Galvanic Leaching of Copper in Waste Printed Circuit Boards Using Manganese Dioxide in Spent Zinc-Carbon Batteries

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Abstract
Spent zinc-carbon batteries and alkaline batteries contain manganese dioxide, but they are buried in landfill sites without being recycled in Japan. Manganese dioxide is nobler than metal copper. The contact between both materials causes galvanic interactions, and manganese dioxide acts cathode to be reduced while copper reacts as anode to be oxidized. We have investigated the galvanic leaching of copper in shredded printed circuit boards using manganese dioxide recovered from spent zinc-carbon batteries. The dissolution of copper was enhanced in the presence of manganese dioxide in sulfuric acid solution with pH 1.0. The extraction yield of copper was 90% in the presence of manganese dioxide in 8 hour leaching while 16% of copper dissolved in the absence. Effects of factors such as pH, amount of manganese dioxide and temperature on the leaching of copper were also examined.

Key words: Galvanic leaching, Waste printed circuit boards, Copper, Spent zinc-carbon batteries

Introduction
Waste printed circuit boards (PCB) contain several metals such as copper, aluminum, tin, lead, gold, silver and so on. Copper is the major constitution in PCBs and is recovered by pyrometallurgical or hydrometallurgical treatment. Hydrometallurgical operations for the metals recovery from wastes are characterized by lower energy consumption, higher metal selectivity and low air pollution. In hydrometallurgical process copper in PCBs is leached followed by solvent extraction and electrowinning. It is crucial to dissolve copper efficiently from wastes. Sulfuric acid, hydrochloric, nitric acid solutions and aca rejia are often used as leaching reagents in hydrometallurgical processes of PCBs. Acid leaching in the presence of an oxidant is extensively used for the extraction of copper from PCBs. In addition, oxidative ammonia leaching can be suitable for the selective recovery of copper from PCBs. In acid leaching the nitric and hydrochloric acids are not suitable due to its corrosive nature and stringent environmental regulations, whereas sulfuric acid is acceptable for industries due to its less hazardous nature. Leaching processes of base metals from PCBs by using sulfuric acid and hydrogen peroxide as oxidant have been conducted by several researchers. Birloaga et al investigated the effects of sulfuric acid concentration, hydrogen peroxide volume and temperature on copper extraction yield. They found that volume of hydrogen peroxide has a positive effect on copper dissolution.

Spent zinc-carbon batteries and alkaline batteries are mostly collected as incombustible waste by municipal authorities and are buried in landfill sites without being recycled in Japan. These batteries contain valuable materials such as manganese, zinc and iron. Alkaline batteries use powdered zinc as negative electrode, manganese dioxide (MnO2) with graphite (black paste) as the positive electrode, and highly conductive potassium hydroxide (KOH) as the electrolyte. Zinc-carbon batteries consist of a carbon rod cathode with a moist paste (black paste) of MnO2 and NH4Cl mixed with carbon to improve conductivity and retain moisture in the acid electrolyte. During discharging of zinc-carbon batteries and alkaline batteries, chemical reactions between the anode and cathode could occur to give ZnO, and Mn3O4 or Mn2O3.
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\[ 2\text{Zn} + 3\text{MnO}_2 \rightarrow \text{Mn}_3\text{O}_4 + 2\text{ZnO} \quad (1) \]

\[ \text{Zn} + 2\text{MnO}_2 \rightarrow \text{Mn}_2\text{O}_3 + \text{ZnO} \quad (2) \]

Galvanic interactions among different minerals are well-known phenomena. Paramguru and Nayak\textsuperscript{10} reported galvanic interaction between sphalerite and manganese dioxide through leaching and found a substantial increase in leaching of both the minerals. Galvanic leaching of manganese nodule and cobalt-rich crust, which contain manganese dioxide, has been investigated. Nakazawa et al\textsuperscript{11} showed that the dissolution of manganese in cobalt-rich crust was accelerated in the presence of pyrite. Since manganese dioxide was nobler than pyrite, manganese dioxide acts as a cathode to be reduced resulting into release of manganese ions in the contact with pyrite. On the other hand, pyrite acts as an anode to be oxidized.

In this study we have investigated the galvanic leaching of copper in waste PCBs using black paste in spent dry batteries. \( \text{Mn}_2\text{O}_3 \) and \( \text{Mn}_3\text{O}_4 \) in black paste in spent batteries dissolve to form \( \text{MnO}_2 \) in sulfuric acid solutions according to Eqs. (3)–(4)\textsuperscript{12,13}.

\[ \text{Mn}_2\text{O}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{MnO}_2 + \text{MnSO}_4 + \text{H}_2\text{O} \quad (3) \]

\[ \text{Mn}_3\text{O}_4 + \text{H}_2\text{SO}_4 \rightarrow \text{MnO}_2 + 2\text{MnSO}_4 + 2\text{H}_2\text{O} \quad (4) \]

Since manganese dioxide is noble than copper, manganese dioxide acts as a cathode in contact between the both materials resulting in the oxidation of copper. The effects of several parameters such as initial pH, type of PCB, and dosage of the black paste on the leaching of copper have been investigated. Besides the enhancement of copper dissolution, leaching of aluminum in PCBs was accelerated in the galvanic contact.

**Materials and Methods**

Two samples of shredded PCBs which were provided by a waste treatment firm were used in this study. Samples were sieved to obtain \(-2\) mm size fraction for the experiments. Fig. 1 presents photographs of two PCB samples. PCB (A) contains flake-shaped copper, and PCB (B) includes copper wires as well as flake-shaped copper. Chemical analysis of two samples was conducted by dissolving them with aqua regia at 1/10 solid/liquid ratio on a hot plate. Table 1 shows average contents of several metals contained in samples. For PCB (B), copper and aluminum were major contents.

Spent zinc-carbon batteries were manually dismantled. Dismantling products such as a carbon electrode, plastic films, ferrous scraps and paper pieces were discarded. Black paste that contains mainly manganese and zinc was collected from the dismantled dry batteries. The black paste was dried at 80°C for 24 h followed by grinding with a porcelain mortar and a pestle. XRD analysis indicated the peaks of unreacted MnO\textsubscript{2} and one zinc-chlorine compound. Broad peaks were observed at 2θ 20–26°, and they could correspond to peaks of Mn\textsubscript{2}O\textsubscript{3} and Mn\textsubscript{3}O\textsubscript{4}. Chemical composition of the black paste was as follows; Mn 37.94%, Zn:9.5%, Fe:0.50%.

For the stoichiometric analysis of galvanic

![Fig. 1 Shredded waste printed circuit boards: (I) PCB (A), (II) PCB (B)](image_url)

Table 1 Chemical compositions of PCB(A) and PCB(B)

|         | PCB(A) % | PCB(B) % |
|---------|----------|----------|
| Cu      | 26.07    | 33.99    |
| Al      | 3.20     | 10.40    |
| Fe      | 1.69     | 1.40     |
| Zn      | 0.70     | 1.68     |
| Mn      | 0.96     | 0.83     |
leaching of copper in PCBs, copper powder and granular MnO$_2$ in chemical grade were used for leaching experiments. Copper powder (Cu grade 99.85%) was purchased from Kanto Chemical Corporation. Granular MnO$_2$ (Mn: 46.16%, Fe: 3.80%) was ground and sieved to obtain $-53 + 32 \mu m$ size fraction for leaching tests.

Leaching experiments were carried out in 300 ml Erlenmeyer flasks with 200 ml sulfuric acid solution agitated using a magnetic stirrer at room temperature or at 50°C in a water bath. In all leaching test leachate samples were withdrawn from time to time. Any evaporation was compensated for with the solution. Leachate samples were centrifuged at 10000 rpm for 10 min. Copper, manganese and aluminum ions in the supernatant were analyzed by ICP-AES. The pH was adjusted with sulfuric acid or sodium hydroxide solution.

Rest potential was measured using granular MnO$_2$ and copper wire electrodes prepared by mounting these materials in 6.25 mm ID Lucite tubing (Fig. 2). Electrical contact was made using a few drops of mercury to contact to a platinum wire. Electrochemical measurements were made with respect to saturated calomel electrode (SCE) in sulfuric acid solution with pH 0.8. Rest potentials of the electrodes were measured using ORP meter (DKK-TOA Co., Ltd). Before each measurement, the electrode surfaces were cleaned by polishing with 400 and 600 grit abrasive papers and then on a metallurgical polishing wheel with 0.5 $\mu m$ diamond powder as the abrasive.

**Results and Discussion**

The steady-state rest potentials of MnO$_2$ in chemical grade and copper wire after one hour in sulfuric acid solution with pH value of 0.8 were 716 mV and 72 mV (SCE), respectively. In contact with both materials MnO$_2$ can act as a cathode while copper wire serves as an anode suggesting that copper could be oxidized to dissolve.

Leaching experiments were carried out using copper powder and MnO$_2$ powder. Fig. 3 shows the effect of MnO$_2$ powder on the leaching of copper powder. The pulp density of copper powder was 1% (1 g copper powder/100 mL). Copper dissolved gradually in the absence of MnO$_2$, but the coexistence of MnO$_2$ enhanced the dissolution of copper in 6 h. Thereafter the copper concentration increased gradually and the dissolution rate was the same as that in the absence of MnO$_2$, suggesting that copper was leached by sulfuric acid. MnO$_2$ did not dissolve at all in the absence of cop-
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per powder, indicating that MnO$_2$ was not leached by acid solution. In the presence of 1 g copper powder, the manganese concentration increased remarkably up to 4.4 g/L in 6 h and it amounted to 92% of MnO$_2$ added. In the contact with both materials nobler MnO$_2$ could act as a cathode to be reduced while copper could work as an anode to be oxidized resulting into the release of manganese ions and copper ions according to the equations below;

$$\text{Cu} \rightarrow \text{Cu}^{2+} + 2e^- \quad (5)$$

$$\text{MnO}_2 + 4\text{H}^+ + 2e^- \rightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O} \quad (6)$$

$$\text{MnO}_2 + \text{Cu} + 4\text{H}^+ \rightarrow \text{Mn}^{2+} + \text{Cu}^{2+} + 2\text{H}_2\text{O} \quad (7)$$

The molar ratio of dissolved manganese ions to copper ions after 6 h was 0.97 and the value was almost coincident with the ratio calculated from the equations described above.

Leaching experiments were carried out using PCB (A) and black paste. Fig. 4 shows the effect of black paste on the dissolution of Cu from PCB (A). Copper concentration increased gradually to 0.7 g/l in the absence of black paste in the experiment period. In the presence of 1 g black paste the copper concentration increased remarkably in 8 h and was 1.15 g/L. Thereafter the dissolution rate declined. The period for the high dissolution rate of copper coincides that of rapid dissolution of Mn. The extraction yields of copper and manganese were 90% and 68% and the molar ratio of dissolved manganese ions to copper ions was 1.27 in 8 h. It was larger than the stoichiometric value of galvanic reaction between copper and manganese dioxide because manganese dioxide could react with other metals such as aluminum and zinc included in PCB (A). It was found that the dissolutions of copper and manganese from wastes were accelerated simultaneously by the galvanic interactions.
In order to examine the effect of initial pH, leaching experiments were conducted by varying the initial pH value between 1.0 and 1.8. The results are presented in Fig. 5. For the initial pH over 1.4, pH values rose substantially to over 5.0 in the early stage of experiments because the galvanic reactions between copper and MnO$_2$ consume protons. For the initial pH values 1.6 and 1.8, copper concentration increased in 4 days and then decreased. Increasing pH could cause the depression of copper dissolution and the formation of copper hydroxide. The results indicated that the optimum pH for the leaching of copper in PCB was below 1.2.

Fig. 6 represents the effect of the magnetic stirring on the leaching of copper in the PCB (A). The magnetic stirring rate was 450 rpm. Copper was completely extracted with the stirring in day first while the extraction yield was 23% without the stirring. The stirring caused the increase in collision rate of PCB particles and manganese dioxide particles, resulting in the acceleration of galvanic interactions between the both materials.

Fig. 7 shows the effect of the black paste dosage on the leaching of PCB (B). Copper in PCB (B) was refractory, and copper concentration was 46 mg/L in 6 day leaching in the absence of black paste. Deveci et al.\textsuperscript{14} reported that copper extrac-
tion from scrap TV boards at 0.53M H₂SO₄ was very limited without oxidants such as hydrogen dioxide.

Since copper on the surface of PCB is covered with laminate it is required to remove the laminate for the leaching of copper. Copper in PCB (B) must be coated to more extent than that in PCB (A). Copper concentration rose with increase in amount of the black paste. MnO₂ is a strong oxidant and could remove the coating on the surface of copper. However, copper dissolution rate was lower in comparison with that in the leaching experiments using the PCB (A). In addition to laminate cover, one of the reasons for low dissolution rate of copper is that specific surface area of copper wires contained in PCB (B) could be smaller than that of flake-shaped copper in PCB (A), resulting in the reduction of collision rate between black paste particles and copper wires. PCB (B) contains aluminum about 10.4%. Aluminum concentration increased rapidly up to 0.40 g/L in 2 days with 1 g black paste while 0.11 g/L in the absence of black paste. The dissolution of Al was enhanced by the galvanic interactions with MnO₂ according to the equation below:

\[ 3\text{MnO}_2 + 2\text{Al} + 12\text{H}^+ \rightarrow 3\text{Mn}^{2+} + 2\text{Al}^{3+} + 6\text{H}_2\text{O} \]

The differences in each amount of dissolved Al and Cu between the experiments with and without black paste in 2 day leaching were 2.08 mmol (56 mg) and 0.84 mmol (53 mg), respectively. Assuming that MnO₂ could dissolve according to reactions (7) and (8), calculated amount of dissolved Mn ions was 3.95 mmol (1.08 g/L), and it was close to the measured value 4.19 mmol (1.15 g/L).

In order to enhance the dissolution of copper in the PCB (B), the effect of the elevated temperature was examined. The experiment results conducted at 50°C were illustrated in Fig. 8. Increasing temperature improved the dissolution of Al in the absence of black paste, but not the copper dissolution rate. The addition of black paste accelerated copper dissolution remarkably, and copper concentration reached 0.7 g/L in the leaching of 34 h at 50°C in the presence of black paste while 0.1 g/L at ambient temperature in 48 h. Mecucci and Scott showed that elevating temperature from 23°C to 80°C accelerated copper dissolution significantly from PCB with HNO₃ because it could facilitate the removal of the epoxy coating on the copper from the board surface. Aluminum concentration increased significantly and leveled off after the leaching of 6 h. The extraction yields of copper and aluminum were 65% and 76% respectively in

![Fig. 8](image)

34 h at 50°C.

Galvanic interactions of PCBs and black paste enhance the dissolution rates of copper and manganese. After leaching, separation methods are required to recover metals from leach solutions. Several separation treatments can be used such as precipitation, liquid-liquid extraction and electrowinning. Sayilgan et al. investigated the sepa-
ration of manganese and zinc ions from the leachate of spent batteries. It was found that at a pH value of 8 almost complete zinc precipitation occurred while manganese precipitation completely at a pH over about 10. It is predicted that Cu$^{2+}$ could be readily separated from Mn$^{2+}$ by precipitation method. Inoue and Kawahara$^{18}$ examined the recovery of copper from the leachate of cobalt crust that contained copper, cobalt, manganese and nickel and indicated that more than 99% of copper was recovered using 10% LIX84-I kerosene solution at nearly pH 2.0.

**Conclusions**

In this study we have investigated the galvanic leaching of copper in waste PCBs using black paste in spent dry batteries. Black paste contains manganese dioxide. Since manganese dioxide is noble than copper, manganese dioxide acts as a cathode in contact between the both materials resulting in the oxidation of copper. The dissolution of copper in waste PCBs was accelerated in the presence of black paste. The dissolution rate of aluminum that was contained in PCBs also increased in the presence of black paste. Elevating temperature and magnetic stirring improved the dissolution rate of copper.

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