

Selective Separation and Recovery of Copper from Iron and Copper Mixed Waste by Ammonia Solution

Assistant Professor Hirokazu KONISHI
Graduate School of Engineering, Osaka University

1. Introduction

Recycling of ferrous scrap is an important issue. Copper metal mixed with shredded ferrous scrap from car motors and cables is difficult to selectively remove by magnetic filtration. The presence of copper impurities as low as 0.1 mass % prevents the recycling of ferrous scrap, as it spreads into the iron crystal grain boundary and reduces its resistivity to stretching. Therefore, a process to remove copper from ferrous scrap at low cost is required.¹⁾ A number of processes for selective separation of copper from ferrous scrap have been proposed and carried out, these include: the chlorination method,²⁾ vacuum distillation, the slag-metal refinement method³⁾ and the metal immersion method.⁴⁾ These pyrometallurgical processes have advantages such as high reaction rates and the utilization of existing facilities. However, they also have very high energy consumption and therefore have not been applied to practical uses. As an alternative, hydrometallurgical processes are attractive in terms of both high separation yield and low energy consumption even though they have low reaction rates.

Among hydrometallurgical processes, the ammonia leaching process is well known. Ammonia solution dissolves copper with very high selectivity where iron and aluminum are not dissolved. Many studies have been conducted on the dissolution of copper in ammonia solutions.⁵⁻⁸⁾ However, problems relating to the separation of copper and iron using ammonia solutions have not been solved.

On the basis of this background, we focused on the selective separation of copper from iron and copper mixed waste using the ammonia leaching process. Dissolution of copper in ammonia solutions containing ammonium chloride or sulfate was examined in the present study.

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^{9,10)} (**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

were stirred at 298~353 K. After stirring, the plates were rinsed with water and acetone, and the weights were measured. The leaching speed of copper was calculated from the obtained weight loss data. Optimum concentrations of NH_3 and NH_4Cl were determined for dissolution of copper.

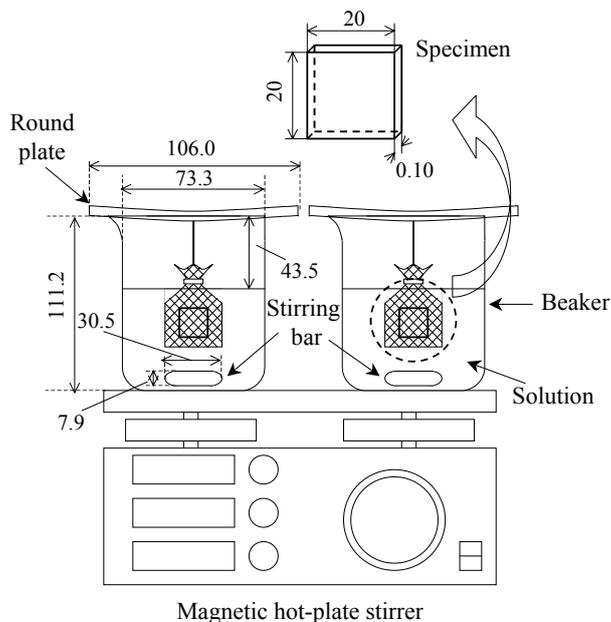


Fig. 2. Schematic representation of experimental apparatus for leaching of Cu and Fe plates in ammoniacal alkaline solutions; dimensions in mm.

4. Results and Discussion

4.1. Dissolution of Cu in an Ammonia Solution Containing Ammonium Sulfate

In order to investigate the leaching behavior of copper, copper plates were immersed and stirred in a solution of $7 \text{ kmol m}^{-3} \text{ NH}_3$ and $1 \text{ kmol m}^{-3} (\text{NH}_4)_2\text{SO}_4$ containing $0.5 \text{ kmol m}^{-3} \text{ Cu(II)}$ at 313 K. The leaching ratio of copper increased with stirring speed in **Fig. 3**. The copper plate was completely dissolved in the ammoniacal alkaline solution 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. 4**. The elevated bath temperature increased the leaching speed due to ion activation and a decrease in the viscosity of the ammoniacal alkaline solution.

Copper weight loss per unit surface area was measured under the above mentioned conditions. In **Fig. 5**, the relationship between copper weight loss per unit surface area and immersion time at 313 K was approximately linear in all conditions. The weight loss at 600 rpm was three-times as much as that at 0 rpm. Moreover, the slopes (indicating leaching speeds) were steeper at increased stirring speeds. The leaching speed at 600 rpm was calculated to be $0.80 \text{ kg m}^{-2} \text{ h}^{-1}$. At

353 K similar results were observed in Fig 6. However, line slopes (leaching speed) at 353 K were found to be steeper than those at 313 K. The leaching speed at 600 rpm and 353 K was calculated to be $1.65 \text{ kg m}^{-2} \text{ h}^{-1}$, more than twice that at 600 rpm and 313 K.

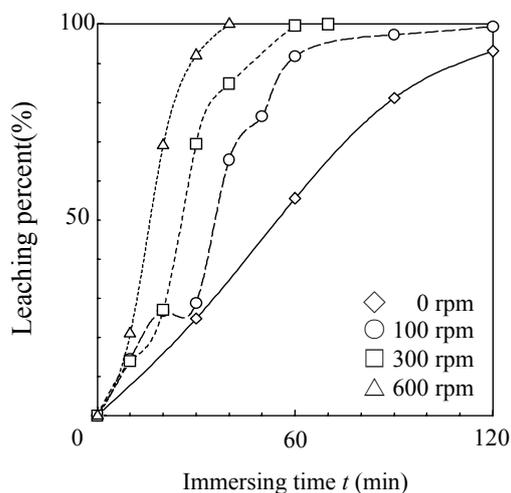


Fig. 3. Relationship between leaching percent and immersion time t in $7 \text{ kmol m}^{-3} \text{ NH}_3$ and $1 \text{ kmol m}^{-3} (\text{NH}_4)_2\text{SO}_4$ containing $0.5 \text{ kmol m}^{-3} \text{ Cu(II)}$ at 313 K.

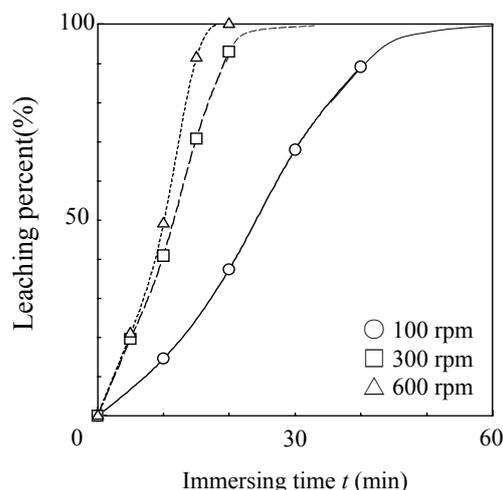


Fig. 4. Relationship between leaching percent and immersion time t in $7 \text{ kmol m}^{-3} \text{ NH}_3$ and $1 \text{ kmol m}^{-3} (\text{NH}_4)_2\text{SO}_4$ containing $0.5 \text{ kmol m}^{-3} \text{ Cu(II)}$ at 353 K.

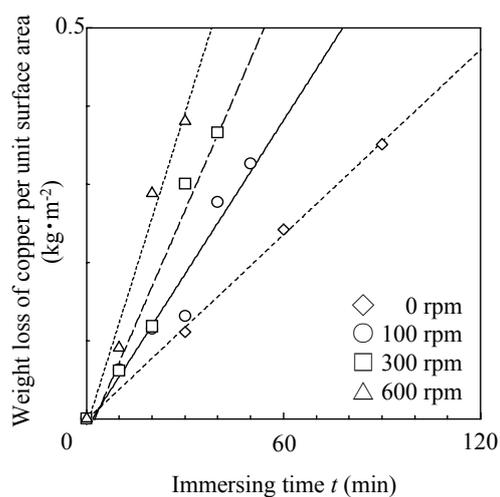


Fig. 5. Relationship between weight loss of copper per unit surface area and immersion time t in $7 \text{ kmol m}^{-3} \text{ NH}_3$ and $1 \text{ kmol m}^{-3} (\text{NH}_4)_2\text{SO}_4$ containing $0.5 \text{ kmol m}^{-3} \text{ Cu(II)}$ at 313 K.

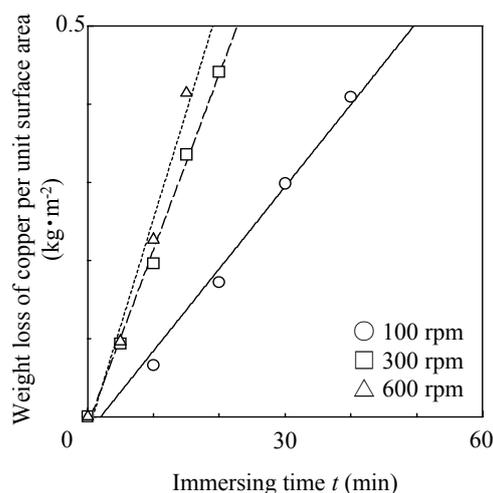


Fig. 6. Relationship between weight loss of copper per unit surface area and immersion time t in $7 \text{ kmol m}^{-3} \text{ NH}_3$ and $1 \text{ kmol m}^{-3} (\text{NH}_4)_2\text{SO}_4$ containing $0.5 \text{ kmol m}^{-3} \text{ Cu(II)}$ at 353 K.

4.2. Dissolution of Cu in an Ammonia Solution Containing Ammonium Chloride

In order to optimize the NH_3 concentration for leaching copper, copper plates were immersed and stirred in 1~6 kmol m^{-3} NH_3 and 1 kmol m^{-3} NH_4Cl containing 0.5 kmol m^{-3} Cu(II) at 313 K. In stirring at 300 rpm, the leaching speed was fastest with 4 kmol m^{-3} NH_3 (**Fig. 7**). Moreover, to optimize the NH_4Cl concentration, copper plates were immersed and stirred in 4 kmol m^{-3} NH_3 and 0~3 kmol m^{-3} NH_4Cl containing 0.5 kmol m^{-3} Cu(II) at 313 K. In this case, the fastest leaching speed at 300 rpm was obtained at approximately 1 kmol m^{-3} NH_4Cl in **Fig. 8**.

These results suggest that concentrations of 4 kmol m^{-3} NH_3 and 1 kmol m^{-3} NH_4Cl containing 0.5 kmol m^{-3} Cu(II) are the most suitable for ammonia leaching of copper.

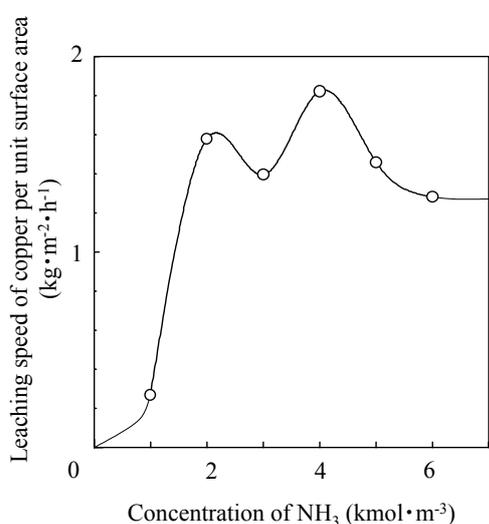


Fig. 7. Relationship between leaching speed of copper per unit surface area and NH_3 concentration in 1 kmol m^{-3} NH_4Cl containing 0.5 kmol m^{-3} Cu(II) at 313 K.

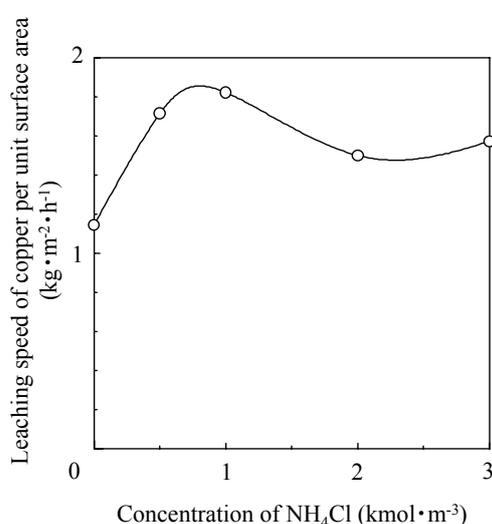


Fig. 8. Relationship between leaching speed of copper per unit surface area and NH_4Cl concentration in 4 kmol m^{-3} NH_3 containing 0.5 kmol m^{-3} Cu(II) at 313 K.

Using these optimized concentrations, copper plates were immersed and stirred at 353 K. This ammoniacal alkaline solution almost dissolved a copper plate after 8 min at 600 rpm in **Fig. 9**. Under these conditions, the weight loss of copper per unit surface area varied with immersion time at 353 K in **Fig. 10**. The slope (leaching speed) was dependent on the stirring speed, and was the highest observed of all in this study. A leaching speed of 3.98 $\text{kg m}^{-2} \text{h}^{-1}$ was obtained at 600 rpm, faster than the 1.65 $\text{kg m}^{-2} \text{h}^{-1}$ obtained at 600 rpm in 7 kmol m^{-3} NH_3 and 1 kmol m^{-3} $(\text{NH}_4)_2\text{SO}_4$ containing 0.5 kmol m^{-3} Cu(II) at 353 K.

In consideration of these results, an ammonia solution containing ammonium chloride is better than an ammonia solution containing ammonium sulfate for the selective separation of copper from ferrous scrap by ammonia leaching.

Finally, we investigated potential selective separation of copper from ferrous scrap using the ammonia leaching process. Both copper and iron plates were immersed and stirred in solutions at the optimal concentrations of $4 \text{ kmol m}^{-3} \text{ NH}_3$ and $1 \text{ kmol m}^{-3} \text{ NH}_4\text{Cl}$ containing $0.5 \text{ kmol m}^{-3} \text{ Cu(II)}$ at 353 K. The variation of leaching ratio with immersed time is shown in **Fig. 11**. The leaching ratio of copper reached 100 % after 12 min at 300 rpm. In contrast, the iron plate hardly dissolved in the ammoniacal alkaline solution. These results suggest that it is possible to achieve selective separation of copper and iron using the ammonia leaching process.

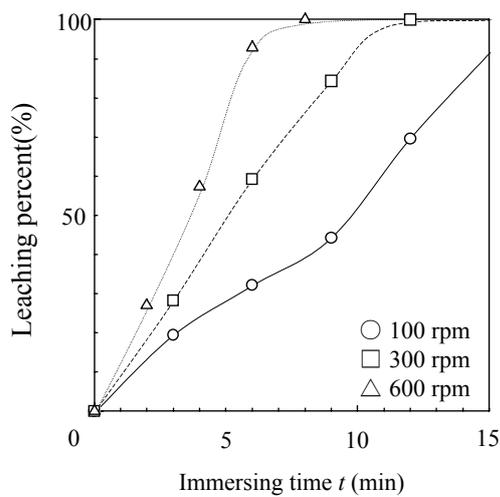


Fig. 9. Relationship between leaching percent and immersion time t in $4 \text{ kmol m}^{-3} \text{ NH}_3$ and $1 \text{ kmol m}^{-3} \text{ NH}_4\text{Cl}$ containing $0.5 \text{ kmol m}^{-3} \text{ Cu(II)}$ at 353 K.

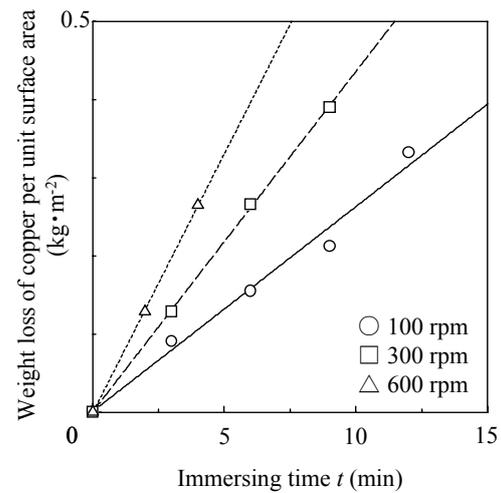


Fig. 10. Relationship between weight loss of copper per unit surface area and immersion time t in $4 \text{ kmol m}^{-3} \text{ NH}_3$ and $1 \text{ kmol m}^{-3} \text{ NH}_4\text{Cl}$ containing $0.5 \text{ kmol m}^{-3} \text{ Cu(II)}$ at 353 K.

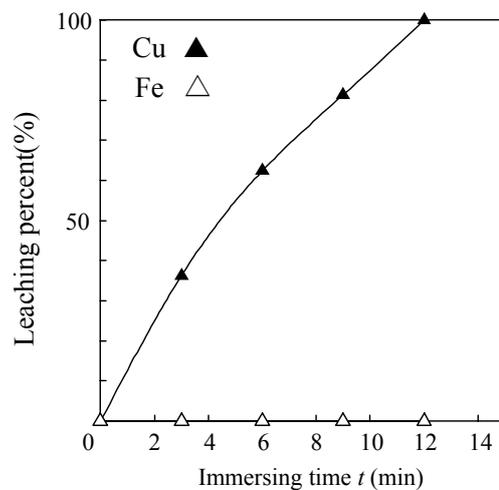


Fig. 11. Relationship between leaching percent and immersion time t in $4 \text{ kmol m}^{-3} \text{ NH}_3$ and $1 \text{ kmol m}^{-3} \text{ NH}_4\text{Cl}$ containing $0.5 \text{ kmol m}^{-3} \text{ Cu(II)}$ at 353 K and 300 rpm.

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) At 313 K in a solution of $7 \text{ kmol m}^{-3} \text{ NH}_3$ and $1 \text{ kmol m}^{-3} (\text{NH}_4)_2\text{SO}_4$ containing $0.5 \text{ kmol m}^{-3} \text{ Cu(II)}$ a copper plate completely dissolved after stirring for 120 min at 100 rpm, 60 min at 300 rpm, and 40 min at 600 rpm. The leaching percent of copper increased with stirring speed. The weight loss at 600 rpm was three-times as much as that at 0 rpm. Moreover, the line slopes (indicating leaching speed) were steeper at increased stirring speeds. The leaching speed at 600 rpm was calculated to be $0.80 \text{ kg m}^{-2} \text{ h}^{-1}$.
- (2) The leaching percent at 600 rpm and 353 K reached 100 % after 20 min in $7 \text{ kmol m}^{-3} \text{ NH}_3$ and $1 \text{ kmol m}^{-3} (\text{NH}_4)_2\text{SO}_4$ containing $0.5 \text{ kmol m}^{-3} \text{ Cu(II)}$. The slopes (leaching speed) were found to be steeper than those at 313 K. The leaching speed at 600 rpm was estimated to be $1.65 \text{ kg m}^{-2} \text{ h}^{-1}$ at 353 K.
- (3) Optimum solution concentrations at 313 K for ammonia leaching of copper were $4 \text{ kmol m}^{-3} \text{ NH}_3$ and $1 \text{ kmol m}^{-3} \text{ NH}_4\text{Cl}$ containing $0.5 \text{ kmol m}^{-3} \text{ Cu(II)}$.
- (4) At 353 K, under the optimum concentrations stated in (3), the ammoniacal alkaline solution almost dissolved a copper plate after 8 min at 600 rpm. In this case, the leaching speed at 600 rpm was estimated to be $3.98 \text{ kg m}^{-2} \text{ h}^{-1}$.
- (5) The leaching percents of copper and iron plates were estimated to be 100 and 0 %, respectively, after 12 min under the optimum concentrations stated in (3) at 300 rpm and 353 K.

ACKNOWLEDGEMENTS

Financial support from JFE 21st Century Foundation is gratefully appreciated.

REFERENCES

- 1) S. Uchida, I Takemura, M. Tokuda and K. Osseo-Asare: *ISIJ Int.*, **36** (1996), 522.
- 2) H-J. Li, H. Suito and K. Tokuda: *ISIJ Int.*, **35** (1995), 1079.
- 3) K. Kitamura, T. Takenouchi and Y. Iwanami: *Tetsu-to-Hagané*, **75** (1989), 82.
- 4) M. Iwase and K. Tokinori: *Steel Research*, **62** (1991), 235.
- 5) H. Majima, S. Nigo, T. Hirato, Y. Awakura and M. Iwai: *Shigen-to-Sozai*, **109** (1993), 191.
- 6) S. Nigo, H. Majima, T. Hirato, Y. Awakura and M. Iwai: *Shigen-to-Sozai*, **109** (1993), 337.
- 7) K. Zhou, K. Shinme, S. Anezaki: *Shigen-to-Sozai*, **111** (1995), 49.
- 8) K. Zhou, K. Shinme, S. Anezaki: *Shigen-to-Sozai*, **111** (1995), 55.
- 9) K. Koyama, M. Tanaka and J-C. Lee: *Mater. Trans.*, **47** (2006), 1788.
- 10) K. Koyama, M. Tanaka, Y. Miyasaka and J-C. Lee: *Mater. Trans.*, **47** (2006), 2076.