Leaching of Copper from Cuprous Oxide in Aerated Sulfuric Acid

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The leaching behavior of copper from Cu₂O in H₂SO₄ solution was investigated to establish the leaching process for cathode powders produced by the recycling of waste printed circuit boards. When air was not introduced in sulfuric acid solution, the dissolution of copper from Cu₂O was inhibited by the formation of elemental copper (Cu⁰). The dissociated cuprous ions (Cu⁺) transformed into elemental copper (Cu⁰) or cupric ions (Cu²⁺) owing to the instability of Cu⁺ in H₂SO₄. Cu⁺ can be reduced to elemental copper (Cu⁰) by accepting an electron generated from the oxidation of another Cu⁺ to Cu²⁺, which is known as a disproportionation reaction. The introduction of air enhanced the leaching efficiency of copper due to the role of oxygen in the air as oxidant by accepting the electron generated from the oxidation of Cu⁺ to Cu²⁺. In the leaching test using Cu₂O reagent, the leaching efficiencies of copper increased with increasing air flow rate, temperature and agitation speed, but decreased with increasing pulp density. Copper leaching efficiency increased to up to 99% within 60 min in the aerated sulfuric acid solution at 30°C, 400 rpm, and pulp density of 2%.

(Received May 8, 2017; Accepted July 18, 2017; Published August 25, 2017)

Keywords: cuprous oxide, disproportionation reaction, sulfuric acid medium, aeration

1. Introduction

The rapid growth in the rate of global electronic waste (e-waste) generation is a growing concern. E-wastes, such as spent printed circuit boards (PCBs), may contain more valuable metals than their typical ores¹-³. As shown in Table 1⁴), even though PCBs contain rather small amounts of precious metals, recovery of precious metals with a high recovery ratio is important because they account for 93% of the total economic value of PCBs⁴). Conventional studies and processes have adopted the approach of extensive comminution followed by leaching for the recovery of precious metals from waste PCBs³,⁵). However, loss of precious metals has been reported in the process, especially during grinding⁵).

A recycling process comprising of smelting and subsequent electrorefining, as depicted in Fig. 1, was established by the Korea Institute of Geoscience and Mineral Resources (KIGAM)⁶). In this process, precious metals are concentrated as anode slimes after smelting and electrorefining, which alleviated the loss of these metals. Other metals such as copper, nickel, and iron are recovered as cathode powder. The copper was found to be cuprous oxide (Cu₂O) and elemental copper (Cu⁰) in the preliminary study.

Only a few studies examined the leaching of cuprite (Cu₂O)⁷-¹⁰). In these studies, leaching tests were carried out using various solutions, such as sulfuric acid with ferric sulfate⁷), sulfuric acid with perchloric acid⁸,⁹), and sulfuric acid with sulfur dioxide¹⁰). The leaching efficiency of copper was reported to be about 50% in the case of leaching in sulfuric acid solution without other oxidants⁷-⁹). Although Sullivan and Oldright⁷) and Majima et al.⁹) observed that the introduction of oxygen or air enhanced the leaching efficiency of copper by employing single experimental set without further discussion, they did not investigate the effects of gas type or gas flow rate as their work focused on the effects of ferric

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Table 1 Distribution of mass versus value share.

<table>
<thead>
<tr>
<th></th>
<th>Mass%</th>
<th>Fe</th>
<th>Al</th>
<th>Cu</th>
<th>Plastics</th>
<th>Ag/ppm</th>
<th>Au/ppm</th>
<th>Pd/ppm</th>
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<td>10</td>
<td>28</td>
<td>280</td>
<td>20</td>
<td>10</td>
<td></td>
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<tr>
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<td>20</td>
<td>23</td>
<td>1000</td>
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<td>110</td>
<td></td>
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<tr>
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<td>210</td>
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<td>5</td>
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<td>115</td>
<td>15</td>
<td>4</td>
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<table>
<thead>
<tr>
<th></th>
<th>Value Share</th>
<th>Fe</th>
<th>Al</th>
<th>Cu + Sum PM</th>
<th>Ag</th>
<th>Au</th>
<th>Pd</th>
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<td>42%</td>
<td>43%</td>
<td>8%</td>
<td>27%</td>
<td>8%</td>
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<tr>
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<td>1%</td>
<td>14%</td>
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<td>5%</td>
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<td>4%</td>
<td>36%</td>
<td>47%</td>
<td>5%</td>
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sulfate and perchloric acid as oxidants. Temperature and agita-
tion speed can also be considered as indirect parameters 
because increasing the temperature decreases dissolved oxy-
gen concentration, and increasing the agitation speed in-
creases the air inflow into solution by the formation of swirl-
ing motions.

It is expected that the economic efficiency will be im-
proved if the leaching efficiency of copper is enhanced by 
introducing air without adding any oxidizing agent, such as 
HClO₄ and Fe³⁺ used in the conventional studies⁷–⁹). 
Therefore, in the present study, leaching tests using cuprous 
oxide were conducted in sulfuric acid solution and the ef-
ects of leaching parameters, such as air flow rate, gas type, 
temperature, agitation speed, sulfuric acid concentration, 
and pulp density, on the leaching efficiency of copper were 
discussed with the aim of improving the dissolution of cop-
per from the cathode powder obtained from the recycling 
process shown in Fig. 1.

2. Experiments

2.1 Materials

The cathode powder sample used in the experiments was 
acquired from KIGAM. The sample was sieved using a 
75 µm screen. Figure 2(a) shows the SEM image (with JSM- 
6490, JEOL Ltd.) of the cathode powder, where agglomer-
ated submicron particles were observed. The X-ray diffrac-
tion (XRD) pattern (see Fig. 3) of the cathode powder 
sample revealed that copper existed in the form of cuprous 
oxide and elemental copper (Cu⁰). The sample was digested 
with HNO₃ and HF to measure the metal content. Acid di-
gestion was performed by Yucheon Tech Co. (Daejeon, 
Korea). The chemical composition of the sample is pre-
sented in Table 2. It contained 89.4% copper, 2.32% iron, 
0.9% tin, 0.77% nickel, and 0.51% zinc; other metals were 
not detected. Cuprous oxide and sulfuric acid used in the ex-
periments were of reagent grade. As shown in Fig. 2(b), the 
reagent-grade cuprous oxide consists of 1–3 µm particles.

2.2 Leaching and analysis procedures

Experiments on the dissolution of the cathode powder 
sample and Cu₂O reagent in H₂SO₄ solution were conducted 
in a 500-mL three-necked Pyrex reactor set in a heating 
mantle. The reactor was fitted with an agitator and reflux 
condenser. The reflux condenser was inserted in one port to 
prevent solution losses at high temperatures. In a typical run, 
200 mL of acid solution (1–5 M H₂SO₄) was poured into the 
reactor and permitted to attain thermal equilibrium (30– 
90°C). Predetermined amount of the cathode powder sample 
or Cu₂O reagent was added to the reactor, and the agitator 
was set to operate at speeds of 200–1000 rpm. Nitrogen gas, 
air, or oxygen gas was introduced into the reactor at a flow 
rate of 0–1000 cc/min. During the experiment, 3 mL of the 
sample solution was withdrawn periodically at a desired 
time interval by means of a syringe. The sample solution 
was filtered using a 0.45-µm membrane filter, and then, the 
filtrate was diluted with 5% HNO₃ for copper, iron, nickel, 
lead, and zinc analyses or 15% HCl solution for tin analysis.

The sample solutions were analyzed by atomic absorption 
spectrometry (AA7000, Shimadzu Co., Ltd., Japan) and in-
ductively coupled plasma-atomic emission spectrometry 
(ICP-AES, Optima 8300DV, PerkinElmer Co., Ltd., USA). 
The leaching residue was also characterized by XRD (D/ 
Max-2500PC, Rigaku Co., Japan).

3. Results and Discussions

As shown in Fig. 3, copper was present in the form of 
Cu₂O and elemental copper (Cu⁰) in the cathode powder

![Fig. 3 XRD pattern of cathode powder sample used in this study.](image)

![Fig. 2 SEM images of cathode powder and Cu₂O reagent.](image)

<table>
<thead>
<tr>
<th>Element</th>
<th>Cu</th>
<th>Fe</th>
<th>Sn</th>
<th>Ni</th>
<th>Zn</th>
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<tbody>
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<td>Mass%</td>
<td>89.4</td>
<td>2.32</td>
<td>0.9</td>
<td>0.77</td>
<td>0.51</td>
</tr>
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</table>

Table 2 Chemical composition of cathode powder sample.
sample. Therefore, the copper leaching tests were performed in sulfuric acid with a Cu$_2$O reagent to investigate the optimum conditions for the dissolution of the cathode powder sample, aiming to improve the economic efficiency of the recycling process shown in Fig. 1.

The effects of temperature on the leaching efficiency of copper were investigated under the following conditions: 1 M H$_2$SO$_4$, 400 rpm, pulp density of 2%, and without the introduction of air. As shown in Fig. 4, the leaching efficiencies first increased rapidly and then gradually afterwards. Generally, an increase in temperature can enhance metal dissolution in an exothermic reaction; however, in the current study, results showed the opposite. The leaching efficiency for copper at 120 min was found to be 82.3% at 30°C but it decreased to 69.4% at 90°C. The leaching residues were examined by XRD and were compared to the reagent-grade Cu$_2$O, to find what caused the opposite effect of temperature on leaching. The XRD patterns are shown in Fig. 5. As can be seen in this figure, peaks of Cu metal are present in all leaching residues. This observation has been reported in previous studies$^{9,10}$, and it can be represented by the reaction as expressed in eq. (1):

$$\text{Cu}_2\text{O} + 2\text{H}^+ = \text{Cu}^{2+} + \text{Cu} + \text{H}_2\text{O} \quad (1)$$

Generally, cuprous ions (Cu$^+$) are unstable in sulfuric acid$^{11}$. If there is no any other oxidant in the system, when one of two Cu$^+$ oxidizes to cupric ions (Cu$^{2+}$) by losing an electron, the other Cu$^+$ must reduce to elemental copper (Cu$^0$) by gaining the electron; this balances out the reaction. This kind of reaction is known as a "disproportionation reaction." During agitation, a swirl is formed which introduces oxygen from air into the leach solution and acts as an oxidant. In this case, Cu metal is not formed and all copper can be dissolved as Cu$^{2+}$ as follows:

$$\text{Cu}_2\text{O} + 4\text{H}^+ + \frac{1}{2}\text{O}_2 = 2\text{Cu}^{2+} + 2\text{H}_2\text{O} \quad (2)$$

However, the increase in temperature reduced the concentration of dissolved oxygen, and higher leaching efficiency was obtained at the lower temperature as shown in Fig. 4. As shown in Fig. 6, when air was introduced into the reactor at a low rate of 1000 cc/min, the copper leaching efficiencies increased up to 99% within 30 min with an increase in temperature at the beginning of the leaching test. This result indicates that the introduction of air could enhance the dissolution of Cu$_2$O in sulfuric acid.

The effects of agitation speed on the leaching efficiency of copper were investigated alongside the leaching test to examine the effects of liquid film boundary diffusion surrounding the solid particles on the leaching efficiency of the Cu$_2$O reagent in 1 M H$_2$SO$_4$ solution at 30°C with a pulp density of 5% and air flow rate of 1000 cc/min. The results

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*Fig. 4* Effect of temperature on leaching efficiency of copper in 1 M H$_2$SO$_4$ solution at 400 rpm with pulp density of 2% and without the introduction of air.

*Fig. 5* XRD pattern of precipitates recovered from leaching test performed under conditions of 1 M H$_2$SO$_4$ solution, 400 rpm, pulp density of 2%, and without the introduction of air.

*Fig. 6* Effect of temperature on leaching efficiency of copper in 1 M H$_2$SO$_4$ solution at 400 rpm with pulp density of 2% and air flow rate of 1000 cc/min.

*Fig. 7* Effect of agitation speed on leaching efficiency of copper in 1 M H$_2$SO$_4$ solution at 30°C with pulp density of 5% and air flow rate of 1000 cc/min.
of this leaching test are shown in Fig. 7. The leaching efficiencies increased rapidly within 10 min and then gradually with time. The leaching efficiencies also increased when the agitation speed was increased to 800 rpm. A higher agitation speed could possibly improve the distribution of dissolved oxygen. However, no improvement was observed when the agitation speed was increased from 800 rpm to 1000 rpm.

Figure 8 shows the effects of the air flow rate on the leaching efficiency of copper in 1 M H\(_2\)SO\(_4\) at 30°C and 800 rpm with a pulp density of 2%. The leaching efficiency increased with increasing air flow rate. However, the improvement in the leaching efficiency was not significant after 60 min when the air flow rate was increased further from 100 cc/min to 1000 cc/min. At these air flow rates, leaching efficiencies higher than 99% were observed within 60 min.

Figure 9 shows the effects of gas type on the leaching efficiency. The introduction of oxygen gas significantly enhanced the leaching efficiency compared to the introduction of air; the leaching efficiency of copper increased to almost 100% within 15 min with oxygen flow rate of 50 cc/min, whereas it took 120 min to dissolve all copper sample with air flow rate of 50 cc/min when temperature and pulp density were fixed at 30°C and 2%, respectively. Furthermore, the introduction of nitrogen gas suppressed the dissolution of copper. These results are in good agreement with the reactions in eqs. (1) and (2).

Figure 10 shows the effects of sulfuric acid concentration on the leaching efficiency in sulfuric acid solution at 30°C and 1000 rpm with a pulp density of 5% and air flow rate of 1000 cc/min. The difference in leaching efficiencies was negligible at sulfuric acid concentrations of 1–4 M after 30 minutes; however, at the concentration of 5 M, the leaching efficiency decreased to 53% at 120 min. The leaching residue was collected and investigated by XRD, and it was determined to be copper sulfate hydrate (CuSO\(_4\)·5H\(_2\)O), as shown in Fig. 11.

Since pulp density is an essential factor to consider for system upgrades, the leaching behavior of copper was investigated in 1 M H\(_2\)SO\(_4\) solution at 30°C and 400 rpm with an air flow rate of 1000 cc/min. Figure 12 shows that the leaching efficiencies decreased with an increase in pulp density from 1% to 10%. A leaching efficiency over 99% was obtained at the pulp density of 5% at 60 min, while an efficiency of 68.3% was obtained at the pulp density of 10% at 120 min, in which case the pH was measured to be 3.5. Equation (2) indicates that hydrogen ions are consumed during the dissolution of copper in the case where oxygen is introduced in sulfuric acid solution. The increase in pH decreased the leaching efficiency of copper with higher pulp density.

To affirm the results of leaching tests using Cu\(_2\)O reagent, a leaching test using the cathode powder obtained from the recycling process shown in Fig. 1 containing copper, nickel,
4. Conclusion

The dissolution of Cu$_2$O in sulfuric acid has been reported to be suppressed by a disproportionation reaction, wherein half of the cuprous ions are reduced to elemental copper (Cu$^0$). In this study, effects of oxygen introduction on the leaching behavior of copper were evaluated via examination of the effects of leaching factors such as the air flow rate, sulfuric acid concentration, temperature, agitation speed, and pulp density on the leaching efficiency.

The leaching efficiencies of copper increased with increasing air flow rate, temperature, and agitation speed but decreased with increasing pulp density. Sulfuric acid concentrations of 1–4 M did not affect the leaching efficiency after 30 minutes, but at a concentration of 5 M, the efficiency decreased owing to the formation of cupric sulfate precipitate. Since oxygen in the air acts as an oxidant for cuprous ions, the introduction of oxygen or air could enhance the dissolution of Cu$_2$O in sulfuric acid solution.

Acknowledgments

This research was supported by the Basic Research Project of the Korea Institute of Geoscience and Mineral Resources (KIGAM) funded by the Ministry of Trade, Industry & Energy (MOTIE) of Korea.

REFERENCES


Fig. 12 Effect of pulp density on leaching efficiency of copper in 1 M H$_2$SO$_4$ solution at 30°C and 400 rpm with air flow rate of 1000 cc/min.

Fig. 13 Leaching behaviors of copper, nickel, iron, tin, and zinc in 1 M H$_2$SO$_4$ leaching test at 50°C and 1000 rpm with pulp density of 5% and air flow rate of 1000 cc/min.

iron, zinc, tin (Table 1). The leaching conditions for the test were 1 M H$_2$SO$_4$ solution, 50°C, 1000 rpm, pulp density of 5% and air flow rate of 1000 cc/min. As shown in Fig. 13, the leaching efficiencies of copper, nickel, iron, and zinc increased to values over 99% within 10 min. This leaching rate was found to be very fast compared to that of the leaching of reagent-grade Cu$_2$O and can be attributed to the much smaller particle size of the cathode powder as shown in Fig. 2. Furthermore, iron dissolved from the cathode powder, could be changed into ferric ions by aeration, and the ferric ion has been known as a strong oxidant$^{12,13}$ enhancing the leaching rate of copper.

The leaching efficiency of Sn first increased and then decreased to almost 0%. Sn has been reported to have lower solubility in sulfuric acid compared to hydrochloric acid$^{13}$, and generally, Sn$^{4+}$ ions precipitate to SnO$_2$$^{14–16}$. The leaching efficiencies of copper, nickel, iron, and zinc were relatively low owing to the formation of elemental copper (Cu$^0$) in the sulfuric acid leaching test without the introduction of oxygen (or air) (data not shown); however, the introduction of air resulted to sufficiently enhanced leaching efficiencies. Therefore, dissolution of copper from cuprous oxide was achieved successfully by sulfuric acid leaching with the introduction of air.