Behavior of Copper Dissolution in an Ammonia Solution Containing Ammonium Chloride or Sulfate

Hirokazu KONISHI1, Takashi BITOH1, Hideki ONO1, Tetsuo OISHI2, Kazuya KOYAMA2 and Mikiya TANAKA2

1 Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan
2 National Institute of Advanced Industrial Science and Technology, 16-1 Onogawa, Tsukuba, Ibaraki 305-8569, Japan

Abstract
The leaching solution was prepared from either copper chloride (NH4Cl solution and NH4Cl or copper sulfate (NH4 solution and (NH4)2SO4). Copper plates were immersed in these solutions and stirred at 298~353 K. The leaching speed of copper was calculated from the obtained weight loss data. Moreover, influence concentrations of NH3 and NH4Cl were investigated for the dissolution of copper.

The dissolution of copper was investigated in solutions containing differing concentrations of NH3 between 0.5 kmol m\(^{-3}\) and 1 kmol m\(^{-3}\) and NH4Cl containing 0.5 kmol m\(^{-3}\) at 313 K, leaching speed increased with increasing NH3 concentration up to 2 kmol m\(^{-3}\) and NH4Cl concentration up to 0.5 kmol m\(^{-3}\). Leaching speed of copper at 600 rpm was calculated to be 3.98 kg m\(^{-2}\) h\(^{-1}\) at 353 K in a solution of 4 kmol m\(^{-3}\) NH3 and 1 kmol m\(^{-3}\) NH4Cl containing 0.5 kmol m\(^{-3}\) Cu(II). The leaching speed of 3.98 kg m\(^{-2}\) h\(^{-1}\) was faster than the 1.65 kg m\(^{-2}\) h\(^{-1}\) obtained at 600 rpm in a solution of 7 kmol m\(^{-3}\) NH3 and 1 kmol m\(^{-3}\) (NH4)2SO4 containing 0.5 kmol m\(^{-3}\) Cu(II) at 353 K. The relationships between \(v^{1/3}\) (stirring speed) and \(R\) (leaching speed) were approximately linear in both baths. On the other hand, the elevated bath temperature increased the leaching speed in a solution of 7 kmol m\(^{-3}\) NH3 and 1 kmol m\(^{-3}\) (NH4)2SO4 containing 0.5 kmol m\(^{-3}\) Cu(II). The leaching speed of copper in an ammonia solution containing ammonium chloride was higher than that in an ammonia solution containing ammonium sulfate.

Key words
Copper Dissolution, Ammonia Solution, Waste, Leaching, Hydrometallurgical Process

1. Introduction
The metals recovery from waste materials is important for preserving the metal resources and the environment. Especially, waste materials originated from various electric appliances, cables and motor vehicles contain a large amount of copper. However, the minable years of copper resource are only 30 years. Therefore, the copper recovery from the waste materials is undoubtedly necessary.

Here, a number of processes for selective separation of copper from waste materials have been proposed and carried out, these include: the chlorination method [1], vacuum distillation, the slag-metal refinement method [2] and the metal immersion method [3]. These pyrometallurgical processes have advantages of high reaction rates and the utilization of existing facilities. However, they also have very high energy consumption. As an alternative, hydrometallurgical processes are attractive for both separation and low energy consumption even though they have lower reaction rates than pyrometallurgical processes such as the metal immersion method [3].

Among hydrometallurgical processes, the ammonia leaching process is well known. The ammonia solution dissolves copper with a very high selectively; iron and aluminum are not dissolved. Many studies have been performed on the dissolution of copper in ammonia solutions [4-7]. Majima reported that leaching speed increased with increasing NH3 concentration up to 7 kmol m\(^{-3}\) and the optimum (NH4)2SO4 concentration existed corresponding to NH3 concentration [4]. Zhou focused on an ammonia solution containing ammonium carbonate, and reported that the leaching speed increased with increasing Cu(II) concentration, O2 gas flow rate and bath temperature [6]. However, the copper dissolution in an ammonia solution containing ammonium chloride has not been reported yet.

In the present study, we focused on an ammonia solution containing ammonium chloride, and examined the behaviors of copper dissolution in ammonia solutions containing ammonium chloride and containing ammonium sulfate in one of optimum conditions of NH3 and (NH4)2SO4 concentration by way of comparison.

2. Potential-pH Diagram of the Cu-NH3-H2O System
The potential-pH diagram assists in understanding the mechanism of various reactions in aqueous solutions. The potential-pH diagram of the Cu-NH3-H2O system [8, 9] in Fig. 1 is obtained under a Cu activity of 0.5 and a total NH3 and NH4+ concentration of 7 kmol m\(^{-3}\). The broken lines indicate the following reactions.
Cu(I) and Cu(II) complexed with NH₃ are stable ionic species in neutral and alkaline solutions. In the presence of excess ammonia, Cu(I) and Cu(II) are also stable as Cu(NH₃)₂⁺ and Cu(NH₃)₃⁺. The oxidation-reduction reactions of Cu(II)/Cu(I) and Cu(I)/Cu are expressed as follows:

\[
\text{Cu} + \text{Cu(NH}_3\text{)}_2^{2+} \rightarrow 2\text{Cu(NH}_3\text{)}_2^{2+}
\]  (5)

The oxidation-reduction potential of Cu(NH₃)₂⁺/Cu(NH₃)₃⁺ is more positive than that of Cu(NH₃)₂⁺/Cu. This indicates that Cu(NH₃)₂⁺ can oxidize metallic copper in an ammoniacal alkaline solution. Moreover, the oxidation-reduction potential of Cu(I)/Cu is more positive than that of hydrogen evolution (eq. (1)), indicating Cu(I) can be preferentially reduced to metallic copper. In the aqueous solutions of CuSO₄-NH₃-(NH₄)SO₄ and CuCl₂-NH₃-HCl used in this work, Cu(II) was present as stable Cu(NH₃)₂⁺. The pH was in the region of 8–10 and Cu was leached by Cu(NH₃)₂⁺ as in reaction (5).

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

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

4. Results and Discussion

4.1 Dissolution of Cu in an ammonium solution containing ammonium sulfate

In order to investigate a leaching behavior of copper, copper plates were immersed and stirred in a solution of 7 kmol m⁻³ NH₃ and 1 kmol m⁻³ (NH₄)₂SO₄ containing 0.5 kmol m⁻³ Cu(II) at 313 K. The leaching ratio of copper increased with increasing stirring speeds in Fig. 2. The copper plates were completely dissolved after stirring for 120 min at 100 rpm, 60 min at 300 rpm, and 40 min at 600 rpm. At 353 K the leaching ratio reached 100 % after stirring for 20 min at 600 rpm in Fig. 3. We calculated the leaching speed from the copper weight loss per unit surface area measured under the above mentioned conditions. Here, we omitted the datum of leaching ratio over 85 % since it is difficult to measure the surface area by the large shape change of samples. In Fig. 4, the relationship between copper weight loss per unit surface area and immersion time at 313 K was approximately linear in all conditions.

\[
R = k [\text{Cu(NH}_3\text{)}_2^{2+}]^{1/2} V^{2/3}
\]  (6)

\(R\): leaching speed \\
\(V\): stirring speed \\
\(k\): reaction rate constant

The weight loss at 600 rpm was three-times as much as that at 0 rpm. Moreover, the slopes, i.e., indicating leaching speeds were higher with increasing stirring speed. The leaching speed at 600 rpm was calculated to be 0.80 kg m⁻² h⁻¹. At 353 K similar results were observed. However, line slopes (leaching speed) at 353 K were found to be higher than those at 313 K. The leaching speed at 600 rpm and 353 K was calculated to be 1.65 kg m⁻² h⁻¹, more than twice that at 600 rpm and 313 K. The elevated bath temperature also increased the leaching speed as a reference [6] due to increase of ion diffusion rate and decrease of viscosity of the ammoniacal alkaline solution. In these conditions, the stirring speed affects the leaching speed as (6) formula, because Cu was leached by Cu(NH₃)₂⁺ as in reaction (5) [10, 11].
So, the relationships between $V^{2/3}$ and $R$ at 313 K and 353 K were shown in Fig. 5. The both relationships were approximately linear followed by (6) formula.

Fig. 4 Relationship between weight loss of copper per unit surface area and immersion time $t$ in 7 kmol m$^{-3}$ NH$_3$ and 1 kmol m$^{-3}$ (NH$_4$)$_2$SO$_4$ containing 0.5 kmol m$^{-3}$ Cu(II) at 313 K

Fig. 5 Relationship between $V^{2/3}$ and leaching speed $R$ at 313 K and at 353 K in 7 kmol m$^{-3}$ NH$_3$ and 1 kmol m$^{-3}$ (NH$_4$)$_2$SO$_4$ containing 0.5 kmol m$^{-3}$ Cu(II) at 313 K

4.2 Dissolution of Cu in an ammonia solution containing ammonium chloride

In order to investigate the influence of NH$_3$ concentration for leaching copper, copper plates were immersed and stirred at 300 rpm in solutions of 1~6 kmol m$^{-3}$ NH$_3$ and 1 kmol m$^{-3}$ NH$_4$Cl containing 0.5 kmol m$^{-3}$ Cu(II) at 313 K. Figure 6 shows the relationship between leaching speed of copper per unit surface area and NH$_3$ concentration. The leaching speed in 0.5 kmol m$^{-3}$ NH$_4$Cl was faster than that in 0 kmol m$^{-3}$ NH$_4$Cl. But the leaching speed almost didn’t change over 0.5 kmol m$^{-3}$ NH$_4$Cl. Majima reported that leaching speed increased with increasing NH$_3$ concentration up to 7 kmol m$^{-3}$ and the optimum (NH$_4$)$_2$SO$_4$ concentration existed corresponding to NH$_3$ concentration in an ammonia solution containing ammonium sulfate [4]. On the other hand, we found that leaching speed increased with increasing NH$_3$ concentration up to 2 kmol m$^{-3}$ and NH$_4$Cl concentration up to 0.5 kmol m$^{-3}$. The small change of NH$_3$ and NH$_4$Cl concentration are related to small change pH in an ammonia solution. Moreover, NH$_4^+$ concentration affects (5) reaction as an oxidation agent. So it is considered that leaching speed affects NH$_3$ and NH$_4$Cl concentration.

Fig. 6 Relationship between leaching speed of copper per unit surface area and NH$_3$ concentration in 1 kmol m$^{-3}$ NH$_4$Cl containing 0.5 kmol m$^{-3}$ Cu(II) at 313 K

Fig. 7 Relationship between leaching speed of copper per unit surface area and NH$_4$Cl concentration in 4 kmol m$^{-3}$ NH$_3$ containing 0.5 kmol m$^{-3}$ Cu(II) at 313 K

Copper plates were immersed and stirred in a solution of 4 kmol m$^{-3}$ NH$_3$ and 1 kmol m$^{-3}$ NH$_4$Cl containing 0.5 kmol m$^{-3}$ Cu(II) at 313 K.
kmol m$^{-3}$ Cu(II) as one of optimum concentration conditions at 353 K. This solution almost dissolved a copper plate after 8 min in Fig. 8. We calculated the leaching speed from the copper weight loss per unit surface area. Here, we omitted the datum of leaching ratio over 85% since it is difficult to measure the surface area by the large shape change of samples. Under these conditions, the weight loss of copper per unit surface area varied with 

\[ \frac{\text{Weight loss of copper per unit surface area}}{\text{Immersion time}} \]

The relationship between leaching speed at 353 K was shown in Fig. 9. The slopes (leaching speed) were dependent on the stirring speed. The relationship between $V^{2/3}$ and $R$ at 353 K was shown in Fig. 10. The relationship was approximately linear followed by (6) formula in a similar behavior to the above mentioned result in an ammonia solution containing ammonium sulfate. Moreover, leaching speed of 3.98 kg m$^{-2}$ h$^{-1}$ at 600 rpm was faster than the 1.65 kg m$^{-2}$ h$^{-1}$ obtained at 600 rpm in a solution of 7 kmol m$^{-3}$ NH$_3$ and 1 kmol m$^{-3}$ (NH$_4$)$_2$SO$_4$ containing 0.5 kmol m$^{-3}$ Cu(II) at 353 K. This result suggested that leaching speed affects the differences of Cu ion diffusion rate and viscosity of the ammoniacal alkaline solution. We have already reported the difference by electrochemical method [12]. Compared with the sulfate system, the current density was higher in the chloride system by anodic polarization. The difference between the chloride and sulfate systems was attributed to the existence of ternary Cu(I)/NH$_3$/Cl$^-$-complexes [14].

In consideration of these results, an ammonia solution containing ammonium chloride is better than an ammonia solution containing ammonium sulfate for copper leaching. These results suggest that it is possible to achieve selective separation of copper from waste materials using the ammonia leaching process.

Fig. 8 Relationship between leaching ratio and immersion time at 353 K in 4 kmol m$^{-3}$ NH$_3$ and 1 kmol m$^{-3}$ NH$_4$Cl containing 0.5 kmol m$^{-3}$ Cu(II) at 353 K

Fig. 9 Relationship between weight loss of copper per unit surface area and immersion time $t$ in 4 kmol m$^{-3}$ NH$_3$ and 1 kmol m$^{-3}$ NH$_4$Cl containing 0.5 kmol m$^{-3}$ Cu(II) at 353 K

Fig. 10 Relationship between $V^{2/3}$ and leaching speed $R$ at 313 K and at 353 K in 4 kmol m$^{-3}$ NH$_3$ and 1 kmol m$^{-3}$ NH$_4$Cl containing 0.5 kmol m$^{-3}$ Cu(II) at 353 K

5. Conclusions

The dissolution of copper in an ammonia solution containing ammonium chloride or sulfate has been examined. The results obtained are summarized as follows:

1. Leaching speeds of Cu at 600 rpm were calculated to be 0.80 and 1.65 kg m$^{-2}$ h$^{-1}$ at 313 and 353 K in a solution of 7 kmol m$^{-3}$ NH$_3$ and 1 kmol m$^{-3}$ (NH$_4$)$_2$SO$_4$ containing 0.5 kmol m$^{-3}$ Cu(II). The leaching speed at 353 K was found to be higher than those at 313 K. The relationships between $V^{2/3}$ (stirring speed) and R (leaching speed) at 313 K and 353 K were approximately linear.

2. Leaching speed increased with increasing NH$_3$ concentration up to 2 kmol m$^{-3}$ and NH$_4$Cl concentration up to 0.5 kmol m$^{-3}$.

3. Leaching speed of Cu at 600 rpm was calculated to be 3.98 kg m$^{-2}$ h$^{-1}$ at 353 K in 4 kmol m$^{-3}$ NH$_3$ and 1 kmol m$^{-3}$ NH$_4$Cl containing 0.5 kmol m$^{-3}$ Cu(II). The leaching speed of 3.98 kg m$^{-2}$ h$^{-1}$ at 600 rpm was faster than the 1.65 kg m$^{-2}$ h$^{-1}$ obtained at 600 rpm in 7...
kmol m⁻³ NH₃ and 1 kmol m⁻³ (NH₄)₂SO₄ containing 0.5 kmol m⁻³ Cu(II) at 353 K.

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References