



Selective recovery of gold from waste mobile phone PCBs by hydrometallurgical process

Eun-young Kim^a, Min-seuk Kim^b, Jae-chun Lee^{b,*}, B.D. Pandey^c

^a Department of Material Science and Engineering, Penn State, University Park, PA 16802, USA

^b Mineral Resources Research Division, Korea Institute of Geoscience & Mineral Resources (KIGAM), Daejeon 305-350, Republic of Korea

^c Metal Extraction & Forming Division, National Metallurgical Laboratory (NML), Jamshedpur 831007, India

ARTICLE INFO

Article history:

Received 13 May 2011

Received in revised form

27 September 2011

Accepted 10 October 2011

Available online 15 October 2011

Keywords:

Gold

Copper

PCBs (printed circuit boards)

Electro-generated Cl₂ leaching

Amberlite XAD-7HP

ABSTRACT

The leaching of gold from the scrap mobile phone PCBs by electro-generated chlorine as an oxidant and its recovery by ion exchange process was investigated. The leaching experiments were carried out by employing separate leaching reactor connected with the anode compartment of a Cl₂ gas generator. The leaching of gold increased with increase in temperature and initial concentration of chlorine, and was favorable even at low concentration of acid, whereas copper leaching increased with increase in concentration of acid and decrease in temperature. In a two-stage leaching process, copper was mostly dissolved (97%) in 165 min at 25 °C during the 1st stage leaching in 2.0 mol/L HCl by electro-generated chlorine at a current density of 714 A/m² along with a minor recovery of gold (5%). In the 2nd stage gold was mostly leached out (93% recovery, ~67 mg/L) from the residue of the 1st stage by the electro-generated chlorine in 0.1 mol/L HCl. Gold recovery from the leach liquor by ion exchange using Amberlite XAD-7HP resin was found to be 95% with the maximum amount of gold adsorbed as 46.03 mg/g resin. A concentrated gold solution, 6034 mg/L with 99.9% purity was obtained in the ion exchange process.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Due to rapid economic growth, technological advances and the obsolescence of electronic equipment in the market, the amount of waste mobile phone generation has been growing. It has resulted in hundreds of millions of mobile phones that are taken out of use each year [1]. Besides, increased production of mobile phone would also increase the amount of the waste generation during the manufacturing process. Mobile phone typically consists of a body, printed circuit boards (PCBs), liquid crystal display (LCD), key board, antenna, etc. Among these parts PCBs contain hazardous materials as well as a variety of valuable metals. Therefore, efficient recycling of mobile phone PCBs should be required to secure the metallic resources and to prevent environmental pollution at the same time. Especially, the gold recovery from the used PCBs from the electronic industry has received the most attention because of the presence of a considerable quantity (300–350 mg/kg) of this metal which is generally 100 times higher in concentration than that of the gold ore [2].

Currently, recycling technology for recovery of valuable metals from waste PCBs can be divided into two major steps: (i) upgrading

the metal content by mechanical pre-treatment, and (ii) extraction and refining to recover the metals by pyro-/hydro-metallurgical method. In the pyrometallurgical process, a conventional method, it is difficult to recover some metals such as Al, Fe, and rare metals, besides a loss of precious metals. In the last few decades, hydrometallurgical processes have been given considerable attention to recover precious metals as well as rare metals from the waste PCBs [2].

Leaching is the first step in the extraction of gold using hydrometallurgical process. Cyanide leaching [3] has been the predominant method for more than one century due to the selectivity and stability of dicyanoaurate complex in spite of the use of toxic reagents [4]. Several substitutes have recently been proposed as the non-cyanide lixiviants such as thiosulfate [5,6] and aqua regia [7]. Hung et al. [5] reported the leaching of gold from non-populated scraps of PCBs by thiosulfate. The process has the disadvantages such as excessive consumption of reagent with the oxidation of thiosulfate and preferred leaching of copper, the major component of PCBs, high cost of the reagent, and difficulty in recovery process [8]. Aqua regia leaching of gold from computer circuit board scrap [7,9] was also reported to be an effective option, but generation of toxic waste [4] could be a deterrent because of more stringent environmental regulations.

Our research group has been carrying out the leaching of metals from waste PCBs by utilizing electro-generated chlorine [10–12].

* Corresponding author. Tel.: +82 42 868 3613; fax: +82 42 868 3415.
E-mail address: jclee@kigam.re.kr (J.-c. Lee).

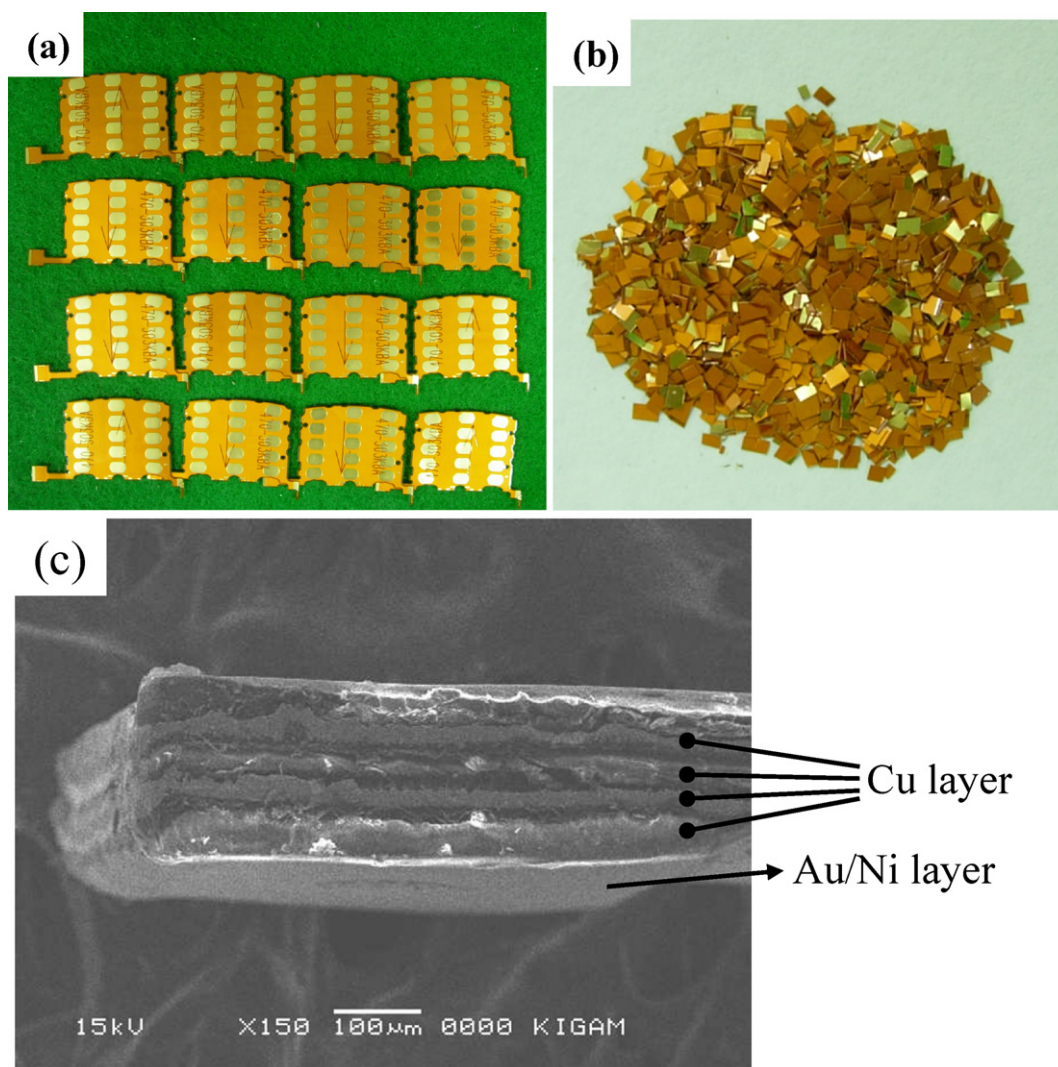


Fig. 1. Scrapped PCBs of mobile phones used for the experiment: (a) as received, (b) after cutting, and (c) SEM image.

The process has the advantage of leaching precious as well as base metals from waste PCBs because of acquiring high oxidation potential. Also, it is considered environment friendly because the electro-generated Cl_2 leaching [10–12] can operate in the closed system and chlorine can be reduced during leaching. The previous studies focused on the leaching mechanism and behavior of copper by electro-generated chlorine using two different reactors: (i) a combined reactor facilitated with simultaneous electro-generation of chlorine and leaching; (ii) a separate leaching reactor connected with anode compartment of a chlorine gas generator [11]. In the combined reactor, the decrease of current efficiency by the oxidation of Cu(I) leached from PCBs to Cu(II) and the low solubility of CuCl were noticed, whereas in the separate reactor no such drawbacks appeared.

This study is focused on the development of a process for selective leaching of gold using the electro-generated chlorine employing the separate reactor and then recovering gold by ion exchange resin. The effect of the process parameters such as acid concentration, temperature, concentration of chlorine, and pulp density has been investigated to understand the mechanism of metal leaching; results are discussed in this paper. Ion exchange process is introduced for separation and enrichment of gold. A more effective process for recovery of gold from waste PCBs could then be established.

2. Experimental

2.1. Leaching by electro-generated chlorine

The non-populated mobile phone PCBs scrap used for the leaching experiment was defective materials obtained from a manufacturer of PCBs (Fig. 1(a)). The chemical composition of the sample is listed in Table 1. The PCBs consist of 66% Cu, 2.30% Ni and 0.045% Au. For leaching experiment, the sample was cut into small pieces of size 2–3 mm unless stated otherwise (Fig. 1(b)). The SEM image of the sample as shown in Fig. 1(c) clearly indicated that copper was inserted between the resin and ceramic materials and gold/nickel was plated on the surface as a thin layer.

Fig. 2 shows the schematic diagram of reactors. The separate reactor consisted of an electrolytic cell for chlorine generation and a separate vessel (reactor) for the metal leaching. The electrolytic

Table 1
Chemical composition of the sample.

	Au	Cu	Ni	Others ^a
wt.%	0.045	66.00	2.30	31.66

^a Ceramics (Al_2O_3 , SiO_2) and resin.

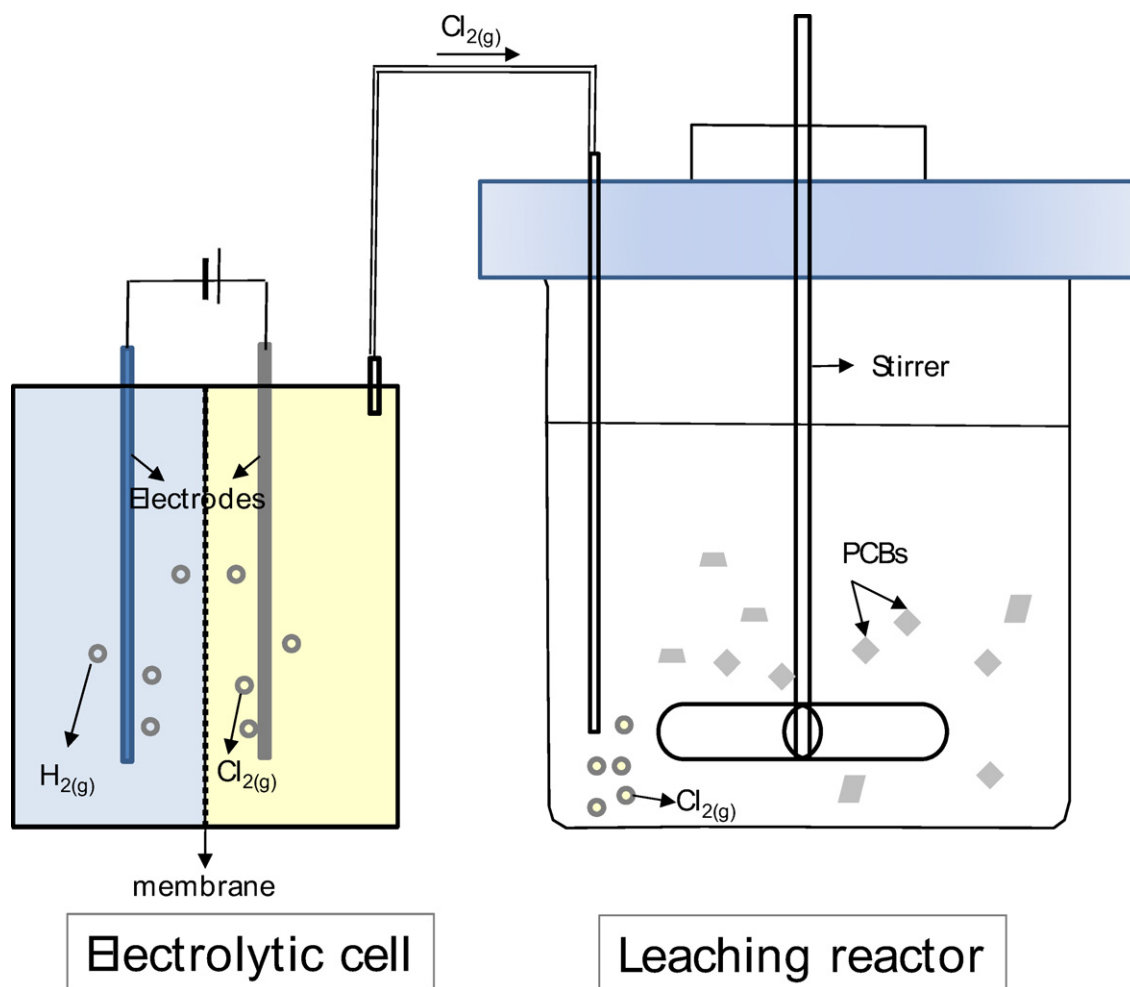


Fig. 2. Leaching apparatus.

cell of acrylic of size 18 cm × 9 cm × 12.5 cm was divided into two compartments with anion exchange membrane (Neosepta AMX, Tokuyama Co.). Two cathodes and anodes were used in these experiments. Both electrodes were made of high purity graphite rods (20 cm (*l*) × 0.8 cm (*d*)) with effective area in the solution being 14.0 cm²/electrode. The anode and cathode compartment of the electrolytic cell was poured 200 mL of 4.0 mol/L, 6.0 mol/L hydrochloric acid solution, respectively and then the anode compartment was saturated with electro-generated chlorine before starting the leaching by supplying constant current. After saturation of anode compartment of the electrolytic cell, 300 mL of hydrochloric acid was poured into the leaching reactor and the solution was heated to the desired temperature by electrically controlled heating bath. A 5.0 g sample except for the experiments of the effect of pulp density was then added for the experiment. The electro-generated chlorine gas from the electrolytic cell was passed to the leaching reactor through a tube. The solution in the leaching reactor was agitated by a PTFE-coated steel impeller at a rotating speed of 500 rpm.

The samples at the predetermined time periods were taken out from the reactors and were analyzed by atomic absorption spectrometer (AAS, AAnalyst 400, PerkinElmer Inc.). The oxidation and reduction potential (ORP, mV vs. Ag/AgCl) in the leach solution was measured and total concentration of oxidants (residual Cl₂(aq) + Cu(II)) was analyzed by the iodide–thiosulfate titration method [13].

2.2. Recovery of gold from leach liquor

2.2.1. Ion exchange of gold by ion exchange resins

In order to investigate the recovery of gold by ion exchange process three resins (Amberlite XAD-7HP, Bonlite BA304, and Purolite A-500) were used. The resins were thoroughly washed with water and dried in oven at 50 °C. A glass column [1 cm (ID) × 25 cm (height)] with a stopcock and a porous disk affixed at the bottom was used in all experiments. The glass column was loaded with 1.0 g (1 bed volume of resin, BV = 4.6 mL) of the resins. After each experiment, the resin filled in the column was washed with a large volume of distilled water and stored in water for the next set of experiment. For each experiment a 5 BV of leach liquor was prepared through 2nd stage leaching by electro-generated chlorine. The solution was passed through the column at a rate of 1.0 mL/min.

Purolite A-500, a macroporous strong base resin was supplied by Purolite Company, whereas Bonlite BA304 (a gel strong base resin) and Amberlite XAD-7HP (a nonionic resin) were obtained from Born Chemical Company and Rohm and Hass, respectively.

2.2.2. Elution in column

The loaded resin was eluted by 0.1 mol/L HCl. The eluted solution was then diluted to 5 vol.% HCl and was analyzed for copper and gold by AAS. The adsorbed gold complex on the column after elution by 0.1 mol/L HCl was eluted again with 1.0 mol/L HCl in acetone and acetone in the eluted solution was evaporated near to dryness.

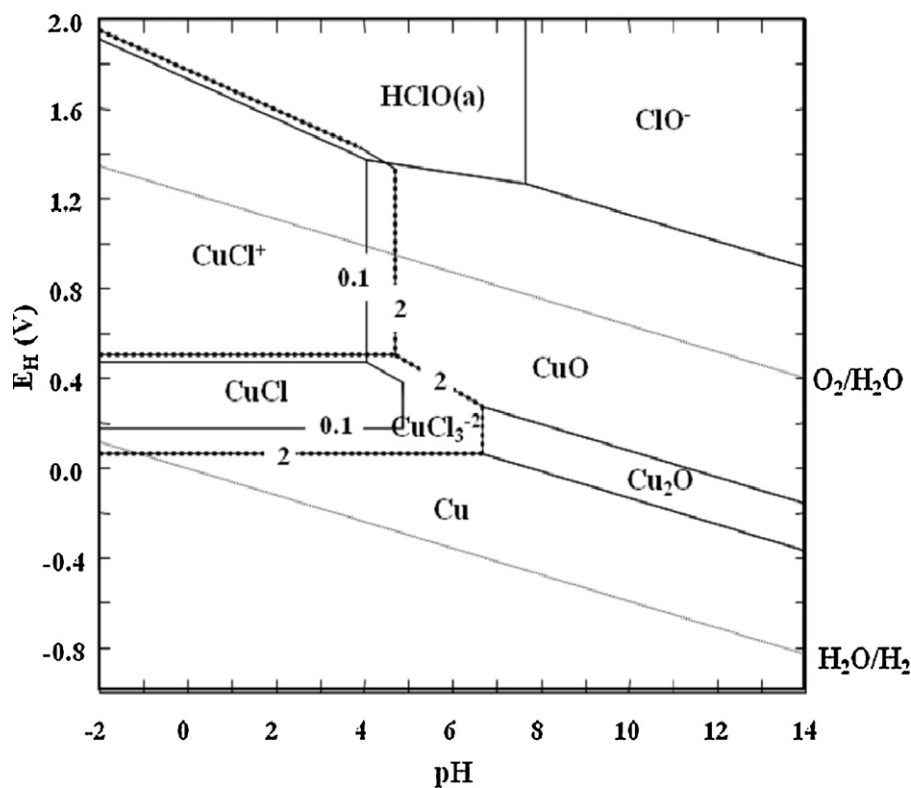


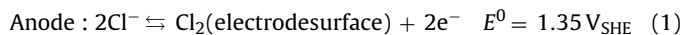
Fig. 3. Cu–Cl–H₂O system at 25 °C ($\{Cl^-\} = 0.1, 2 \text{ mol/L}$, $\{Cu\} = 0.1 \text{ mol/L}$).

The residue was dissolved in 5 vol.% HCl and the final solution was analyzed for copper and gold by AAS.

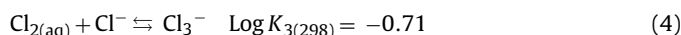
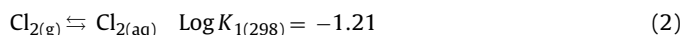
3. Results and discussion

3.1. Leaching by electro-generated chlorine

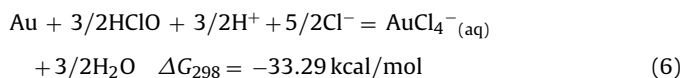
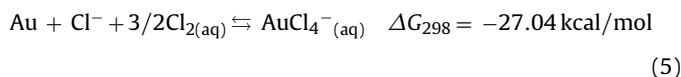
Chlorine generation from hydrochloric acid solution can be represented by the following reaction:



The chlorine gas by Eq. (1) dissolves in water as follows (where $\text{Log } K_{1-3}$ being the equilibrium constants at 298 K):

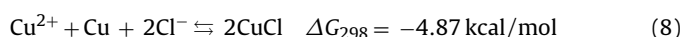
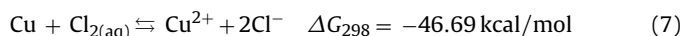


The dissolution of gold takes place as [14]:



where ΔG is the Gibbs free energy change at 298 K.

The dissolution of copper can be expressed as follows in chloride media [11]:



Thus, thermodynamically the reaction of chlorine with copper (Eq. (7)) is more favorable (lower ΔG_{298} value) than that of gold (Eq. (5)) whereas, the feasibility of reaction of hypochlorous acid (HClO) with gold is higher (Eq. (6)) than the reaction with chlorine (Eq. (5)) under the same condition.

In the presence of chloride, gold and copper dissolve to form Au(III) and Cu(I), Cu(II) chloride complexes, $AuCl_4^-$, $CuCl^+$, $CuCl_3^{2-}$, and $CuCl$ which is evident from the potential (E_h)–pH diagram shown in Figs. 3 and 4 [15]. As the chloride concentration increased from 0.1 to 2.0 mol/L, the stability region of Cu(I) complexes (Fig. 3) and $AuCl_4^-$ (Fig. 4) increased with respect to pH and the redox potential. The E_h –pH diagrams also show that copper as cuprous ion can be leached out at lower potential and higher chloride concentration for complexation and gold needs relatively higher redox conditions and remains in the solution even at low acid concentration.

3.1.1. Effect of acid concentration

Fig. 5 shows the percentage leaching of copper and gold as a function of acid concentration in the range 0.01–2.0 mol/L at a fixed chloride concentration of 2.0 mol/L by adding NaCl and 25 °C when electro-generated chlorine at 714 A/m² current density (2.0 A current) was passed in the leach reactor. Raising the acid concentration to 1.0 mol/L at a fixed chloride concentration (2.0 mol/L) has increased the copper leaching with a substantial decrease of gold leaching till the period of 60 min. One of the most important factors in the chloride leach system is the pH level, since chlorine chemistry is pH dependant [8,16,17]. Fig. 6 shows the chlorine distribution with pH in acidic range which is calculated from the equilibrium constants given in Eqs. (2) through (4). When the pH falls below 2, dominant species of chlorine are $Cl_{2(aq)}$, Cl_3^- , and above pH 2 HClO is the dominant species. Besides, hypochlorous acid (HClO) (Eq. (6)) has a higher oxidizing power towards gold which is evident from the lower ΔG value than that with aqueous chlorine to form $AuCl_4^-$ complex (Eq. (5)). As acid concentration increases, the distribution

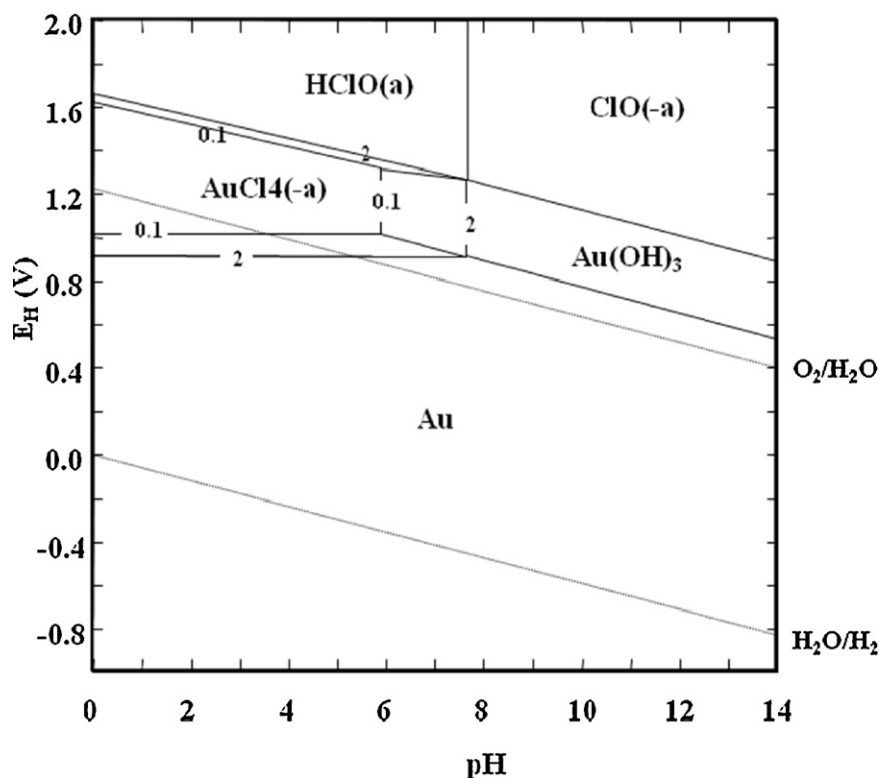


Fig. 4. Au–Cl–H₂O system at 25 °C ($\{Cl^{-}\} = 0.1, 2 \text{ mol/L}$, $\{Au\} = 0.5 \times 10^{-3} \text{ mol/L}$).

of the hypochlorous acid decreases and disappeared at the concentration of acid $>1.0 \text{ mol/L}$. Since the gold leaching increased with decreasing acid concentration (Fig. 5(b)) thus gold leaching seems to mainly depend on the concentration of hypochlorous acid and consequently on the oxidation potential as well. On the other hand, copper leaching increased with increasing acid concentration as shown in Fig. 5(a). Therefore, copper leaching may be dependent on the solubility of chlorine regardless of oxidation power of chlorine species.

3.1.2. Effect of temperature

Fig. 7 shows the pattern of the percentage leaching of copper (Fig. 7(a)) and gold (Fig. 7(b)) from the PCBs sample in solution as a function of temperature at a fixed HCl concentration of 2.0 mol/L and applied current density of 714 A/m^2 (2.0 A current) to generate chlorine gas. As can be seen a decrease in temperature increased the percentage leaching of copper while gold leaching mostly decreased. It is evident from Fig. 7(a) that the leaching of copper followed the order for temperature $25^\circ\text{C} > 35^\circ\text{C} > 50^\circ\text{C}$ in 120 min, with the copper leaching of 75.4%, 58.5%, and 53.5%, respectively. The leaching of gold (Fig. 7(b)) was retarded in initial stages at all temperatures when the copper leaching was active. In particular the low gold leaching rate was noticed up to 40 min at 25°C correspond to the lowest concentration of residual chlorine and thereafter it increased drastically with increasing concentration of residual chlorine which meant high oxidizing condition. It was reported that the leaching of copper and gold was controlled by diffusion [18] and chemical reaction [19], respectively. Accordingly, the gold leaching would be more affected by temperature than that of copper. However, in this system the chlorine solubility [20] and residual chlorine concentration (Fig. 7(b)) seem to play the major role.

3.1.3. Effect of initial concentration of chlorine

The percentage leaching of copper and gold as a function of initial concentration of chlorine in 2.0 mol/L HCl solution at 25°C and 714 A/m^2 current density (2.0 A current) is given in Fig. 8. The initial chlorine supplied from the anode in the electrolytic cell was titrated by the iodide–thiosulfate method to analyze total aqueous chlorine concentration [13]. As presented in Fig. 8(a), raising the initial concentration of chlorine increased the extent of copper leaching till 60%. Subsequently, the increase of copper leaching was almost similar regardless of the initial concentration of chlorine. Interestingly the gold leaching (Fig. 8(b)) was rapid with increasing initial concentration of chlorine due to presence of sufficient oxidants. Also, when the initial concentration of chlorine was increased from 0 to 3.46 g/L , the leaching of gold started rapidly and the retardation of gold leaching disappeared. This indicated that copper and gold can be selectively leached by adjusting the concentration of chlorine in the solution.

3.1.4. Effect of particle size

The percentage leaching of copper and gold as a function of particle size at 25°C , 2.0 mol/L HCl, 17 g/L pulp density and 714 A/m^2 (2.0 A current) current density is given in Fig. 9. As is evident from Fig. 9(a), decreasing the particle size increased the extent of copper leaching from 30% to 97% in 120 min. Gold leaching (Fig. 9(b)) was retarded with decreasing particle size although, the effect was not that severe when sample without cutting (average size – $35 \text{ mm} \times 40 \text{ mm}$) was treated. Mention may particularly be made of the retarded dissolution of gold from the finest size particles ($-2/+1 \text{ mm}$) with increased surface area due to the favorable copper leaching with the presence of insufficient chlorine thereafter to leach out gold. This may also be attributed to the galvanic effect for dissolving copper preferentially as compared to gold.

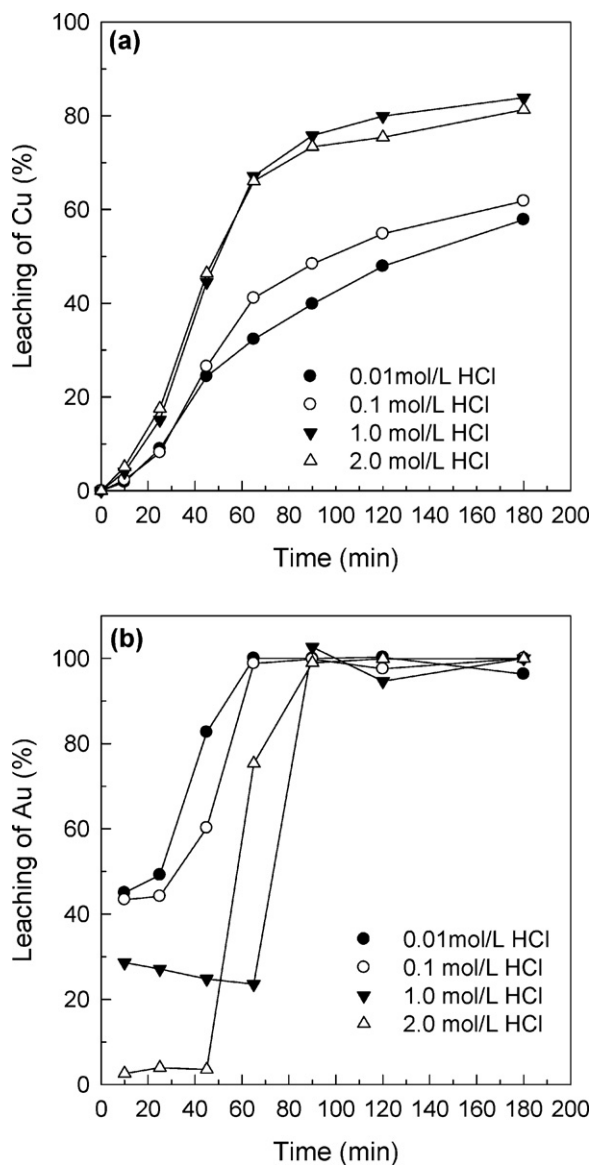


Fig. 5. Effect of acid concentration on (a) Cu and (b) Au leaching in fixed chloride concentration, 2.0 mol/L $[\text{Cl}^-]$ (current density, 714 A/m²; leaching time, 180 min; stirring speed, 600 rpm; pulp density, 17 g/L; temperature, 25 °C; particle size, $-3/+2$ mm).

3.1.5. Effect of pulp density

The leaching behavior of copper and gold was investigated while varying the pulp density in 2.0 mol/L HCl solution at 25 °C and 180 min leaching time by electro-generated chlorine at 714 A/m² (2.0 A current) current density. Fig. 10 shows the copper leaching with time and copper concentration in 180 min with increase in the pulp density. As can be seen the increase in pulp density from 17 to 40 g/L resulted in the copper leaching of around 97% or slightly lower in 180 min. At a pulp density above 40 g/L the leaching rate decreased due to the insufficient concentration of chlorine. Therefore, the pulp density of 40 g/L may be considered as optimum for copper leaching at 25 °C in 180 min under the above conditions with the maximum leaching of 95% and the concentration of 25 g/L Cu in the solution.

The leaching of gold from the PCBs sample was investigated at 25 °C with time under the same condition as given in Fig. 10 and results are plotted in Fig. 11. It is apparent that the starting point of gold leaching was retarded with increasing pulp density from 17 to 45 g/L. In all cases the leaching of gold was very low (Fig. 11)

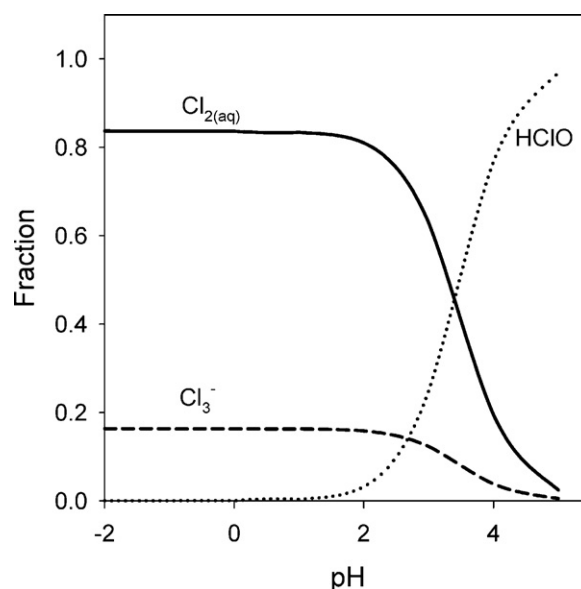


Fig. 6. Chlorine distribution with pH at 25 °C.

till major part of copper dissolved (Fig. 10) and then increased to almost completely within a short time. The leaching of gold was particularly below 5% in 165 min and after that it drastically increased to 99% even at the high pulp density of 40 g/L. From this result it appears that gold and copper can be selectively leached by electro-generated chlorine in 2.0 mol/L hydrochloric acid solution for 165 min at 40 g/L pulp density and 25 °C.

To recover copper and gold selectively, the leaching process by electro-generated chlorine was divided into two stages (Table 2), leach-1 and leach-2. The 1st stage leaching with electro-generated chlorine with the particles of size $-2/+1$ mm was terminated at the optimum condition such as: pulp density – 40 g/L, leaching time – 165 min, temperature – 25 °C, and acid concentration – 2.0 mol/L HCl, for which the ORP value was below 350 mV_{Ag/AgCl}. In the leach liquor the concentrations of copper and gold were found as 24.0 g/L and 0.9 mg/L, respectively. After filtration, the residue was leached again in 0.1 mol/L HCl solution by electro-generated chlorine with 714 A/m² (2.0 A current) current density (2nd stage leaching) at 25 °C, leaching time 10 min and pulp density 160 g/L. Gold was leached out almost completely (93%, ~67 mg/L) with more diluted concentration of copper (607 mg/L) in solution than that obtained in stage-1. It may be noted that the copper concentration in the 2nd stage leaching was 40 times lower than that of the 1st stage and gold was concentrated 4 times higher.

3.2. Gold recovery from the leach liquor

3.2.1. Adsorption by Amberlite XAD-7HP

In order to recover gold after leaching, preconcentration and separation procedure is necessary. Gold can be recovered from leach liquors using ion exchange resins. For selective Au(III) adsorption, three different resins such as a nonionic (Amberlite XAD-7HP) and strong base resins (Bonlite BA304 and Purolite A-500) were used [21]. The results from the gold sorption experiments are summarized in Table 3. As can be seen, these resins are non-selective for gold and the adsorption values are almost similar. Copper ions are more selectively adsorbed on the resins rather than gold ions due to their high concentration. The gold and copper ions loaded onto the resins can be selectively desorbed using different eluents for the two metals [22]. As reported earlier the Au(III) ions on the non-ionic resin such as Amberlite XAD-7HP, can be eluted easily rather than that of the strong base resins without loss of

Table 2
Leaching results by electro-generated chlorine from waste mobile phone PCBs.

Leaching stage	Optimum condition	Leaching		Concentration	
		Cu (%)	Au (%)	Cu (g/L)	Au (mg/L)
1st stage (ORP < 350 mV _{Ag/AgCl})	40 g/L; 714 A/m ² ; 2.0 mol/L HCl; 165 min; 25 °C	94.91	5.0	24.0	0.9
2nd stage (ORP > 1100 mV _{Ag/AgCl})	160 g/L; 714 A/m ² ; 0.1 mol/L HCl; 10 min; 25 °C	0.58	93.06	0.61	67

subsequent loading capacity [21,22]. Therefore, Amberlite XAD-7HP was chosen for the separation of copper and gold. In order to get more concentrated gold solution with lower concentration of copper as described above, the process of the 2nd stage leaching by electro-generated chlorine was adapted repeatedly to generate sufficient leach liquor which after filtration was subjected to the ion exchange process. To determine the metal loading capacity of Amberlite XAD-7HP, the leach liquor was passed to the column containing 1 BV (4.6 mL) of the resin and the metal recoveries were investigated. The adsorption capacity is the maximum metal quantity taken up by 1 g (1 BV) of the resin and expressed as mg

Au/1 BV resin. The breakthrough curve (plot of C_e/C_0 vs. BV) presented in Fig. 12 shows the loading behavior of gold that may be recovered from the solution in a fixed bed. After a solution BV of 115, an increase of gold concentration in the raffinate was observed (Fig. 12, where C_e : the final concentration of metal in the solution (mg/L) and C_0 : the initial concentration (mg/L) in the solution). Gold

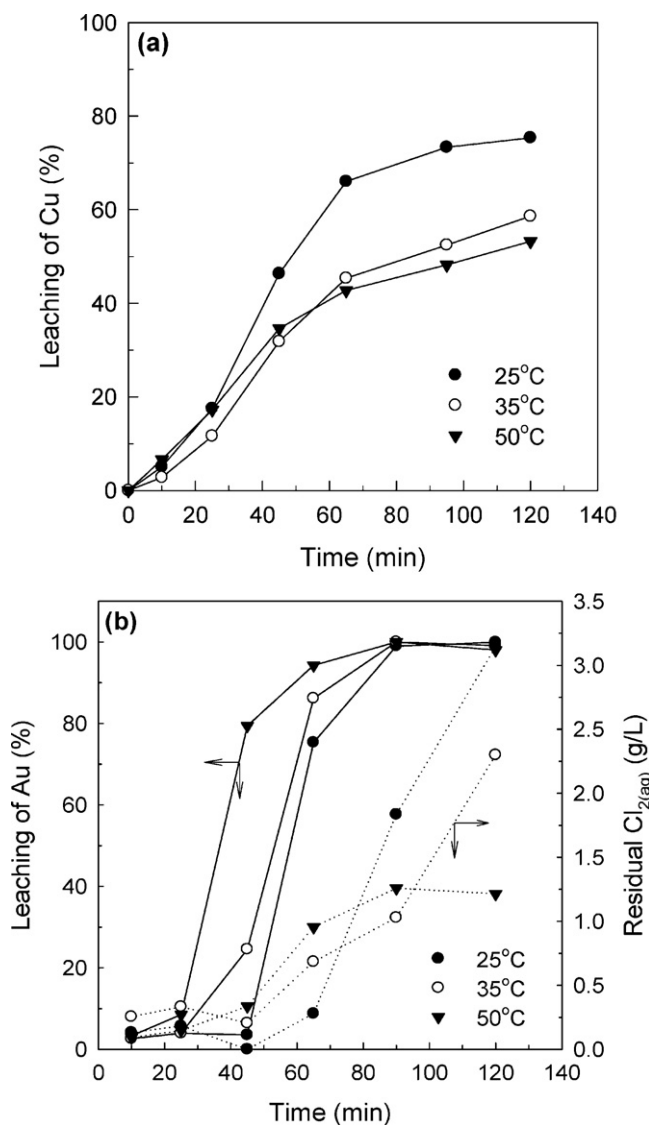


Fig. 7. Effect of temperature on (a) Cu and (b) Au leaching and residual Cl_{2(aq)} in 2.0 mol/L HCl (current density, 714 A/m²; leaching time, 120 min; stirring speed, 600 rpm; pulp density, 17 g/L; particle size, -3/+2 mm).

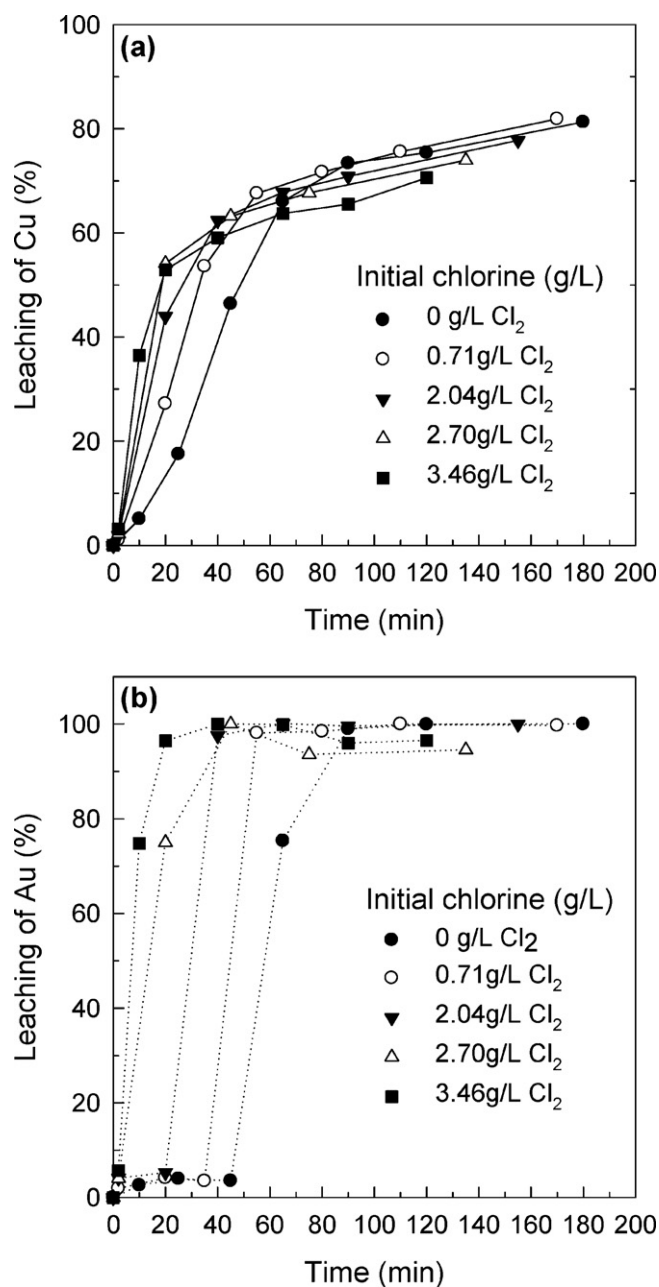


Fig. 8. Effect of initial concentration of chlorine on (a) Cu and (b) Au leaching in 2.0 mol/L HCl (current density, 714 A/m²; leaching time, 180 min; stirring speed, 600 rpm; pulp density, 17 g/L; temperature, 25 °C; particle size, -3/+2 mm).

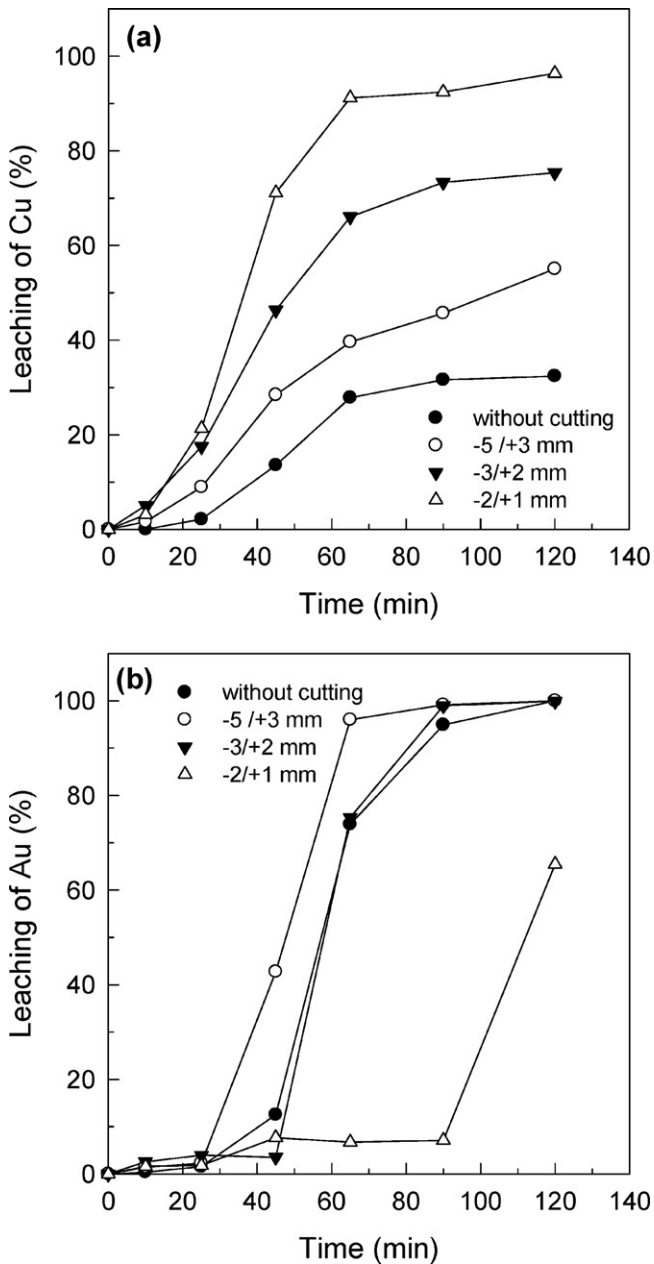


Fig. 9. Effect of particle size on (a) Cu leaching and (b) Au leaching in 2.0 mol/L HCl (current density, 714 A/m²; stirring speed, 600 rpm; temperature, 25 °C; pulp density, 17 g/L; leaching time, 120 min).

recovery from the leach liquor by ion exchange using Amberlite XAD-7HP resin was thus 95%. The maximum amount of gold loaded on 1 g resin was calculated to be 46.03 mg. Under this condition the copper also adsorbed on the resin along with gold, which was around 5% (30 mg/L) of the initial copper concentration of the leach liquor.

Table 3

Adsorption results by various resins from 2nd stage leach liquor (leach liquor composition: 610 mg/L Cu, 67 mg/L Au, 0.5 pH).

Name of resin	Types	Adsorption			
		Cu (mg/L)	Au (mg/L)	Cu (%)	Au (%)
Amberlite XAD-7HP	Non-ionic	596	5.3	97.70	7.9
Bonlite BA304	Strong base	596	4.9	97.70	7.3
Purolite A-500	Strong base	580	4.7	95.08	7.0

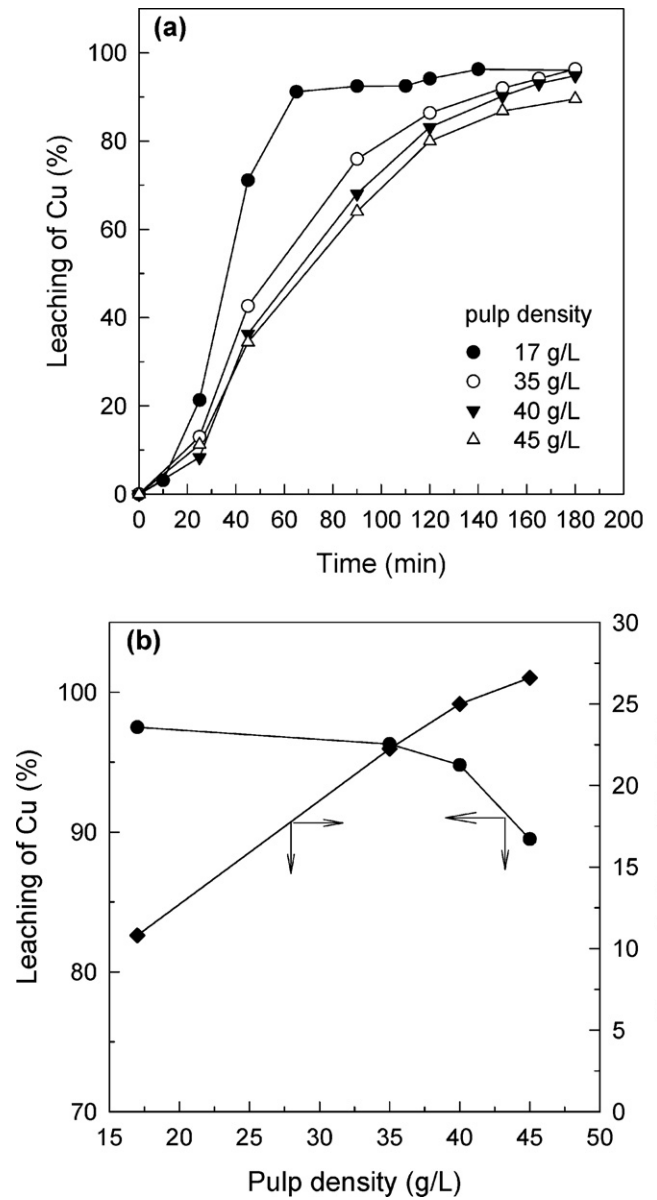


Fig. 10. (a) Leaching of Cu vs. time and (b) leaching and concentration of copper vs. pulp density at 180 min (current density, 714 A/m²; stirring speed, 600 rpm; temperature, 25 °C; leaching time, 180 min; particle size, -2/+1 mm).

3.2.2. Elution and enrichment of the gold from the resin

The elution experiments were carried out to separate gold and copper from the loaded resins. The hydrochloric acid is effective reagent for the elution of copper but not suitable for gold [22]. Harris et al. [23] suggested the use of a mixture of acetone and diluted hydrochloric acid for achieving gold elution. Therefore, the loaded resin was eluted initially with a hydrochloric acid solution and then with a mixture of acetone and hydrochloric acid for recovery of copper and gold, respectively. Preliminary experimental results show that the elution of copper from the loaded resin was not affected by the concentration of hydrochloric acid. Therefore, the concentration of hydrochloric acid was selected as 0.1 mol/L HCl for eluting copper (770 mg/L). During the elution of copper prior to gold elution no Au(III) was eluted. And then the loaded resin was eluted again with a mixture of acetone and hydrochloric acid (1.0 mol/L) at a ratio of 9:1 for the gold recovery. The elution curve of gold from Amberlite XAD-7HP is presented in Fig. 13. The eluent flow rate through the column was maintained at 1 mL/min

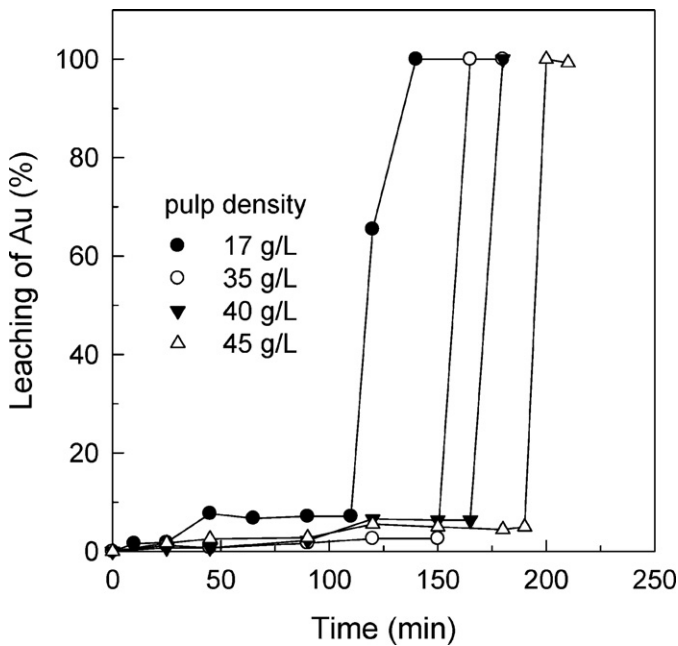


Fig. 11. Effect of pulp density on Au leaching in 2.0 mol/L HCl (current density, 714 A/m²; stirring speed, 600 rpm; temperature, 25 °C; particle size, -2/+1 mm).

and total elution occurred at 2 BV of eluent. A maximum 170-fold concentration (11,700 mg/L Au/BV, Fig. 13) of the initial gold solution was obtained in the ion exchange/elution process. After elution with 1.0 mol/L HCl in acetone, the concentration of 6034 mg Au/L could be enriched with 99.9% purity, which is 100 times higher in comparison to the concentration of this metal in the 2nd stage leach liquor.

3.3. Suggested process for the recovery of gold from mobile phone PCBs

Fig. 14 shows the suggested process flow-sheet for the recovery of gold and copper from mobile phone PCBs. During the 1st stage

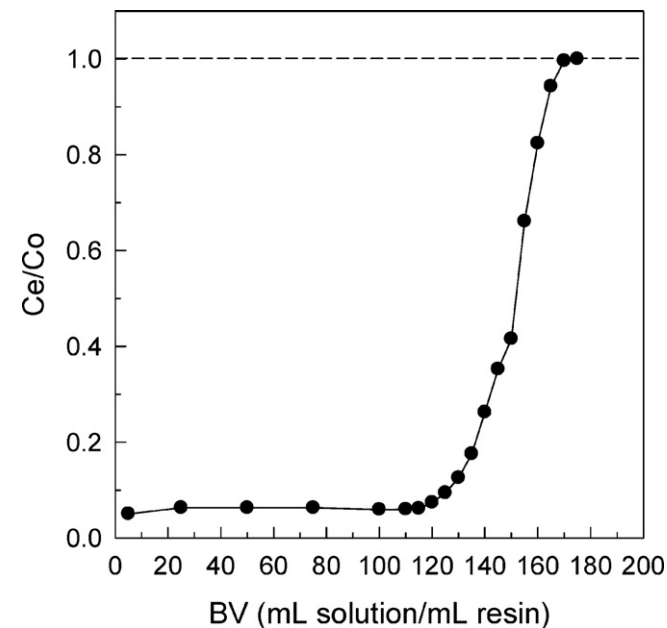


Fig. 12. Breakthrough profiles of gold (feed concentration: Au=67 mg/L, Cu=607 mg/L, Flow rate=60 mL/min, wt. of Amberlite XAD-7HD packed in the column=1.0 g).

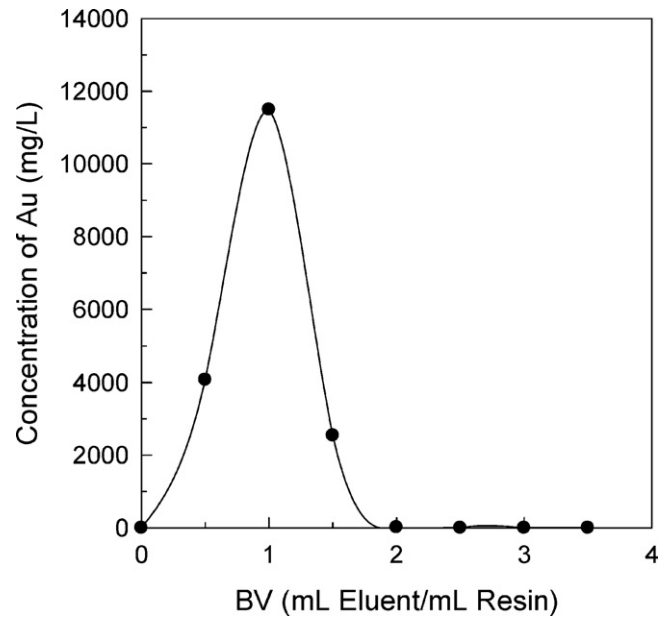


Fig. 13. Elution profiles of Au(III) loaded on Amberlite XAD-7HD by 1.0 mol/L HCl in acetone (eluent: a mixture of acetone and 1.0 mol/L HCl, ratio of acetone and hydrochloric acid = 1:9, flow rate = 1.0 mL/min).

of electro-generated chlorine leaching, copper can be dominantly leached out to get a high concentration (around 24.0 g/L) with negligible amount of gold (<5%). The concentrated copper solution in the leach liquor (1st stage) can be subjected to the copper recovery process such as electrowinning at the cathode in the electrolytic cell after purification, whereas the gold in the residue from the leach-1 stage can be processed through the 2nd stage leaching by

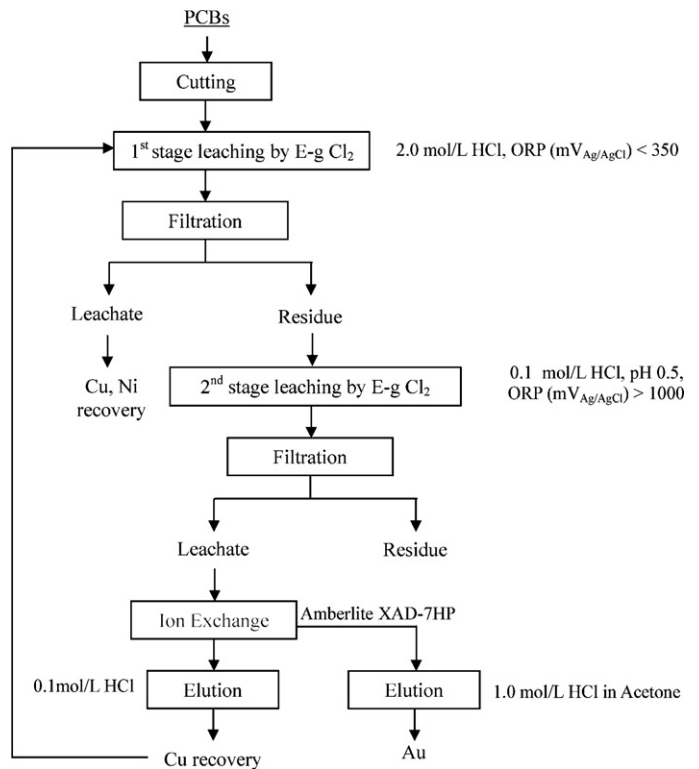


Fig. 14. The suggested process for the recovery of gold and copper from mobile phone PCBs.

electro-generated chlorine. The 2nd stage of leaching by electro-generated chlorine has the advantages as follows:

- (1) Concentrating gold solution (more than 4 times than that of 1st stage) by increasing the pulp density of residue
- (2) Lowering the metal concentration ratio of [Cu]/[Au] from 1000 to ~10 in the leach solution
- (3) Recovery of copper in cuprous state which saves electrical energy to generate chlorine as well as to recover copper
- (4) Operation in low acidity conditions

The solutions from the 2nd stage of leaching can then be treated for gold recovery by ion exchange resin using Amberlite XAD-7HP. The elution of metals from the loaded resin separately with hydrochloric acid and a mixture of hydrochloric acid and acetone, provides an effective method to separate and recover copper and gold, respectively. The copper solution (~770 mg/L) after elution by hydrochloric acid can be recovered as metal powder [24] by reduction with hydrogen gas, which is generated in the cathode compartment of the electrolytic cell (Fig. 2). The elution of the gold complex loaded in resin again with a mixture of hydrochloric acid and acetone, facilitates gold concentration to 6034 mg/L without contamination with copper. Pure gold metal can be obtained from the enriched solution by electrowinning process or reduction with $H_{2(g)}$ obtained from cathode compartment of the electrolytic cell.

4. Conclusions

In this work, leaching of gold from mobile phone PCBs by electro-generated chlorine and enriching the concentration of purified gold solution from the hydrochloric acid media by ion exchange procedure using Amberlite XAD-7HP, a non ionic resin were investigated. The following conclusions are drawn:

- (1) The leaching efficiency of gold increased with increasing temperature and dissolved initial chlorine concentration, besides lowering the amount of acid in a fixed chloride concentration.
- (2) In a two-stage leaching process the selective dissolution of copper and gold using electro-generated chlorine was achieved. In the 1st stage leaching the maximum copper recovery in 2 mol/L HCl solution was 97% in 165 min at 25 °C and 40 g/L pulp density, while the gold leaching was below 5%. High leaching of gold (93%, ~67 mg/L) was obtained along with residual copper (770 mg/L) in the 2nd stage of leaching with a diluted acid solution (0.1 mol/L HCl) at 25 °C and a higher pulp density of 160 g/L. The experimental results clearly demonstrate that copper and gold can be mostly separated during leaching stage itself by adjusting the solution acidity and chlorine concentration.
- (3) Gold was recovered from the solution of the 2nd stage of chlorine leaching by ion exchange using Amberlite XAD-7HP. The concentration of gold was enriched during elution with 1.0 mol/L HCl in acetone (1:9) to 6034 mg/L (99.9% purity) without any contamination with copper. Prior to gold elution the small amount of copper loaded to the resin was selectively recovered by contacting with 0.1 mol/L hydrochloric acid.

A process flow-sheet is suggested to recover gold and copper from the mobile phone PCBs.

Acknowledgements

This paper is based on work supported by the Korea Institute of Energy Technology Evaluation and Planning (KETEP) under the project entitled "Development of Technology for the Recycling of Valuable Metals from End-of-Life Small Electric & Electronic Equipment (No. 2010501010006B)".

References

- [1] F. Ongondo, I. Williams, Mobile telephone collection, reuse, and recycling in the UK, in: Third BOKU Waste Conference, 2009.
- [2] J. Cui, L. Zhang, Metallurgical recovery of metals from electronic waste: a review, *J. Hazard. Mater.* 158 (2008) 228–256.
- [3] P. Quinet, J. Proost, A.V.X. Lierde, Recovery of precious metals from electronic scrap by hydrometallurgical processing routes, *Miner. Metal. Process.* 22 (2005) 17–22.
- [4] S. Kulandaisamy, J.P. Rethinaraj, P. Adaikkalam, G.N. Srinivasan, M. Raghavan, The aqueous recovery of gold from electronic scrap, *JOM* 8 (2003) 35–41.
- [5] V.H. Hung, J.-c. Lee, J. Jeong, H.T. Hai, M.K. Jha, Thiosulfate leaching of gold from waste mobile phones, *J. Hazard. Mater.* 17B (2010) 1115–1119.
- [6] C. Abbruzzese, P. Fornari, R. Massidda, F. Veglió, S. Ubaldini, Thiosulphate leaching for gold hydrometallurgy, *Hydrometallurgy* 39 (1995) 265–276.
- [7] P.P. Sheng, T.H. Etsell, Recovery of gold from computer circuit board scrap using aqua regia, *Waste Manage. Res.* 25 (2007) 380–383.
- [8] M.I. Jeffery, P.L. Breuer, W.L. Choo, A kinetic study that compares the leaching of gold in the cyanide, thiosulfate, and chloride systems, *Metal. Mater. Trans.* 32B (2001) 979–986.
- [9] A.G. Chmielewski, T.S. Urbanski, W. Migdal, Separation technologies for metals recovery from industrial wastes, *Hydrometallurgy* 45 (1999) 333–344.
- [10] E.-y. Kim, M.-s. Kim, J.-c. Lee, M.K. Jha, K. Yoo, J. Jeong, Effect of cuprous ions on Cu leaching in the recycling of waste PCBs, using electro-generated chlorine in hydrochloric acid solution, *Miner. Eng.* 21 (2008) 121–128.
- [11] E.-y. Kim, M.-s. Kim, J.-c. Lee, M.K. Jha, K. Yoo, J. Jeong, Leaching behavior of copper using electro-generated chlorine in hydrochloric acid solution, *Hydrometallurgy* 100 (2010) 95–102.
- [12] E.-y. Kim, M.-s. Kim, J.-c. Lee, K. Yoo, M. Kumar, Leaching of metal components from waste printed circuit boards using electrogenerated chlorine in hydrochloric acid solution, in: Proceedings of the Conference on Jim Evans Honorary Symposium, TMS 2010 Annual Meeting & Exhibition, Seattle, Washington, USA, February 17, 2010, pp. 233–239.
- [13] I.M. Kolthoff, E.B. Sandell, E.J. Meehan, S. Bruckenstein, Quantitative Chemical Analysis, The MacMillan Company, New York, 1971.
- [14] R. Radulescu, A. Filcenco-Olteanu, E. Panturu, L. Grigoraş, New hydrometallurgical process for gold recovery, *Chem. Bull. "POLITEHNICA"* 53 (2008) 135–139.
- [15] HSC Chemistry 5.1, Chemical Reaction and Equilibrium Software, Outotec, 2002.
- [16] R. Winand, Chloride hydrometallurgy, *Hydrometallurgy* 27 (1991) 285–316.
- [17] H. Majima, Y. Awakura, K. Tsugui, E. Peters, Fundamental studies on chlorine behavior as related to zinc electrowinning from aqueous chloride electrolytes, *Metal. Trans.* 21B (1990) 251–258.
- [18] O. Herreros, R. Quiroz, J. Viñals, Dissolution kinetics of copper, white metal and natural chalcocite in Cl_2/Cl^- media, *Hydrometallurgy* 51 (1999) 345–357.
- [19] J. Viñals, C. Núñez, O. Herreros, Kinetics of the aqueous chlorination of gold in suspended particles, *Hydrometallurgy* 38 (1995) 125–147.
- [20] M. Alkan, M. Oktay, M. Çopur, Solubility of chlorine in aqueous hydrochloric acid solutions, *J. Hazard. Mater.* 119 (2005) 13–18.
- [21] N.V. Nguyen, J. Jeong, M.K. Jha, J.-c. Lee, K. Osseo-Asare, Comparative studies on the adsorption of Au(III) from waste rinse water of semiconductor industry using various resins, *Hydrometallurgy* 105 (2010) 161–167.
- [22] N.V. Nguyen, J.-c. Lee, S.-k. Kim, M.K. Jha, K.-S. Chung, J. Jeong, Adsorption of gold(III) from waste rinse water of semiconductor manufacturing industries using Amberlite XAD-7HP resin, *Gold Bull.* 43 (2010) 200–208.
- [23] B.G. Harris, J.P. Barry, S. Monette, Recovery of gold from acidic solutions, US Patent 5,028,260 (1990).
- [24] A. Agrawal, V. Kumar, B.D. Pandey, K.K. Sahu, A comprehensive review on the hydrometallurgical process for the production of nickel and copper powders by hydrogen reduction, *Mater. Res. Bull.* 41 (2006) 879–892.