



“Gheorghe Asachi” Technical University of Iasi, Romania



## LEACHING OF METALS FROM WASTE PRINTED CIRCUIT BOARDS (WPCBs) USING SULFURIC AND NITRIC ACIDS

Manoj Kumar<sup>1</sup>, Jae-chun Lee<sup>2\*</sup>, Min-Seuk Kim<sup>2</sup>, Jinki Jeong<sup>2</sup>, Kyoungkeun Yoo<sup>3</sup>

<sup>1</sup>CSIR-National Metallurgical Laboratory (CSIR-NML), Metal Extraction and Forming Division, 831007 Jamshedpur, India

<sup>2</sup>Korea Institute of Geoscience and Mineral Resources (KIGAM), Mineral Resources Research Division, 124 Gwahang-no, Yuseong-gu, 305-350 Daejeon, Korea

<sup>3</sup>Korea Maritime University, Department of Energy & Resources Engineering, 606-791 Busan, Korea

### Abstract

This study aims to understand the acid-leaching behavior of metals from 2 to 4 mm waste printed circuit boards (WPCBs) containing  $22.0\% \pm 1.1$  Cu,  $6.7\% \pm 0.2$  Ca,  $0.68\% \pm 0.02$  Sn,  $0.59 \pm 0.01$  % Pb,  $2.71\% \pm 0.08$  Al,  $0.22\% \pm 0.01$  Fe, etc.. Copper leaching was increased for sulfuric acid concentrations up to 1.2 mol/L and hydrogen peroxide concentrations of 10.0 vol% for a pulp density of 100 g/L at 50°C over 4 h, whereas for the same concentrations of sulfuric acid and hydrogen peroxide copper leaching was decreased from 75.7 to 56.7% with an increase in pulp density from 25 to 125 g/L. Under the same optimum conditions and a 100 g/L pulp density, the leached copper concentration was 16.66 g/L (75.7%) and the concentrations of Pb, Al, Fe, and Ca were 0.1 g/L, 0.64 g/L, 0.13 g/L, 0.79g/L, respectively. Above 50°C and 500 rpm, the amount of leached copper decreased. With nitric acid, 98.3% copper leaching was obtained under the optimum conditions of 3 mol/L nitric acid and an agitation speed of 800 rpm at 60°C for 5 h at 25 g/L pulp density. Under optimum conditions and 100 g/L pulp density, the concentration of Cu in the leachate was 21.12 g/L (96%), and the concentrations of Pb, Al, Fe and Ca were 0.52 g/L, 0.91 g/L, 0.13 g/L, 1.70 g/L, respectively. At the same pulp density, nitric acid enabled better leaching of copper and other metals than sulfuric acid with 10.0 vol% hydrogen peroxide. The solid precipitates obtained in the leach liquors of PCBs included stannic oxide and calcium aluminum oxide in nitric acid and gypsum in sulfuric acid.

*Key words:* hydrogen peroxide, metal(s), nitric acid leaching, sulfuric acid leaching, waste PCBs

*Received:* November, 2011; *Revised final:* June, 2012; *Accepted:* July, 2012

### 1. Introduction

Waste printed circuit boards (WPCBs), which are generated in large numbers due to the rapid development of information technology and industrialization, are the key components of electronic equipment and serve as the boards on which many surface and micro components are mounted. The total quantity of waste electrical and electronic equipments (WEEEs) generated in the world is approximately 20–50 million tons per year (Huang, 2009).

Computer WPCBs have been widely recognized as posing a global environmental problem

and as contributing to the loss of valuable precious and base metal resources (Cui and Zhang, 2008; Huang et al., 2009; Lee et al., 2007). There has been growing concern for the development of viable processes that utilize the waste materials in an environmentally friendly way.

Due to the complexity of the heterogeneous mixtures of metals and other materials present in computer WPCBs, which include approximately 30% metals, 30% plastic and 30% ceramic material (Yoo et al., 2009), recovery of the metals has been a serious challenge. The pyrometallurgical technology for recovering non-ferrous metals, particularly precious metals from WPCBs has several drawbacks,

\* Author to whom all correspondence should be addressed: e-mail: [jclee@kigam.re.kr](mailto:jclee@kigam.re.kr); Phone: +82-42-868-3613; Fax: +82-42-868-3415

which include the loss of noble metals into slag, low recovery of several metals and high amounts of gaseous effluents whose treatment requires a significant investment in heavy equipment (Sum, 1991).

As a part of the processes of recovering metals from WPCBs, the enrichment of metallic components from ground WPCBs using several mechanical separation methods has been reported (Eswaraiah, et al., 2008; Veit et al., 2005; Wu et al., 2008). Dhawan et al. (2009) reported that nitric acid is more effective in leaching metals from waste TV WPCBs in comparison to hydrochloric and sulfuric acid. Demir et al. (2004) studied the effect of temperature, nitric acid concentration, solid-to-liquid ratio, and stirring speed on the dissolution of spherical copper particles. Oishi et al. (2007) found that the leaching of WPCBs by ammonium sulfate and chloride solutions containing copper (II) ammine complexes as the oxidizing agent produces a leach liquor with 40 – 50 g/L copper; other metallic contents include ~1 g/L zinc and ~0.1 g/L of lead and manganese. A solution of 2 mol/L sulfuric acid and 0.2 mol/L hydrogen peroxide was used to dissolve 100% copper and zinc at the optimized condition of 85°C and 8 h, whereas 95% iron, nickel and aluminum were leached in 12 h from waste computer PCBs that were shredded to particle sizes of less than 1 mm (Oh et al., 2003).

Reducing the size of WPCBs was reported to be beneficial to recycling cost (Dalrymple, 2007). However, processing larger waste PCBs would eliminate dust generation, providing a more environmentally friendly approach for processing WPCBs. Most conventional leaching methods are based on the leaching of WPCBs ground to 1 mm or smaller. Thus, the purpose of this study was to investigate the leaching behavior of metals that are leached from 2 to 4 mm PCBs. Additionally, the extent of copper leaching and the leaching of other metals using sulfuric acid and nitric acid was investigated. Because sulfuric acid was ineffective in leaching the metals, hydrogen peroxide was added as an oxidizer.

However, in the granular WPCBs containing copper in a multilayered form, nitric acid leached almost all of the copper in and above the resin material. In a few cases, the initial effect of temperature, concentration and agitation speed on the percentage of leached metals (such as Sn, Ni and Mn) excluding copper, was not evident because of the low initial concentration of these metals and their negligible leaching capacity.

Because copper is present in large quantities, its leaching behavior was investigated in detail with regards to the process parameters. The use of different acids for metal leaching will help determine the suitability of using either nitric acid or sulfuric acid as a medium for the recovery of metals in downstream processing.

## 2. Experimental

### 2.1. Materials

The WPCBs used in this study were provided by Recom Co. Ltd., Korea. The provided sample was in the form of a heterogeneous mixture of shredded WPCBs and metal chips which are 10 to 50 mm in size. The metals chips were sorted and removed by hand to create a homogeneous sample. The WPCBs with surface-mounted micro components were further reduced in size to 2 – 4 mm in a scutter-cutter mill (Make: Hyosung Corporation, Korea) to increase homogeneity and subsequently washed with tap water. The washed WPCBs were dried in the oven at 110°C for more than 2 h before they were used for the leaching experiment.

For estimating the chemical composition, 2.5 Kg of samples were taken from the ground WPCBs prepared above for the leaching experiment and the quartering method was skillfully performed to obtain a homogeneous sample. 3 samples of 25 g ground WPCBs were incinerated at 450°C and dissolved into aqua regia. The metals were analyzed using a flame atomic absorption spectrometer (AAAnalyst 400, PerkinElmer Inc.), which contained 22.0% ± 1.1 Cu, 6.7% ± 0.20 Ca, 0.68% ± 0.02 Sn, 0.59 ± 0.01 % Pb, 2.71% ± 0.08 Al, 0.22% ± 0.01 Fe, 0.09% ± 0.004 Ni, 0.06% ± 0.003 Mn, 0.02% ± 0.001 Zn, 130 ppm ± 10 Ag, 50 ppm ± 5 Au etc.. The metallic fraction percentage was approximately 33.09%. All of the chemicals and reagents used in this work were reagent grade.

### 2.2. Methods

The leaching tests were performed in a 1-L three-necked pyrex reactor. The reactor was kept in a heating mantle to maintain the required temperature. A Teflon<sup>®</sup>-coated mechanical agitator was inserted through the central opening of the glass reactor lid to achieve the desired agitation speed. One neck was used for attaching the reflux condenser to avoid acid evaporation at higher temperatures. The second neck was used for inserting the Teflon<sup>®</sup>-coated thermocouple connected with the temperature controller. The third neck was used for sampling. The 1-mL sample was removed using a syringe, filtered and diluted to the appropriate concentration for the chemical analysis by flame atomic absorption spectrometry (FAAS).

The pulp density and acid concentrations were selected according to the predetermined experimental conditions. Sulfuric acid and nitric acid were selected as the leachants. Hydrogen peroxide was added as the oxidizing agent with the sulfuric acid. The appropriate contact time was selected based on the experimental conditions and the maximum leaching of metals. The samples were taken at predetermined intervals.

A concentration of 1.0 – 4.0 mol/L nitric acid was used, whereas the concentration of sulfuric acid was in the range of 0.5 – 1.2 mol/L. The quantity of hydrogen peroxide mixed with the sulfuric acid was 4 – 16 vol%. The agitation speed and temperature were in the range of 200 – 800 rpm and 30 – 90°C, respectively. The samples were taken at different time intervals from 10 to 120 minutes when the effect of agitation and temperature with sulfuric acid mixed with hydrogen peroxide was being evaluated and from 15 to 240 minutes when the effect of sulfuric acid and hydrogen peroxide concentration was being evaluated. Similarly, 10 - 120 minutes was selected as the sampling time when evaluating the effect of temperature and nitric acid concentration, and 30 – 300 minutes was selected when evaluating the effect of agitation speed at different nitric acid concentrations.

To determine the effect of the pulp density, a sample was taken at 4 h using sulfuric acid with hydrogen peroxide as the leachant or at 5 h using nitric acid as the leachant. The concentration of hydrogen peroxide was determined using the volumetric titration method with  $\text{KMnO}_4$ . A 1-mL sample was taken using a syringe, filtered and diluted to the required concentration for chemical analysis. The metal ions Pb, Al, Fe and Ca were analyzed using FAAS. The precipitates obtained from the leach liquors after a few days were filtered, washed and dried in the oven above 120°C for more than 2 h.

### 3. Results and discussion

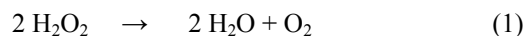
#### 3.1. Leaching of WPCBs by sulfuric acid in the presence of hydrogen peroxide

##### 3.1.1. Effect of agitation speed on copper leaching

The leaching of copper from WPCBs was performed by varying the agitation speed from 200 to 600 rpm at a temperature 50°C in 0.2 mol/L sulfuric acid solution with 5.0 vol% hydrogen peroxide and a pulp density of 100 g/L. This set of experiments was conducted using 0.2 mol/L sulfuric acid mixed with 5.0 vol% hydrogen peroxide to enhance copper leaching. The results are presented in the Fig. 1. An increase in copper leaching from 29.5% to 41.3% was reported at 2 h with an increase in agitation speed from 200 to 500 rpm. However, at 600 rpm, copper leaching (36.6%) was less than that observed at 500 rpm. This difference can be attributed to the accelerated decomposition of hydrogen peroxide at higher agitation speeds, as indicated in reaction (1). In the presence of hydrogen peroxide, as shown in Eq. (2), sulfuric acid forms peroxysulfuric acid ( $\text{H}_2\text{SO}_5$ ), which acts as a strong oxidizing agent for the copper and for the dissolution of other metals (Pauling, 1949).

Copper leaching with  $\text{H}_2\text{SO}_5$  is shown in Eq. (3). The resulting molecular oxygen derived from the increased rate of hydrogen peroxide decomposition at higher agitation speeds is adsorbed onto the copper surface. The oxygen occupancy of the copper surface

hinders contact with the sulfuric acid. A similar effect of oxygen adsorption resulting from hydrogen peroxide decomposition at higher stirring speeds during the leaching of zinc concentrate and chalcopyrite was also reported by researchers (Adebayo et al., 2003; Olubambi et al., 2006).



##### 3.1.2. Effect of temperature on copper leaching

Fig. 2 represents the effect of temperature on copper leaching from WPCBs by 0.5 mol/L sulfuric acid containing 4 vol% hydrogen peroxide for 2 h at a pulp density of 100 g/L and agitation speed of 500 rpm. The content and composition of the leachant was held constant to obtain a wide range of copper leachate compositions. It is evident that the increase in temperature from 30°C to 50°C increases the percentage of leached copper from 35.3% to 45.8%. After increasing the temperature beyond 50°C, i.e., to 70°C or 90°C, the percentage of leached copper was 40 and 30%, respectively. At all of the temperatures investigated, the percentage of leached copper increased with time, but at the end of 2 h, copper leaching became almost constant. The decrease in copper leaching above 50°C can be attributed to the accelerated rate of hydrogen peroxide decomposition at higher temperature. A similar observation was reported by Antonijevic et al. (1997).

An additional set of experiments was conducted to evaluate effect of hydrogen peroxide depletion resulting from the progression of metal leaching and the decomposition of hydrogen peroxide in the leach liquor over time in 1.0 mol/L sulfuric acid containing 10 vol% hydrogen peroxide at a pulp density of 100 g/L, an agitation speed of 500 rpm and a temperature of 50°C. The results of the experiments are reported in the Table 1. The consumption of hydrogen peroxide was found to be proportional to the amount of copper leached from the WPCBs.

##### 3.1.3. Effect of sulfuric acid concentration on copper leaching

The effect of the sulfuric acid concentration (0.8 to 1.2 mol/L) on the percentage of copper leaching is shown in the Fig. 3. With an increase in the sulfuric acid concentration from 0.8 mol/L to 1.0 mol/L, the percentage of copper leaching increases from 34.2% to 54.9% at 100 g/L pulp density, 4 vol%  $\text{H}_2\text{O}_2$ , 50°C and 500 rpm over 4 h. After the concentration was increased to 1.2 mol/L sulfuric acid, the increase in the percentage copper leaching was much less, only 5%. At all of the concentrations, as time increased up to 90 minutes, the rate of increase of copper leaching was significant. Beyond 90 minutes, the rate of copper leaching was still appreciable up to 210 minutes, but not as much as

during the initial 90 minutes. Beyond 210 minutes, the increase in copper leaching was insignificant.

3.1.4. Effect of hydrogen peroxide concentration on cooper leaching

Fig. 4 shows the effect of the hydrogen peroxide concentration on copper leaching from WPCBs. As the leaching duration increased up to 90 minutes, the percentage of copper leaching increased significantly.

At 210 minutes, the increase in copper leaching was still appreciable, and beyond 210 minutes, the percentage of leached copper remained constant. The initial experiment conducted with 4.8 mol/L sulfuric acid and 100 g/L pulp density at room

temperature for 2 h showed low copper leaching efficiency in the absence of hydrogen peroxide. With an increase in hydrogen peroxide concentration from 4 to 10 vol%, the copper leaching increased from 60% to 76% at 100 g/L pulp density, 1.2 mol/L sulfuric acid, 50°C temperature, and 500 rpm agitation speed in 4 h. Further increases in concentration, even up to 16 vol%, were not beneficial, as is evident from the marginal increase in copper leaching to 77% under the same conditions.

The use of 16 vol% hydrogen peroxide with higher concentrations of sulfuric acid was ineffective in increasing the leaching of copper and other metals from an economic point of view.

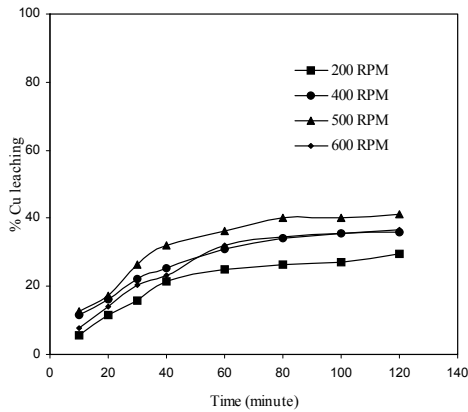


Fig. 1. Effect of agitation speed on copper leaching by sulfuric acid in the presence of hydrogen peroxide [H<sub>2</sub>SO<sub>4</sub>: 0.2 mol/L, H<sub>2</sub>O<sub>2</sub>: 5 vol%, pulp density: 100 g/L, temp.: 50°C]

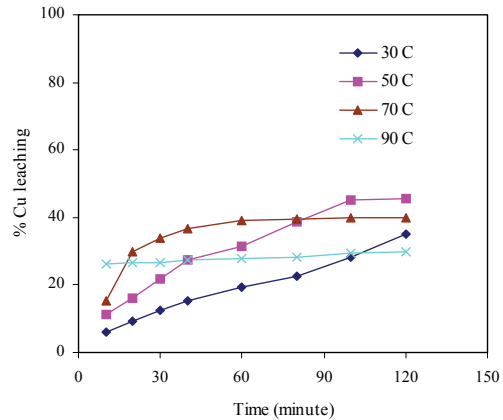


Fig. 2. Effect of temperature on copper leaching from the WPCBs using sulfuric acid [Pulp density: 100 g/L, H<sub>2</sub>SO<sub>4</sub>: 0.5 mol/L, conc. of H<sub>2</sub>O<sub>2</sub>: 4 vol%, agitation speed: 500 rpm]

Table 1. Consumption of hydrogen peroxide during copper leaching from WPCBs

S.No.	Time (min.)	H <sub>2</sub> O <sub>2</sub> (vol%)
1	0	10
2	30	6.5 ± 0.1
3	60	5.4 ± 0.1
4	90	4.9 ± 0.1
5	120	3.9 ± 0.1

Pulp density: 100 g/L, Conc. of H<sub>2</sub>SO<sub>4</sub>: 1.0 mol/L, Conc. of H<sub>2</sub>O<sub>2</sub>: 10 vol.%, Agitation speed: 500 rpm, Temperature: 50°C

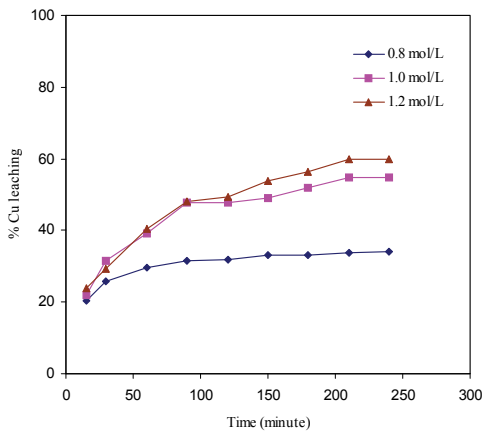


Fig. 3. Effect of concentration of the sulfuric acid on copper leaching from waste PCBs [Pulp density: 100 g/L, conc. of H<sub>2</sub>O<sub>2</sub>: 4 vol%, agitation speed: 500 rpm, temp.: 50°C]

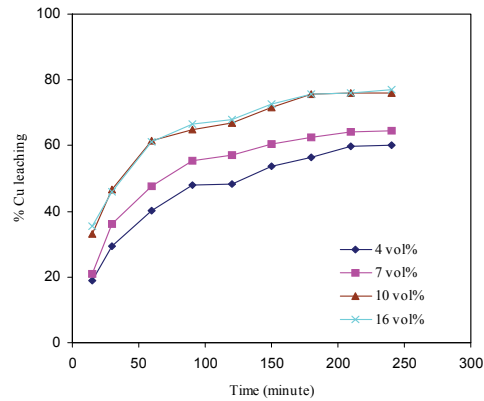


Fig. 4. Effect of hydrogen peroxide concentration on copper leaching from waste PCBs according to time [Pulp density: 100 g/L, conc. of H<sub>2</sub>SO<sub>4</sub>: 1.2 mol/L, agitation speed: 500 rpm, temp.: 50°C]

Experiments performed with 1.5 mol/L and 2.5 mol/L sulfuric acid in combination with 15.0 vol% hydrogen peroxide resulted in 68.7% and 81.7% copper leaching, respectively. Therefore, the subsequent experiments were performed at 1.2 M and 10 vol% hydrogen peroxide.

### 3.1.5. Effect of pulp density

Additional experiments were conducted to evaluate the effect of pulp density on the copper leaching. To increase cost efficiency, a 1.2 mol/L sulfuric acid concentration mixed with 10 vol% hydrogen peroxide was selected as the constant parameters to evaluate the effect of pulp density.

The percentage of copper leaching was nearly the same, i.e., 75.8 to 75.7%, when the pulp density was increased from 25 g/L to 100 g/L at the optimum conditions of 1.2 mol/L sulfuric acid, 50°C temperature, 500 rpm agitation speed, and 10 vol% H<sub>2</sub>O<sub>2</sub> for 4 h.

However, with an increase in pulp density up to 125 g/L, the percentage of copper leaching reduces to 56.7%. Thus, 100 g/L pulp density may be considered as the optimum value for operating the leaching process of waste PCBs and its subsequent downstream recovery.

Under the same conditions, the leaching of other metals increases with increasing the pulp density by the end of 4 h, as depicted in the Fig. 5. It is clear from the figure that with the increase in the pulp density from 25 g/L to 125 g/L, the leaching of Pb increases from 0.002 to 0.10 g/L, Al increases 0.16 to 0.74 g/L, Fe increases 0 to 0.13 g/L and Ca increases 0.13 to 0.92 g/L. At 100 g/L pulp density, the concentrations of Pb, Al, Fe, and Ca that leached were 0.1 g/L, 0.64 g/L, 0.13 g/L, 0.79 g/L, respectively.

The tin leaching was found to be 0.0035 g/L with 1.0 mol/L sulfuric acid at 15.0 vol% H<sub>2</sub>O<sub>2</sub>, 100 g/L pulp density, 500 rpm stirring speed and 50°C temperature for 4 h. The extent to which other metals leached was very low in comparison to that of copper leaching for the same reason as in the other cases. The concentration of Ca and Pb in the sulfuric acid leach liquor was relatively lower than that of the nitric acid (Figs. 5 and 9).

This can be explained by the formation of calcium sulfate and lead sulfate in the leaching process of WPCBs. Therefore, the extraction of copper by a solvent extraction method from leachate containing several metal ions at low concentration would be more effective.

## 3.2. Nitric acid leaching

### 3.2.1. Effect of temperature

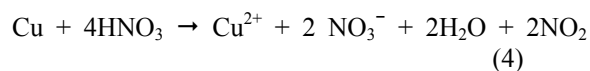
The effect of temperature under the conditions of 1.0 mol/L nitric acid, 100 g/L pulp density, 400 rpm agitation speed and 2 h reaction time are shown in the Fig. 6. With an increase in temperature from 35°C to 90°C, the copper leaching percentage was

increased from 0.81 to 54.8%. At 90°C, the percentage of copper leaching was high, up to 90 min and then remained constant. These experiments were performed in a glass reactor fitted with a reflux condenser, Teflon cork and stirrer, with the entire set-up mounted in a heating mantle and the temperature was varied up to 90°C.

### 3.2.2. Effect of nitric acid concentration

A series of experiments were performed to determine the effect of the nitric acid concentration on copper leaching at 90°C using a 400 rpm agitation speed for 2 h. The copper leaching results for these experiments are shown in the Fig. 7. The leaching percentage increases with an increase in the concentration of nitric acid. In 2 h, copper leaching increased from 62.5 to 96.1% as the concentration of nitric acid increased from 1.0 to 4.0 mol/L.

However, due to the agitation, a significant amount of acid fumes were produced during the reaction, which is not environmentally friendly. Therefore, subsequent experiments were performed at a lower concentration of nitric acid and higher agitation speed to avoid the acid fume emissions. Copper leaching in the nitric acid solution is described in Eq. (4). In this reaction, copper reacts with nitric acid to form copper nitrate and nitrogen peroxide.



### 3.2.3. Effect of agitation speed

The maximum agitation speed was restricted to 800 rpm to avoid splashing of the acid in the 1-L reactor and to prevent the PCB from getting stuck on the upper portion of the reactor, which does not occur later the leaching process. The experiments were performed using 1 to 3 mol/L nitric acid at 60°C for 5 h (Fig. 8). As the concentration increases, the leaching percentage increases. The results in Fig. 8 indicate that using 3.0 mol/L nitric acid at 90°C and 400 rpm for 2 h resulted in 85.4% of the copper leaching from the WPCBs.

However, in this Figure, the percent of copper leached was 85.6% when the leaching process was performed for 5 h with 3.0 mol/L nitric acid at an agitation speed of 800 rpm at 60°C. These experiments were performed to understand the effect of agitation speed on enhancing the leaching of metals. At even higher agitation speeds, the churning action resulted in temporary sticking of the 2 to 4 mm WPCBs on the upper wall of the reactor. There was no emission of brown fumes at this concentration of nitric acid. Therefore, to create the optimum conditions at the lower concentration of nitric acid, the subsequent experiments were performed at 3.0 mol/L nitric acid, 90°C, 800 rpm for 5 h. The advantage of using low concentrations of nitric acid is that the low pH of the resulting leach liquor is favorable for downstream treatment and that

alkaline additives may not be required to increase the pH to near 2 when using the solvent extraction for purifying copper.

3.2.4. Effect of pulp density

A set of experiments was conducted to assess the effect of various pulp densities at the optimum conditions of 800 rpm agitation speed, 90°C for 5 h. In these experiments, the temperature was increased further to 90°C at 3 mol/L (no fumes emission observed) to obtain a better metal leaching percentage. As the pulp density increases from 25 to 100 g/L, the percentage of copper leaching decreases from 98.3 to 96%.

With the additional increase in pulp density to 125 g/L, the percentage of copper leaching decreases from 96% to 76.1%. This is due to a gradual decrease in the residual acid concentration. Ninety-six percent copper leaching resulted in a copper concentration of 21.12 g/L in the leach liquor. The leaching results for other metals are shown in the Fig. 9. The concentrations of Pb, Al, Fe and Ca increase from 0.08 to 0.57 g/L, 0.22 to 1.01 g/L, 0.01 to 0.16 g/L, and 1.01 to 2.07 g/L, respectively, under the

optimum conditions and 100 g/L pulp density.

The concentrations of leached Pb, Al, Fe and Ca were 0.52 g/L, 0.91 g/L, 0.13 g/L, 1.70 g/L, respectively, under the same experimental conditions at the end of the 5 h leaching process, which is very low in comparison to the amount of leached copper, 21.12 g/L (96%).

The tin concentration was determined to be below 0.01 g/L due to the formation of stannic acid (HSnO<sub>3</sub>) during the leaching of WPCBs by the nitric acid (Mecucci and Scott, 2002). In comparison to the other metals that were leached by the sulfuric acid in the presence of hydrogen peroxide under optimum conditions, lead, aluminum and calcium were present at high concentrations, whereas the iron concentration remained the same.

The extraction of other metals in downstream processing may be improved using a sulfuric acid medium rather than of nitric acid medium because of the corrosive nature of nitric acid. Thus, we predict from these study results that sulfuric acid medium in the presence of hydrogen peroxide may be a better leachant for use with WPCBs.

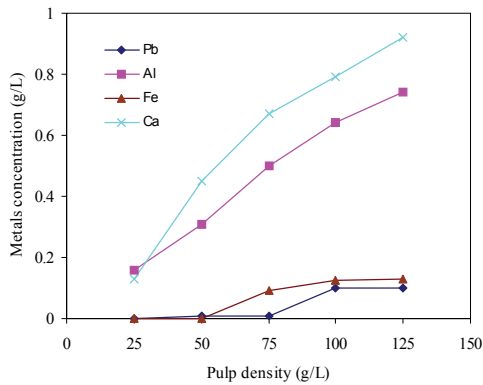


Fig. 5. Effect of pulp density on leaching of metals from the WPCBs [Conc. of H<sub>2</sub>SO<sub>4</sub>: 1.2 mol/L, agitation speed: 500 rpm, H<sub>2</sub>O<sub>2</sub>: 10 vol%, t: 4 h, Temp.: 50°C]

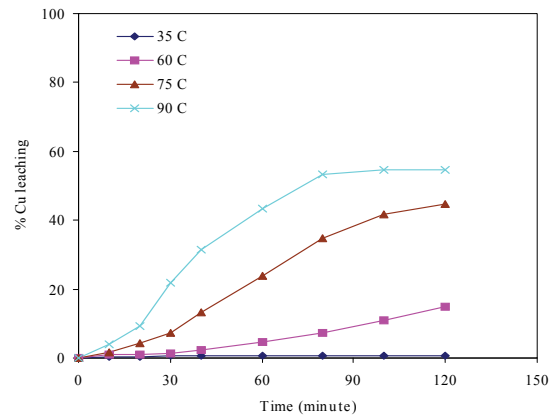


Fig. 6. Effect of temperature on copper leaching from WPCBs [HNO<sub>3</sub> conc.: 1 mol/L, agitation speed: 400 rpm, pulp density: 100 g/L]

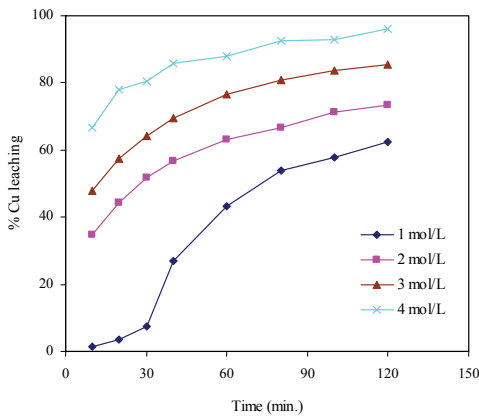


Fig. 7. Effect of nitric acid concentration on copper leaching from WPCBs [Temp.: 90°C, agitation speed: 400 rpm, pulp density: 100 g/L]

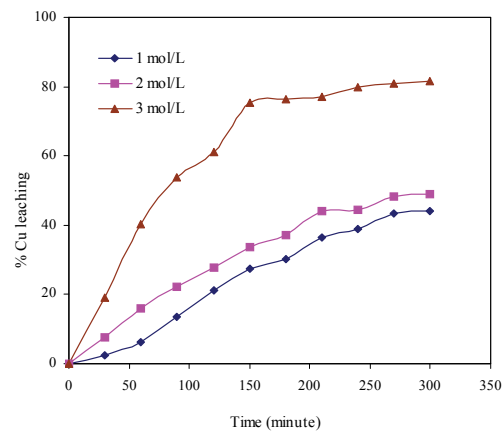
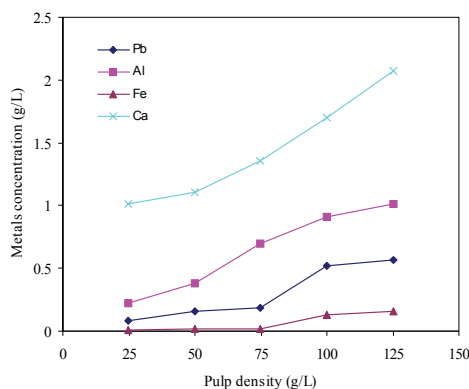


Fig. 8. Effect of agitation speed on copper leaching using different concentrations of nitric acid [Temp.: 60°C, pulp density: 100 g/L, agitation speed: 800 rpm]



**Fig. 9.** Effect of pulp density on extraction of metals from the WPCBs [Conc. of  $\text{HNO}_3$ : 3 mol/L, agitation speed: 800 rpm, temp.:  $90^\circ\text{C}$ , t: 5 h]

## 5. Conclusions

The nitric acid leaching of WPCBs (2 – 4 mm size) enables better leaching of copper and other minor metals than the sulfuric acid leaching in the presence of hydrogen peroxide at optimum conditions.

Nitric acid can leach 96% of copper (21.12 g/L) at 100 g/L pulp density under the optimum conditions of 3 mol/L nitric acid, 800 rpm agitation speed, and  $90^\circ\text{C}$  for 5 h. Conversely, sulfuric acid enables the leaching of 75.7% copper (16.66 g/L Cu) at 100 g/L pulp density under the optimum condition of 1.2 mol/L  $\text{H}_2\text{SO}_4$ , 10 vol%  $\text{H}_2\text{O}_2$ , 500 rpm agitation speed, and  $50^\circ\text{C}$  and 4 h.

## Acknowledgments

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”. One of the authors, Manoj Kumar, is grateful to the KIGAM for the award of post doctoral fellowship during 2009–2010.

## References

- Adebayo A. O., Ipinmoroti K. O., Ajayi O. O., (2003), Dissolution kinetics of chalcopyrite with hydrogen peroxide in sulphuric acid medium, *Chemical and Biochemical Engineering Quarterly*, **17**, 213–218.
- Antonijevic M. M., Dimitrijevic M., Jankovic Z., (1997), Leaching of pyrite with hydrogen peroxide in sulphuric acid, *Hydrometallurgy*, **46**, 71–83.
- Cui J., Zhang L., (2008), Metallurgical recovery of metals from electronic waste: A review, *Journal of Hazardous Materials*, **158**, 228–256.
- Dalrymple I., Wright N., Bains N., Geraghty K., Goosey M., Lightfoot L., (2007), An integrated approach to electronic waste (WEEE) recycling, *Circuit World*, **33**, 52–58.
- Demir H., Ozmetin C., Kocakerim M. M., Yapici S., Copur M., (2004), Determination of a semi empirical kinetic model for dissolution of metallic copper particles in  $\text{HNO}_3$  solutions, *Chemical Engineering and Processing: Process Intensification*, **43**, 1095–1100.
- Dhawan N., Wadhwa M., Kumar V., Kumar M., (2009), *Recovery of Metals from Electronic Scrap by Hydrometallurgical Route*, In: *Proc. Annual Meeting & Exhibition*, TMS 2009, Stanley M.H. (Ed.), EPD Congress, San Francisco, California, USA, 1107–1109.
- Eswaraiah C., Kavitha T., Vidyasagar S., Narayanan S.S., (2008), Classification of metals and plastics from printed circuit boards (PCB) using air classifier, *Chemical Engineering and Processing: Process Intensification*, **47**, 565–576.
- Huang K., Guo J., Xu Z., (2009), Recycling of waste printed circuit boards: A review of current technologies and treatment status in China, *Journal of Hazardous Materials*, **164**, 399–408.
- Lee J-c., Song H. T., Yoo J., (2007), Present status of the recycling of waste electrical and electronic equipment in Korea, *Resources, Conservation and Recycling*, **50**, 380–397.
- Mecucci A., Scott K., (2002), Leaching and electrochemical recovery of copper, lead and tin from scrap printed circuit boards, *Journal of Chemical Technology and Biotechnology*, **77**, 449–457.
- Oh C. J., Lee S. O., Yang H. S., Ha T. J., Kim M. J., (2003), Selective leaching of valuable metals from waste printed circuit boards, *Journal of the Air and Waste Management Association*, **53**, 897–902.
- Oishi T., Koyama K., Alam S., Tanaka M., Lee J-C, (2007), Recovery of high purity copper cathode from printed circuit boards using ammoniacal sulfate or chloride solutions, *Hydrometallurgy*, **89**, 82–88.
- Olubambi P. A., Borode J. O., Ndlovu S., (2006), Sulphuric acid leaching of zinc and copper from Nigerian Complex Sulphide Ore in the presence of hydrogen peroxide, *Journal of The Southern African Institute of Mining and Metallurgy*, **106**, 765–770.
- Pauling L., (1949), *Oxidation-Reduction Reactions*, In: *General Chemistry – A Textbook*, 1<sup>st</sup> Edition, Freeman W.H. and Company, San Francisco, California, 184–185.
- Sum E.Y.L., (1991), The recovery of metals from electronic scrap, *Journal of the Minerals, Metals and Materials Society*, **43**, 53–61.
- Veit H. M., Diehl T.R., Salami A.P., Rodrigues J.S., Bernardes A. M., Tenorio J. A. S., (2005), Utilisation of magnetic and electrostatic separation in the recycling of printed circuit boards scrap, *Waste Management*, **25**, 67–74.
- Wu J., Li J., Xu Z., (2008), Electrostatic separation for multisize granule of crushed printed circuit board waste using two-roll separator., *Journal of Hazardous Materials*, **159**, 230–234.
- Yoo J., Jeong J., Yoo K., Lee J-c., Kim W., (2009), Enrichment of the metallic components from waste printed circuit boards by a mechanical separation process using a stamp mill, *Waste Management*, **29**, 1132–1137.