environment when burned or disposed of in landfills but also valuable metals like copper (Cu), aluminum (Al), iron (Fe), and gold (Au). Recent studies have reported that the average Au content of PCBs is often several tens or hundreds of times higher than natural ores. This means that recycling and recovery of Au from waste mobile phones are needed for resources sustainability and conservation.

To recover the Au from waste mobile phones, both pyrometallurgical and hydrometallurgical techniques have been applied. Pyrometallurgical treatment, however, requires high initial capital and operational costs, so hydrometallurgical technique is a good alternative in areas without any pyrometallurgical facilities. In hydrometallurgy, Au is first leached in suitable aqueous solutions and then recovered by adsorption, precipitation or cementation. Cyanide and the halides (e.g., aqua regia) are two of the most widely used extractants of Au largely because of their high extraction efficiency. Although effective, alternative lixivants have been developed because cyanide is very toxic while the halides are highly corrosive. Among these alternatives, ammonium thiosulfate is attractive because it is non-toxic, less corrosive, and highly selective for Au. Despite these many advantages, its use in recycling is still limited primarily because of two drawbacks: (1) Au extraction is low at high solid-to-liquid ratio (S/L) and (2) there is no acceptable method for recovery of Au ions from leached solution to date. The present study investigated the leaching of Au in waste mobile phones and identified what makes the Au extraction low at high S/L. After that, to minimize the effects of the interfering requisites, pretreatment of the feed materials prior to ammonium thiosulfate leaching was carried out and leaching was conducted to determine the effects of physical separation techniques on Au extraction efficiency. Finally, a novel method of Au ions recovery from leached solution was developed.

Chapter 1 gives the background, importance and objectives of the study.

In Chapter 2, previous studies on waste mobile phone recycling by physical and chemical techniques (i.e., pyrometallurgical and hydrometallurgical techniques) were reviewed.

In Chapter 3, leaching of Au from waste mobile phones were conducted. Leaching experiments were performed by mixing 0.1-1 g of ground samples with 10 ml solution composed of 0–3 M $\text{Na}_2\text{S}_2\text{O}_3$, 0–10 mM CuSO_4 , 2.5–250 mM $(\text{NH}_4)_2\text{SO}_4$, and 5–500 mM NH_4OH . The leaching experiments were done at 25 °C with a shaking time of 0-75 h and a total ammonium concentration of 0.01–1 M (pH 9–10). The Au extraction increased with increasing shaking time, total ammonium, and CuSO_4 concentration. Increasing the concentration of $\text{Na}_2\text{S}_2\text{O}_3$ also enhanced the extraction of Au but only up to ca. 1M. Higher than this value, however, the extraction of Au from waste mobile phones decreased. The maximum amount of Au extracted 86% using 1 M of $\text{Na}_2\text{O}_2\text{O}_3$, 10 mM of CuSO_4 , and 1 M of total ammonium concentration with a sample amount of 0.1 g and treatment time of 24 h.

Chapter 4 identified the interfering metal(s) that causing cementation/precipitation of extracted Au ions during ammonium thiosulfate leaching. After leaching experiments in the previous section, 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 Cu and Al, implying that extracted Au ions were likely re-deposited during leaching onto Cu and Al found in waste mobile phones 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.

After identifying the interfering metals (i.e., coexisting Cu and Al), we conducted various physical separation techniques (i.e., jig, hybrid jig, magnetic separation, flotation, and sink-float separation) aimed at separating those base metals from Au-containing fraction in Chapter 5. Waste mobile phones were coarsely crushed (+2–10 mm) and then treated by jig separation to concentrate printed circuit boards (PCBs). The results showed that over 96% of PCBs was recovered in the bottom layers via jig separation. The concentrated PCBs were further crushed to improve liberation of Au-containing parts and treated by magnetic separation followed by jig separation. Over 99% of Fe-bearing components were separated by magnetic separation while Au was separated from Cu and Al by jig separation and was recovered in the middle layers. The fine fraction generated from 1st crushing operation was treated by flotation and sink-float separation.

Over 99% of combustibles and 80% of Au were recovered as froth while over 80% of Cu and Fe were recovered as tailing. In the subsequent sink-float process, Au-containing plastics were concentrated in the sink while plastics without Au were recovered as floating particles. The fine fraction generated by the 2nd crushing operation was treated by magnetic and hybrid jig separation. Over 99% of Fe components were separated via magnetic separation and over 60% of Au and 52% of Al were concentrated in the upper layers and separated from Cu by hybrid jig separation. Leaching results using ammonium thiosulfate solution showed that Au extraction was significantly improved (about 11-fold) after physical pretreatments.

In the previous section, Chapter 4, results showed that Au extraction suppressed during thiosulfate leaching due primarily to the re-deposition of extracted Au by coexistence of Cu with Al in PCBs via galvanic effect. Based on this result, we could purpose a new idea: that is, efficient Au recover can be expected when Al as a reductant and other material that is cheaper than Cu as well as manageable at the post-recovery stage such as activated carbon is coexisted in thiosulfate system. The present section, Chapter 6, deals with the recovery of Au ions from thiosulfate medium via synergistic effect by Al with activated carbon. Au recovery results were found that when either sole activated carbon or sole Al was present in thiosulfate solution containing Au ions, its recovery is negligible under the following parameters: 0.15 g of activated carbon or Al with 10 ml thiosulfate solution containing 100 mg/l of Au ions at 25 °C for 24 h with 120 rpm. When both 0.15 g of activated carbon and 0.15 g of Al were coexisting in the solution, however, Au recovery significantly increased and obtained over about 99% of Au recovery via two mechanisms: (1) the nano-scratches of the oxide film on Al caused by a collision between particle-particle during shaking are covered with activated carbon, which in turn makes it easier to transfer the electrons from the Al, and finally Au ions are deposited on them, and (2) due to the dielectric property of the thin Al oxide film, accumulated electrons in oxide film donate to the attached activated carbon on Al where Au ions are deposited on it.

Finally, Chapter 7 gives the general conclusion of the present study.

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그리고 마지막으로 항상 응원해주시고 저의 든든한 버팀목이 되어주신 사랑하는 나의 부모님, 그리고 동생에게 진심으로 감사의 말씀을 전합니다.