Copper Leaching Behavior from Waste Printed Circuit Board in Ammoniacal Alkaline Solution

Kazuya Koyama¹, Mikiya Tanaka¹ and Jae-chun Lee²

¹Metals Recycling Group, Research Institute for Environmental Management Technology, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba 305-8569, Japan
²Minerals and Materials Processing Division, Korea Institute of Geoscience & Mineral Resources(KIGAM), 30, Gajeong-dong, Yuseong-gu, Daejeon 305-350, Korea

A novel energy-saving hydrometallurgical recovery process for copper from electronic scrap employing the Cu(I)-amine complex has been presented on the basis of a thermodynamic consideration. In order to experimentally explore the feasibility of the leaching stage in this process, the copper leaching behavior from a printed circuit board (PCB) in ammoniacal alkaline solutions has been investigated under a nitrogen atmosphere. Copper in PCB was oxidized by Cu(II) to form Cu(I)-amine complex ions. The leaching reaction can be expressed as:

\[ \text{Cu} + \text{Cu(II)} + 2\text{NH}_3 \rightarrow 2\text{Cu(NH}_3)_2^{+} \]

The Cu(II)-amine complex significantly enhanced the leaching rate, while the Cu(I)-amine complex slightly depressed it. Crushing of the PCB effectively enhanced the leaching rate, because the exposed metallic copper area is increased by the crushing. The effect of temperature on the leaching rate was insignificant. Consequently, the feasibility of the leaching stage in the proposed copper recovery process has been experimentally confirmed. [doi:10.2320/matertrans.47.1788]

(Received January 5, 2006; Accepted May 10, 2006; Published July 15, 2006)

Keywords: copper recycling, energy-saving, oxidative leaching, printed circuit board, cupric ammine solution, cuprous ammine solution

1. Introduction

The recovery of various metals from waste materials is an important issue in order to conserve the environment and metal resources. Copper is used for cables, electric appliances, etc., and is a very important material for industries in now and the future. A printed circuit board (PCB) also contains copper in addition to many kinds of valuable metals such as gold, silver, palladium, nickel and so on. The copper content in the PCB is 10 to 30 mass%, which is the highest among the metallic elements. There are two ways to recover copper, either pyrometallurgically or hydrometallurgically. Hydrometallurgical treatments generally have more flexibilities during the process scale and control. Sulfuric and hydrochloric acid solutions are often employed as leaching agents in the hydrometallurgical treatment; however, in these cases, the separation processes tend to become complicated because of the poor selectivity during the leaching.

It has been reported that certain kinds of complexing agents are effective for selective leaching. Majima et al. reported the selective leaching of copper from motor scraps using cupric ammine solutions. Zhou et al. studied the removal of copper from ferrous scrap by an ammonia leaching method. In these studies, Cu(I) ions were obtained under an air or oxygen atmosphere as the reaction product, and then metallic copper would be electrowon from a sulfuric acid solution obtained by solvent extraction-stripping. During this electrowinning, one mole of copper deposition at the cathode requires two moles of electrons, and oxygen is evolved at the anode. Its power consumption is 2000 to 2500 kWh ton⁻¹. In order to facilitate the hydrometallurgical copper recycling, a process requiring much less energy should be developed.

In this paper, a novel energy-saving hydrometallurgical process for copper recovery from electronic scraps employing the Cu(I)-amine complex is proposed on the basis of a thermodynamic consideration. As the first step for its experimental verification, the copper leaching behavior from a PCB in the Cu(II)-NH₃-(NH₄)₂SO₄ solutions was studied under a nitrogen atmosphere.

2. Copper Recovery Process

The potential-pH diagram is a useful tool for understanding various reactions such as the electrochemical reaction, neutralization, etc., in aqueous solution.

Figure 1 shows the potential-pH diagram of the Cu-NH₃-H₂O system. This figure is obtained under the conditions that the Cu activity is 0.5 and the sum of the concentrations of NH₃ and NH₄⁺ is 7 kmol m⁻³. The broken lines in this figure show the following reactions:

\[ 2\text{H}^{+} + 2\text{e}^{-} = \text{H}_2 \] (1)

\[ \text{O}_2 + 4\text{H}^{+} + 4\text{e}^{-} = 2\text{H}_2\text{O} \] (2)

Neither Cu(I) nor Cu(II) are stable ionic species in neutral and alkaline solutions without complexing agents, i.e., NH₃ or CN⁻. In the presence of excess ammonia, however, Cu(I) and Cu(II) are stable as Cu(NH₃)₂⁺ and Cu(NH₄)₂⁺ in neutral and alkaline solutions, respectively. The oxidation-reduction reactions of Cu(II)/Cu(I) and Cu(I)/Cu are expressed as follows:

\[ \text{Cu(NH}_3)_2^{2+} + \text{e}^{-} = \text{Cu(NH}_3)_2^{+} + 2\text{NH}_3 \] (3)

\[ \text{Cu(NH}_3)_2^{+} + \text{e}^{-} = \text{Cu} + 2\text{NH}_3 \] (4)

The oxidation-reduction potential of Cu(NH₃)₂²⁺/Cu(NH₃)₂⁺ is greater than that of Cu(NH₃)₂⁺/Cu, which indicates that Cu(NH₃)₂⁺ can work as an oxidizing agent for metallic copper in an ammoniacal alkaline solution. Also, the oxidation-reduction potential of Cu(I)/Cu is greater than that of hydrogen evolution (eq. (1)), which indicates that Cu(I) can be preferentially reduced to metallic copper.

The reactions at the cathode and anode predicted by the thermodynamic consideration, theoretical cell voltage, and the power consumption in the electrowinning stage are
shown in Table 1. The theoretical cell voltage and the power consumption by this work are much lower than those by the conventional process. This is due to the Cu(I) oxidation to Cu(II) at the anode as well as the monovalent electrodeposition at the cathode.

On the basis of the above thermodynamic considerations, the copper recovery process consisting of a leaching and electrowinning from Cu(I) is now presented in Fig. 2. The waste PCB containing metallic copper is immersed in the cupric ammoniacal solution during the leaching stage. The copper in the PCB is dissolved as cuprous ions, and the cupric ions are simultaneously reduced to cuprous ions. Certain types of metals such as nickel and zinc, which form ammine complexes, can be simultaneously dissolved. These ions should be separated during the purification stage. The purified solution, thus obtained for the electrowinning stage, is poured into the cathodic compartment of the electrolytic cell with a diaphragm. Half of the Cu(I) ions are then reduced to metallic copper and the remaining half are transferred to the anodic compartment in order to oxidize to Cu(II). The Cu(II) ions thus obtained are used as the oxidizing agent in the leaching process. The expected advantages of this process are as follows.

a) Selectivity of the copper leaching is high, because iron, and aluminum are not dissolved.

b) Power consumption is low during the electrowinning stage due to electrodeposition from Cu(I) at the cathode and electrolytic oxidation of Cu(I) at the anode.

c) Additional oxidative agents are not necessary, because Cu(II) produced at the anode works as the oxidative agent for copper in the wastes.

3. Experimental

A PCB, on which no electronic device was mounted, consisting of four layers in part, each plated with copper, was crushed to the average particle diameter of 3.4 mm and 1.5 mm. The former was used in the leaching experiment unless otherwise stated. The copper content in the PCB was 9.5 mass%. Copper particles with the average diameter of 0.83 mm (99.85% purity, Kanto Chemical Co., Inc.) were also used in the leaching experiment. The leaching solutions were prepared by dissolving cupric sulfate pentahydrate, CuSO\(_4\)-5H\(_2\)O (98% purity, Wako Pure Chemical Industries, Ltd.), cuprous oxide, Cu\(_2\)O (99% purity, Kanto Chemical Co., Inc.), ammonia solution, NH\(_3\) (25% purity, Wako Pure Chemical Industries, Ltd.), and ammonium sulfate, (NH\(_4\))\(_2\)-SO\(_4\) (99.5% purity, Wako Pure Chemical Industries, Ltd.). All the aforesaid solutions were prepared using deionized water having a specific resistivity of 5 × 10\(^4\) ohm-m. Nitro-
gen gas was bubbled through the deionized water for 24 hours before preparation of solution in order to remove the oxygen in the water.

In the leaching experiment using the copper particles, the Cu(II) concentrations in these solutions were measured by a colorimetric method, because Cu(II) in the ammoniacal alkaline solution shows an absorbance peak at around a 630 nm wavelength and Cu(I) does not show an absorbance peak at this wavelength. On the other hand, the total copper were analyzed using ICP-AES (Seiko Instruments Inc. SPS-4000). Thus, the Cu(I) concentrations were obtained by the difference between the total copper concentrations and Cu(II) concentrations. These leaching experiment and colorimetric measurement were conducted under a nitrogen atmosphere in a glove box to prevent the oxidation of Cu(I).

In the leaching experiment using the PCB, a 200 cm$^3$ aqueous solution and a 10 g PCB were placed in a flask under a nitrogen atmosphere. Nitrogen gas was introduced into the reaction vessel through a saturator of 5 kmol m$^{-3}$ NH$_3$-1 kmol m$^{-3}$ (NH$_4$)$_2$SO$_4$ solution to prevent oxidation of the Cu(I)-ammine complex ions produced during the leaching experiments. The solution was agitated by an impeller at the rotating speed of 200 rpm. The reaction vessel was placed in a water bath kept at a specific temperature. A 5 cm$^3$ aliquot of the solution was periodically removed for analysis. The copper concentrations were analyzed using ICP-AES. The percentage of the leached copper was determined as

$$\text{Cu leaching (\%)} = \frac{\text{Dissolved copper/g}}{\text{The amount of copper in PCB/g}} \times 100 \quad (5)$$

4. Results and Discussion

A leaching experiment using the copper particles was carried out in order to investigate the behaviors of the Cu(I) and Cu(II) concentrations. An aqueous solution of 0.1 kmol m$^{-3}$ CuSO$_4$, 5 kmol m$^{-3}$ NH$_3$, 1 kmol m$^{-3}$ (NH$_4$)$_2$SO$_4$ was used as the leaching solution. Figure 3 shows the time variation of the Cu(I) and Cu(II) concentrations. The Cu(I) and Cu(II) concentrations increased and decreased with time, respectively. As is clear in this figure, copper was dissolved in this aqueous solution. The Cu(I) concentration after leaching for 4-hours was found to be twice that of the initial concentration of Cu(II).

In order to determine the leaching reaction, the ratio of the amount of Cu(I) increase to that of Cu(II) decrease at each interval was shown in Fig. 4. They were found to be a constant value of 2, which means that 2 moles of Cu(I) ions were produced when 1 mole of Cu(II) ions was consumed as the oxidizing agent. The leaching reaction is expressed by the following stoichiometric relation:

$$\text{Cu} + \text{Cu(NH}_3\text{)}_4^{2+} = 2\text{Cu(NH}_3\text{)}_2^{+} \quad (6)$$

This leaching reaction corresponds to the previously described thermodynamic consideration.

The color of the solution changed from navy blue to pale blue. This is because, with the progress of leaching, the concentration of Cu(II)-ammine complex, which is navy blue, decreased and, simultaneously, that of the Cu(I)-ammine complex, which is colorless, increased.

The time variation in the copper leaching from PCB is shown in Fig. 5. An aqueous solution of 0.3 kmol m$^{-3}$ CuSO$_4$, 5 kmol m$^{-3}$ NH$_3$, 1 kmol m$^{-3}$ (NH$_4$)$_2$SO$_4$ was used as the leaching solution. The percentage of the leached copper increased with time and reached 67% and 82% after 2 and 4-hours leaching, respectively. Copper in the crushed PCB consisted of three types: (i) electroplated on the PCB, (ii) liberated from the PCB, and (iii) buried inside the PCB. The leaching rate of copper inside the PCB is much lower than that on the surface due to the limited exposed area of the former, which resulted in the decreasing leaching rate with time. The time variation of the oxidation-reduction potential (ORP) is also shown in this figure. The oxidation-reduction
potential rapidly decreased with time during the initial stage of leaching and then gradually after 30 minutes. The oxidation-reduction reaction, which determines the oxidation-reduction potential, is as follows:

$$\text{Cu}^{2+} + e^- = \text{Cu}^+$$  \hspace{1cm} (7)

$$E = E_0 + \frac{RT}{F} \ln \frac{a_{\text{Cu}^+}}{a_{\text{Cu}^{2+}}}$$  \hspace{1cm} (8)

where the symbols $E$, $E_0$, $R$, $T$, $F$ and $a$ are the potential, standard potential, gas constant, temperature, Faraday constant and activity, respectively. It was assumed that Cu$^+$ and Cu$^{2+}$ activities increased in proportion to the concentrations of the Cu(I)-ammine complex ion and Cu(II)-ammine complex ion, respectively. The Cu(II) concentration only slightly decreased during the experiment since the Cu(II) in the initial aqueous solution was quadruple as much as the copper in the PCB. Therefore, the decrease in the oxidation-reduction potential indicates that the concentration of the Cu(I)-ammine complex ion increased with time, which corresponds to Fig. 3.

Figure 6 shows the effect of the average diameter of PCB on the leaching rate. An aqueous solution of 0.3 kmol m$^{-3}$ CuSO$_4$-5 kmol m$^{-3}$ NH$_3$-1 kmol m$^{-3}$ (NH$_4$)$_2$SO$_4$ was used as the leaching solution. Although the copper contents were the same, the leaching rate for the smaller PCB particles was greater than that for the larger one. The percentage of leached copper in the PCB with a 1.5 mm average diameter was 93% after 2.5-hours leaching, while that in the PCB with a 3.4 mm was 82% after 4-hours leaching. Copper on the surface of the PCB completely dissolved after the experiment using the PCB particles with a 3.4 mm average diameter. Copper inside the layer, however, did not completely dissolve due to the insufficient diffusion of the solution containing the oxidizing agent. The longer crushing time makes the PCB particles smaller and the exposed area of copper inside the PCB greater. From this result, crushing was found to enhance the leaching rate.

Figures 7 and 8 depict the effects of the initial Cu(II) and Cu(I) concentrations on the copper leaching, respectively. Copper(II) acts as an oxidizing agent in this study and Cu(I) is the reaction product. When the initial Cu(II) concentration was varied from 0 to 0.3 kmol m$^{-3}$, the leaching rate was significantly enhanced. The percentages of the leached copper after 4-hours leaching were 1, 30 and 82% for the initial Cu(II) concentrations of 0, 0.1 and 0.3 kmol m$^{-3}$, respectively. Enhancement of the leaching rates with the Cu(II) concentration were reported in the previous paper. When the initial Cu(I) concentration was varied from 0 to 0.2 kmol m$^{-3}$, the leaching rate slightly decreased. The percentages of the leached copper after 4-hours leaching were 82, 71 and 68% for the initial Cu(I) concentrations of 0, 0.1 and 0.2 kmol m$^{-3}$, respectively. Smith et al. studied the kinetics of the dissolution of copper in cupric ammonium carbonate solutions and reported the similar effect of the Cu(I) concentration on the dissolution rate.
The effect of the temperature on the copper leaching from PCB was also studied. Figure 9 shows the leaching rate curves for 0.1 kmol m$^{-3}$ CuSO$_4$, 5 kmol m$^{-3}$ NH$_3$, 1 kmol m$^{-3}$ (NH$_4$)$_2$SO$_4$ at 298 K, 313 K and 328 K. The leaching rates slightly increased with the rise in temperature. As previously reported,$^9$ the activation energy for the leaching of copper with Cu(II) ions in the ammoniacal alkaline solution was 8 to 13 kJ mol$^{-1}$. This suggests that the leaching reaction is limited by the diffusion in the diffusion layer, which seems to be in accord with the present observation.

5. Conclusions

A novel energy-saving hydrometallurgical process for copper recovery from electronic scraps employing the Cu(I)-ammine complex has been proposed on the basis of thermodynamic considerations. As the first step for its experimental verification, the copper leaching behavior from a PCB in ammoniacal alkaline solutions was studied under a nitrogen atmosphere. Copper in the PCB was oxidized by Cu(II) to form Cu(I)-ammine complex ions, resulting in the decreased oxidation-reduction potential during the leaching. The leaching reaction is expressed as: Cu + Cu(NH$_3$)$_2$$^{2+}$ $\rightarrow$ 2Cu(NH$_3$)$_2$$^{+}$. The Cu(II)-ammine complex significantly enhanced the leaching rate, while the Cu(I)-ammine complex slightly depressed it. Increasing the exposed area of metallic copper by crushing the PCB was important in order to enhance the leaching rate. The effect of temperature on the leaching rate was slight. Consequently, the leaching stage in the proposed copper recovery process has been experimentally verified.

REFERENCES

7) A. Yazawa and M. Eguchi: Hydrometallurgy and Wastewater Treatment (Shishiki Seiren to Haisui Shori), (Tokyo, Kyoritsu Shuppan, 1975) 196–197.