

Enhancement of chalcopyrite leaching by ferrous ions in acidic ferric sulfate solutions

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Abstract

The effects of ferrous ions on chalcopyrite oxidation with ferric ions in 0.1 mol dm^{-3} sulfuric acid solutions were investigated by leaching experiments at 303 K in nitrogen. With high cupric ion concentrations, the chalcopyrite oxidation was enhanced by high concentrations of ferrous ions and copper extraction was mainly controlled by the concentration ratio of ferrous to ferric ions or the redox potential of solutions. Ferrous ions, however, suppressed the chalcopyrite oxidation when cupric ion concentrations were low. A reaction model, which involves chalcopyrite reduction to intermediate Cu_2S by ferrous ions and oxidation of the Cu_2S by ferric ions, was proposed to interpret the results. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Chalcopyrite; Oxidation; Leaching; Ferrous ions; Ferric ions; Cupric ions, redox potential

1. Introduction

Dump leaching is used to recover copper from low-grade ores that would otherwise be waste and the importance of leaching in copper production is increasing [1]. However, the leaching rate of chalcopyrite, an abundant copper mineral, is very low. To improve leaching rates, the factors affecting chalcopyrite leaching must be better understood.

In the leaching, chalcopyrite is oxidized by ferric ions and/or dissolved oxygen in sulfuric acid solution to extract cupric ions. During this process, ferrous ions are also extracted from chalcopyrite. Previ-

ously, the authors found that ferrous ions act to promote the chalcopyrite oxidation with dissolved oxygen [2–5], and this phenomenon may contribute to chalcopyrite leaching near the surface of leaching dumps. However, chalcopyrite oxidation with dissolved oxygen is less important in the deep parts of leaching dumps because oxygen concentrations decrease rapidly with increasing depth. In the deep parts, ferric ions are the more important oxidant for leaching chalcopyrite.

There are several reports of the effects of ferrous ions on chalcopyrite oxidation with ferric ions. Dutrizac et al. [6] and Hirato et al. [7] reported that ferrous ions suppress chalcopyrite oxidation with ferric ions in sulfuric acid solution. However, there is a report implying that ferrous ions promote this reaction. Kametani and Aoki [8] investigated the effect of the solution redox potential on chalcopyrite

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leaching in the presence of ferrous and ferric ions, and reported that leaching rates increased with increasing the potential but decreased above a certain critical potential. The potential of solutions containing ferric and ferrous ions increases with increasing concentration ratios of ferric to ferrous ions. Therefore, Kametani's result indicates that the rate of chalcopyrite oxidation with ferric ions is higher in the presence of an adequate amount of ferrous ions than in the absence of ferrous ions.

In the present study, leaching experiments were carried out in nitrogen to establish the effects of ferrous ions on chalcopyrite oxidation with ferric ions in sulfuric acid solutions and it was found that ferrous ions promote the chalcopyrite oxidation in the presence of high concentrations of cupric ions.

2. Method

2.1. Chalcopyrite sample and leaching solution

A very pure massive chalcopyrite sample was ground with an agate mortar. The components of this sample were: copper 33.32%, iron 29.63%, zinc 0.2%, lead < 0.01% and silica 0.28%. With X-ray diffraction analysis, only chalcopyrite was detected in the sample. The ground sample was dry-sieved to obtain the -200 mesh portion, and the $-65 + 100$ mesh chalcopyrite sample was prepared by wet sieving and drying at room temperature.

Leaching solutions were 0.1 mol dm^{-3} sulfuric acid containing various concentrations of ferric, ferrous, and cupric ions. Reagent grade $\text{Fe}(\text{SO}_4) \cdot 7\text{H}_2\text{O}$, $\text{Fe}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, H_2SO_4 (Wako Pure Chemicals Ltd.), and distilled–deionized water were used to prepare the solution.

2.2. Shaking flask leaching experiments

Except where mentioned, the shaking flask leaching experiments were carried out as follows: a 10-cm^3 portion of the solution and 0.1 g of -200 mesh chalcopyrite sample were mixed in a 50-cm^3 Erlenmeyer flask and the flask was capped with a silicon rubber plug. Two injection needles were inserted through the plug and $1 \text{ dm}^3 \text{ min}^{-1}$ of nitrogen was introduced into the flask for about 15 min to remove

oxygen using the needles as inlet and outlet. Then the needles were removed from the plug and the flask was reciprocally shaken in a water bath at 303 K (amplitude 40 mm; shaking speed 120 strokes min^{-1}). After 24 h, the leaching solution was filtered with a membrane filter (pore size: $0.22 \mu\text{m}$) and the copper and total soluble iron concentrations were determined by atomic absorption spectroscopy. The redox potential of the leaching solution was measured at room temperature with a platinum electrode using a saturated Ag/AgCl electrode as the reference electrode and it was converted to values against a standard hydrogen electrode (SHE). Final concentrations of ferric and ferrous ions were calculated based on the solution potential and total soluble iron concentration using the Nernst equation for sulfuric acid solution containing ferric and ferrous ions (Eq. (1)) [9] and the mass balance equation for soluble iron species (Eq. (2)).

$$E = 0.670 + 0.059 \log \left(\frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} \right) \quad (1)$$

$$[\text{Total Fe}] = [\text{Fe}^{2+}] + [\text{Fe}^{3+}] \quad (2)$$

where $[\text{Total Fe}]$, $[\text{Fe}^{3+}]$ and $[\text{Fe}^{2+}]$ indicate the concentrations of total soluble iron, ferric ions and ferrous ions, and E is the solution potential (V vs. SHE).

To determine the amount of elemental sulfur formed during the leaching, shaking flask experiments were carried out with 500-cm^3 Erlenmeyer flasks containing 1.0 g of chalcopyrite and 100 cm^3 of leaching solution in the same manner. After 24 h, the residue was recovered by filtration using 5-A filter paper and washed with 0.1 mol dm^{-3} sulfuric acid and distilled–deionized water, then dried in air at room temperature. Elemental sulfur was extracted to benzene from the dried residue using Soxhlet's extractor and the sulfur concentration was determined from the light absorbance at 330 nm.

2.3. Column leaching experiments

Column leaching was performed with the apparatus outlined in Fig. 1. A glass tube (inner diameter 3.5 mm, height 10 cm) with a glass ball filter was used as the leaching column, and 0.50 g of the chalcopyrite ($-65 + 100$ mesh portion) was placed

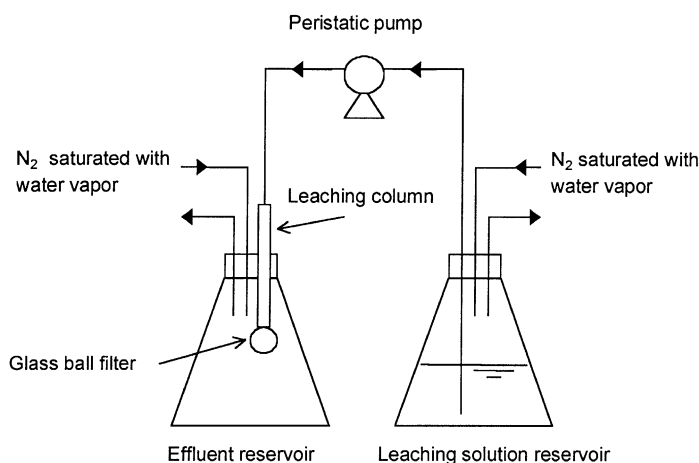


Fig. 1. Column leaching arrangement.

in the column. Leaching solution was pumped to the column at $100 \text{ cm}^3 \text{ day}^{-1}$ from a leaching solution reservoir set in a water bath at 303 K. During the experiments, nitrogen was introduced into the reservoirs to remove oxygen. The solution collected in the effluent reservoir was removed daily, and its volume and copper ion concentration were measured to determine the amount of extracted copper.

2.4. Chalcopyrite rest potential measurements

A chalcopyrite electrode was prepared from the massive ore used for leaching experiments. A regular shape specimen was cut from the ore and ground to a thickness of about 5 mm by using #120, #600, #1000 and #3000 alumina powder in this order. The specimen was washed in distilled–deionized water with ultrasonic washer and rinsed with acetone. A gold thin layer was then sputter deposited on one side of the specimen to give an ohmic contact and copper wire was connected on the gold layer with conducting silver resin. Then the specimen was embedded in insulating resin to expose only one side of the chalcopyrite. Before each measurement, the exposed surface of chalcopyrite was ground with #3000 alumina powder and washed in the same manner described above. The exposed surface area was determined by image analysis to be 0.64 cm^2 .

The chalcopyrite electrode was immersed in 0.1 mol dm^{-3} sulfuric acid containing various concen-

trations of ferric, ferrous and cupric ions and the rest potential was measured using saturated Ag–AgCl electrode as reference electrode at 303 K in nitrogen with stirring. Significant changes in the potential were not observed in 10 min. In this paper, the rest potentials after 10-min immersion were shown in values against SHE.

3. Results

3.1. Shaking flask leaching experiments

Table 1 shows the amounts of copper extracted and the elemental sulfur formed after 24 h in the presence of 0.03 mol dm^{-3} ferric ions with or without 1.00 mol dm^{-3} ferrous ions. The amounts of extracted copper and elemental sulfur were larger with ferrous ions and the mole ratio of extracted copper to elemental sulfur is about 2 both with and without ferrous ions. Because a large amount of

Table 1
Effects of ferrous ions on the amounts of copper extracted and elemental sulfur formed after 24 h in the presence of 0.03 mol dm^{-3} ferric ions (unit: mmol dm^{-3})

Fe(II) added	Cu extracted	S formed
0	0.52	1.03
1000	1.43	3.14

Table 2

Reproducibility of copper extraction in shaking flask experiments using 50-cm³ flask containing 0.1 g chalcopyrite and 10 cm³ leaching solution at 303 K in nitrogen (unit: mmol dm⁻³)

	Condition 1	Condition 2
Run 1	1.13	3.09
Run 2	1.12	2.99
Run 3	1.09	3.09
Run 4	1.10	3.09
Average	1.11	3.06
Standard deviation	0.02	0.05

The solutions were 0.1 mol dm⁻³ sulfuric acid containing 0.03 mol dm⁻³ ferric ions. In the experiments indicated as “Condition 1”, ferrous ions were not added. In the experiments indicated as “Condition 2”, 1 mol dm⁻³ ferrous ions were added.

chalcopyrite sample is needed for elemental sulfur assay, these experiments were carried out in a large scale (500-cm³ Erlenmeyer flasks containing 1.0 g of chalcopyrite and 100 cm³ of leaching solution). However, most of other experiments were carried out in a small scale (50-cm³ Erlenmeyer flasks containing 0.1 g of chalcopyrite and 10 cm³ of leaching solution) for saving the chalcopyrite sample.

Table 2 shows the reproducibility of the small-scale leaching experiments. In this series of experiments, copper extraction after 24 h was investigated in the presence of 0.03 mol dm⁻³ ferric ions with or without 1.00 mol dm⁻³ ferrous ions repeatedly. The results indicate that enough reproducibility was obtained in the small-scale experiments. The difference

in the amounts of extracted copper between large-scale experiments [(Table 1)] and small-scale experiments [(Table 2)] may be interpreted by the difference in solution stirring. The flask shaking condition (amplitude and frequency) was the same in both scales, so solution stirring was weaker in the large-scale experiments than that in the small-scale experiments and this may have caused the smaller amount of extracted copper in the large-scale experiments.

Leaching experiments were carried out in the presence of various concentrations of ferric and ferrous ions without cupric ions. Fig. 2 shows the initial solution potential as a function of the initial concentration ratio of ferric to ferrous ions. A dotted line in the figure corresponds to the Nernst equation shown in Eq. (1) and the experimental results agreed well with Eq. (1).

Fig. 3 shows the amount of extracted copper, ferrous ions and ferric ions after 24 h as a function of the initial ferrous ion concentration. Even without the addition of ferric ions, ferric ions and extracted copper formed after 24 h. With ferric ion addition, the amounts of extracted copper and consumption of ferric ions increased when high concentrations of ferrous ions were added. In all cases, ferrous ion concentration after 24 h was almost the same as the initial concentration.

Figs. 4 and 5 show the amounts of extracted copper after 24 h as a function of the initial ferrous to ferric ion concentration ratio (Fig. 4) and as a function of the initial solution potential (Fig. 5). The

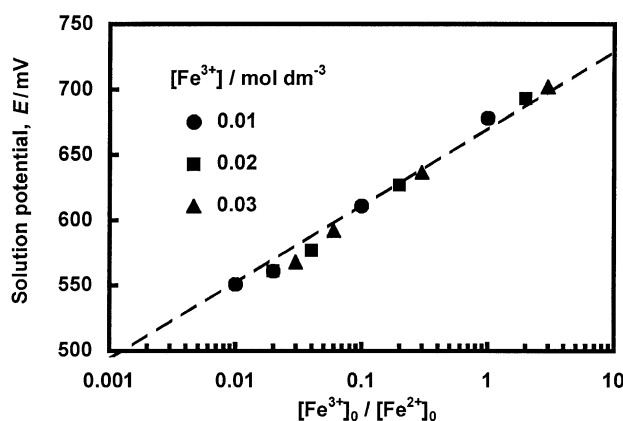


Fig. 2. Relationship between the initial concentration ratio of ferric to ferrous ions ($[\text{Fe}^{3+}]_0/[\text{Fe}^{2+}]_0$) and the initial redox potential (E) in 0.1 mol dm⁻³ sulfuric acid.

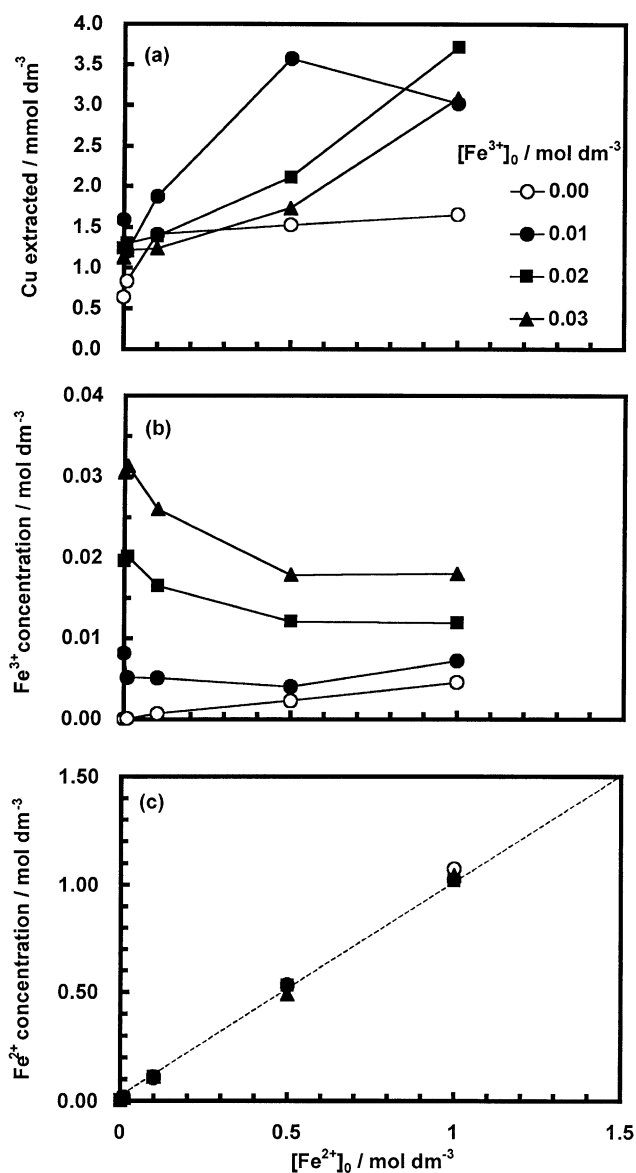


Fig. 3. Effect of initial ferrous ion concentration ($[\text{Fe}^{2+}]_0$) on the leaching of a -200 mesh chalcopyrite sample with 0.1 mol dm⁻³ sulfuric acid containing various initial concentrations of ferric ions ($[\text{Fe}^{3+}]_0$). Leaching time was 24 h.

amount of extracted copper mainly depended on the ferrous to ferric ion ratio or the potential, and increased markedly at the ratios above 10 or at potentials below 610 mV vs. SHE.

During the shaking flask leaching experiments, cupric ions were extracted from chalcopyrite and accumulated in the solutions. To clarify the role of cupric ions on chalcopyrite leaching, a series of

leaching experiments were carried out. The experimental conditions and results are summarized in Table 3. In the absence of oxidant ferric ions (Nos. 1 to 3), the amounts of extracted copper were negligible even with cupric ions or with ferrous and cupric ions. However, in the presence of ferric ions (Nos. 4 to 7), more than 1 mmol dm⁻³ of copper ions was extracted. The amount of extracted copper in the

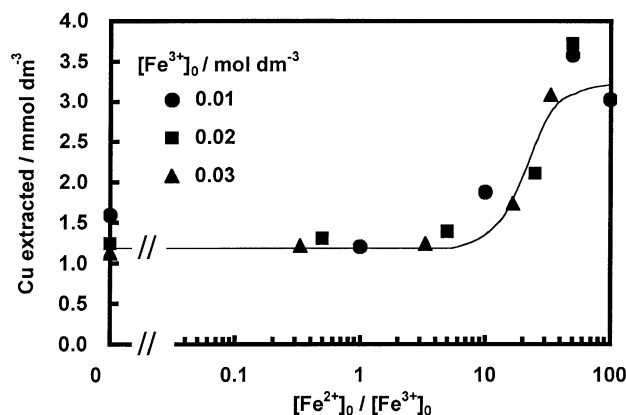


Fig. 4. Relationship between initial ferrous to ferric ion concentration ratios and the amount of copper extracted from a -200 mesh chalcopyrite sample after 24 h in 0.1 mol dm^{-3} sulfuric acid containing various initial concentrations of ferric ions.

presence of ferric ions was the largest when ferrous and cupric ions coexisted (No. 6), and larger with ferrous ions alone (No. 5) than without ferrous and cupric ions (No. 4). With only cupric ions added to the ferric solution (No. 7), the amount of extracted copper was almost the same as that without cupric ions (No. 4).

Fig. 6 shows the effect of cupric and ferrous ions on the copper extraction and solution redox potential behavior in the presence of 0.25 mol dm^{-3} ferric ions. The experiments were performed with 500-cm^3 flasks containing 250 cm^3 of leaching solution and 2.5 g of the chalcopyrite in nitrogen. Temperature and shaking conditions were the same as in other

experiments. At the desired time interval, a 1 to 2 cm^3 of solution was sampled using an injection needle inserted through the silicon rubber plug and nitrogen was introduced for about 15 min for keeping anaerobic conditions. Without ferrous and cupric ions, only about 10% of the copper was extracted even after 27 days. When only ferrous ions were added to the ferric solution, the leaching rate was almost the same as that without ferrous ions during the initial period but became higher after 4 days and about 75% of the copper was extracted after 27 days. When cupric and ferrous ions were added, the leaching rate was higher from the beginning and the fraction of extracted copper reached about 70% after

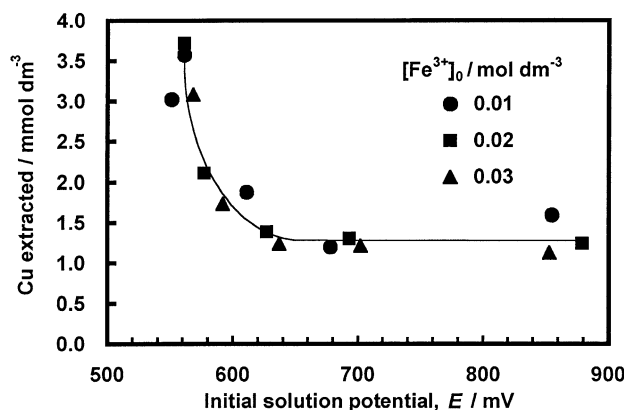


Fig. 5. Relationship between the initial redox potential of solution (E) and the amount of copper extracted from -200 mesh chalcopyrite sample after 24 h in 0.1 mol dm^{-3} sulfuric acid containing various initial concentrations of ferric ions.

Table 3

Effects of ferric, ferrous and cupric ions on chalcopyrite leaching in 0.1 mol dm^{-3} sulfuric acid at 303 K in nitrogen

No.	Experimental conditions			Results
	$[\text{Fe}^{3+}]_0$ (mol dm^{-3})	$[\text{Fe}^{2+}]_0$ (mol dm^{-3})	$[\text{Cu}^{2+}]_0$ (mol dm^{-3})	
				Cu extracted after 24 h (mmol dm^{-3})
1	0.00	0.00	0.00	0.61
2	0.00	0.50	0.01	0.21
3	0.00	0.00	0.01	0.21
4	0.03	0.00	0.00	1.08
5	0.03	0.50	0.00	1.66
6	0.03	0.50	0.01	3.28
7	0.03	0.00	0.01	1.02

25 days. In all cases, solution potential decreased with time.

Fig. 7 shows the results of the shaking flask experiments using the $-65 + 100$ mesh chalcopyrite in 0.03 mol dm^{-3} ferric solutions containing various

concentrations of ferrous ions. The experiments were carried out with a 50-cm^3 flask containing 10 cm^3 solution and 0.1 g of the chalcopyrite sample. The amounts of copper ions accumulated in the solutions were considerably lower than with the -200 mesh chalcopyrite (Fig. 3). As shown in Fig. 7, copper extraction was not enhanced by adding ferrous ions with the $-65 + 100$ mesh chalcopyrite, while it was markedly enhanced with the -200 mesh sample (Fig. 3).

3.2. Column leaching experiments

To investigate the effect of ferrous ions on chalcopyrite leaching behavior at extremely low cupric ion concentrations, column leaching experiments were carried out in 0.01 mol dm^{-3} ferric ion solutions with or without 0.50 mol dm^{-3} ferrous ions. To confirm the reproducibility, experiments were duplicated in each condition. In the column leaching,

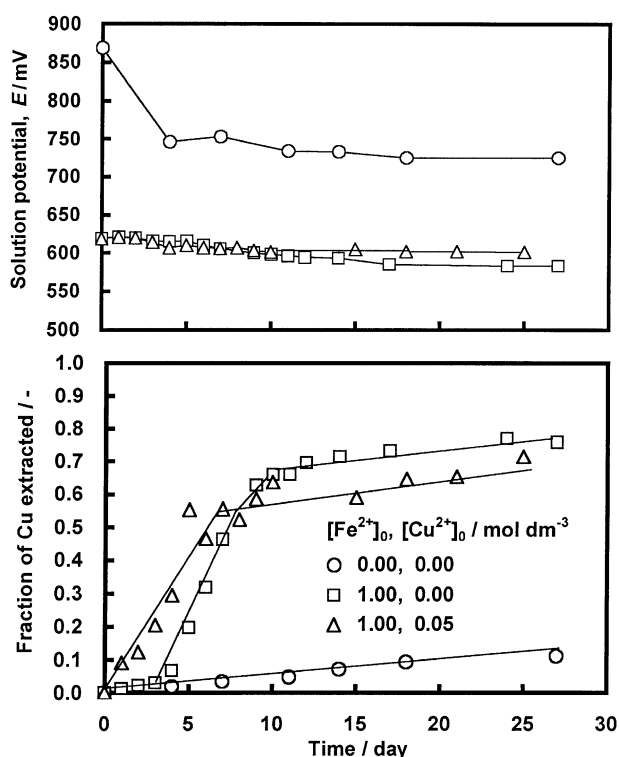


Fig. 6. Effect of ferrous and cupric ion addition on the leaching behavior of a -200 mesh chalcopyrite sample with 0.1 mol dm^{-3} sulfuric acid containing 0.25 mol dm^{-3} ferric ions.

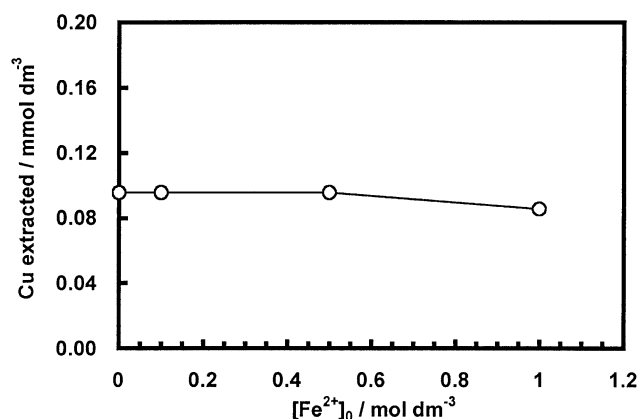


Fig. 7. Effect of initial ferrous ion concentration ($[\text{Fe}^{2+}]_0$) on the amount of copper extracted from $-65 + 100$ mesh chalcopyrite sample after 24 h in 0.1 mol dm^{-3} sulfuric acid. Initial ferric ion concentration: 0.03 mol dm^{-3} .

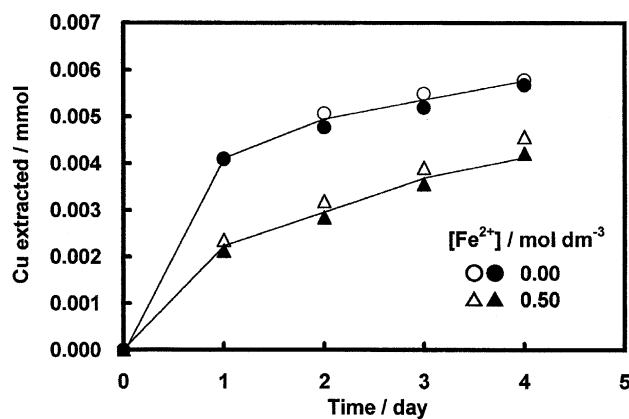


Fig. 8. Effect of ferrous ion on copper extraction in column leaching with 0.1 mol dm^{-3} sulfuric acid containing 0.03 mol dm^{-3} ferric ions at 303 K in nitrogen.

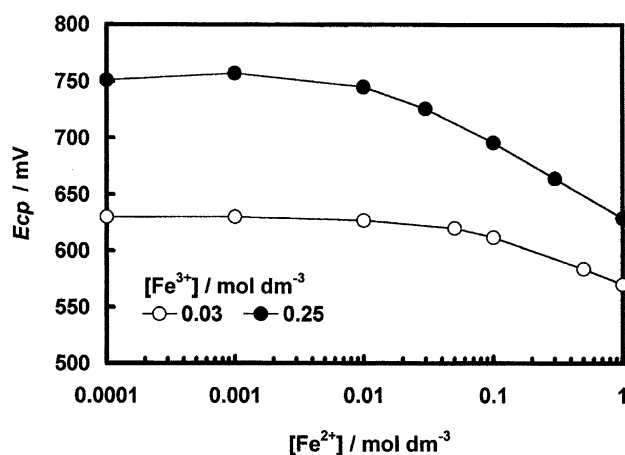


Fig. 9. Rest potential of chalcopyrite (E_{cp}) as a function of ferrous ion concentration ($[\text{Fe}^{2+}]$). Solutions were 0.1 mol dm^{-3} sulfuric acid containing 0.05 mol dm^{-3} cupric ions and various concentrations of ferric and ferrous ions.

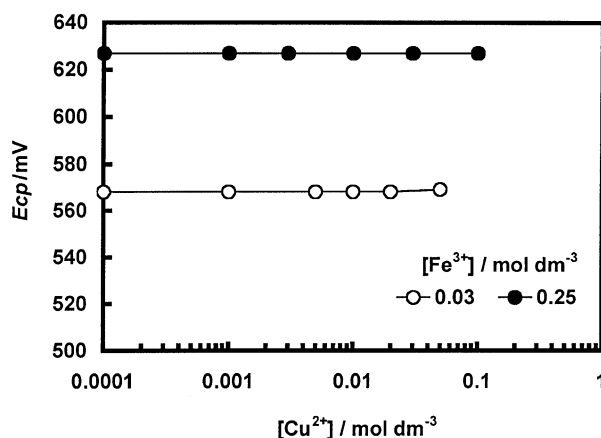


Fig. 10. Rest potential of chalcopyrite (E_{cp}) as a function of cupric ions ($[Cu^{2+}]$). Solutions were 0.1 mol dm^{-3} sulfuric acid containing 1 mol dm^{-3} ferrous ions and various concentrations of cupric and ferric ions.

copper ion concentrations in the effluent were measured daily and less than 60% of those in the shaking flask experiments using the $-65 + 100$ mesh sample (Fig. 7) and less than 10% of those in the shaking flask experiments using the -200 mesh sample (Fig. 3) leached out. Fig. 8 shows the cumulated amounts of extracted copper as a function of time. As shown in this figure, reproducibility was enough and copper extraction was suppressed by ferrous addition at the low copper ion concentrations.

3.3. Rest potential of chalcopyrite

The rest potential of the chalcopyrite electrode was measured in 0.1 mol dm^{-3} sulfuric acid contain-

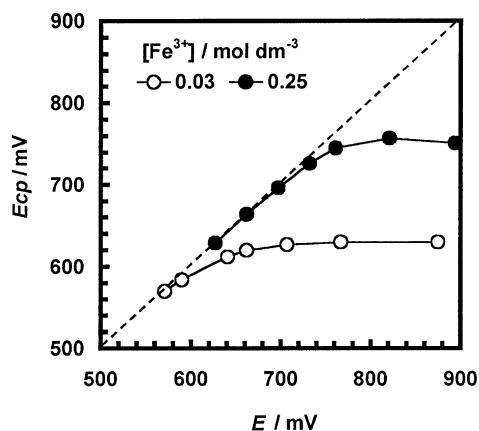
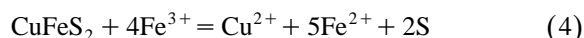
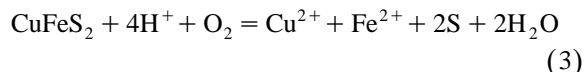


Fig. 11. Relationship between the redox potential of solution (E) and the rest potential of chalcopyrite (E_{cp}). Solutions were 0.1 mol dm^{-3} sulfuric acid containing 0.05 mol dm^{-3} cupric ions and various concentrations of ferrous and ferric ions.

ing various concentrations of ferric, ferrous and cupric ions in nitrogen. As shown in Figs. 9 and 10, the rest potential was determined by the concentrations of ferric and ferrous ions and was not affected by cupric ions. The potential decreased with ferrous ions and increased with ferric ions. Fig. 11 shows the relationship between the solution redox potential and the rest potential of chalcopyrite in the presence of 0.05 mol dm^{-3} cupric ions and 0.03 or 0.25 mol dm^{-3} ferric ions. The solution potential was adjusted by adding various concentrations of ferrous ions. When the solution redox potential was high, the rest potential of chalcopyrite was lower than the solution potential and it had a constant value that was determined by the ferric ion concentration. In the lower potential region, however, the rest potential of chalcopyrite gradually decreased with decreasing solution potential and was close to the solution potential.

4. Discussion

Chalcopyrite oxidation takes place with dissolved oxygen and/or with ferric ions in sulfuric acid solutions:

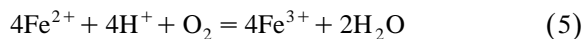


Previous papers [2–5] reported that chalcopyrite oxidation with dissolved oxygen (Eq. (3)) is pro-

moted by ferrous ions. The present study set out to clarify the effect of ferrous ions on chalcopyrite oxidation with ferric ions (Eq. (4)) and all experiments were performed in nitrogen.

As shown in Fig. 3, when ferric ions were added, high concentrations of ferrous ions enhanced copper extraction and ferric ion consumption. Table 1 shows that the amounts of elemental sulfur formed during the leaching was about twice the amount of extracted copper both with and without ferrous ions. These results imply that chalcopyrite oxidation due to ferric ions (Eq. (4)) is enhanced by ferrous ions. However, it is difficult to determine the effect of ferrous ions on the stoichiometry of chalcopyrite leaching based on the results shown in Fig. 3, because the effect of dissolved oxygen on the total copper extraction cannot be ignored in these experiments as discussed below.

If oxygen were completely removed from the system, there would be no copper extraction without ferric ions. As shown in Fig. 3, however, even without ferric ion substantial amounts of copper were extracted from chalcopyrite and ferric ions were formed when ferrous ions were added alone. This indicates the presence of contaminant oxygen and that ferrous oxidation with the contaminant oxygen takes place (Eq. (5)).



Therefore, it should be noted that chalcopyrite oxidation with dissolved oxygen (Eq. (2)) may occur and contribute to copper extraction. Moreover, acid soluble copper, which is due to the surface oxidized matter formed during the preparation of chalcopyrite sample, may contribute to the copper extraction without ferric ions.

Extraction of acid soluble copper would be finished in a short period, so its contribution to total copper extraction may be ignored in a long time leaching. It is also expected that the effect of contaminant oxygen on copper extraction can be ignored in a long time-leaching experiment if the contaminant oxygen is the oxygen remaining in flasks at the beginning of experiments.

Considering the above, leaching experiments were performed in about 1 month to determine the stoichiometry of chalcopyrite leaching (Fig. 6). If we

assume that copper extraction is due to chalcopyrite oxidation with ferric ions (Eq. (4)) and there is no other reaction, the following relations are satisfied during the batch leaching of chalcopyrite.

$$[\text{Cu}^{2+}] = [\text{Cu}^{2+}]_0 + \Delta\text{Cu} \quad (6)$$

$$[\text{Fe}^{2+}] = [\text{Fe}^{2+}]_0 + 5\Delta\text{Cu} \quad (7)$$

$$[\text{Fe}^{3+}] = [\text{Fe}^{3+}]_0 - 4\Delta\text{Cu} \quad (8)$$

where, $[J]_0$ and $[J]$ are the initial concentration and the concentration at a given time for species J , and ΔCu is the amount of extracted copper.

Substituting Eqs. (7) and (8) into Eq. (1), the following equation is obtained.

$$E = 0.670 + 0.059 \log \left(\frac{[\text{Fe}^{3+}]_0 - 4\Delta\text{Cu}}{[\text{Fe}^{2+}]_0 + 5\Delta\text{Cu}} \right) \quad (9)$$

Using this equation, the amount of extracted copper, ΔCu , was calculated from the solution potential, E , and this theoretical amount was compared with the experimental value. As shown in Fig. 12, there are deviations but the theoretical amounts of extracted copper almost match the experimental values both in the case with and without ferrous ion addition. This indicates that copper extraction shown in Fig. 6 is mainly due to the chalcopyrite oxidation

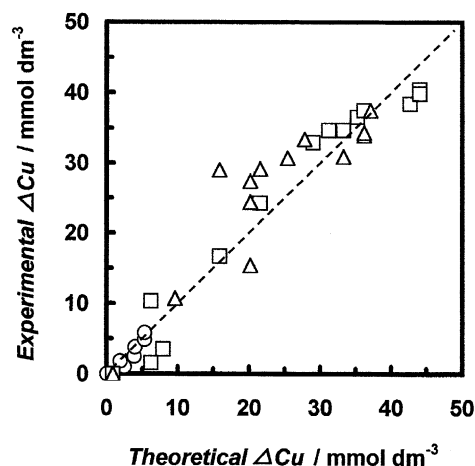


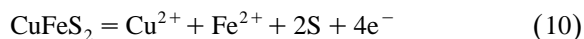
Fig. 12. Plot of the experimental amounts of extracted copper vs. the theoretical amounts using Eq. (9) and the solution potential data shown in Fig. 6. Symbols are the same as in Fig. 6.

with ferric ions (Eq. (4)) and that ferrous ions do not affect the stoichiometry. Because the amount of extracted copper was larger with ferrous ions than without ferrous ions (Fig. 6), we can conclude that the ferrous ions enhance the chalcopyrite oxidation according to Eq. (4).

As shown in Figs. 4 and 5, copper extraction was mainly controlled by the concentration ratio of ferrous to ferric ions or the redox potential of the solutions (a function of the concentration ratio), and the extraction was enhanced at higher ferrous ratios and/or in the lower potential region. Figs. 9–11 show that the rest potential of chalcopyrite is determined by the concentrations of ferric and ferrous ions and that it decreases with increasing ferrous ions, indicating that ferrous ions discharge on chalcopyrite surface, i.e. ferrous ions potentially act as a reductant on the mineral. These results imply that the ferrous-promoted chalcopyrite leaching is an electrochemical phenomenon where ferrous ions act as a reductant.

The results in Table 3 and Fig. 6 show that addition of cupric ions together with ferrous ions enhanced copper extraction more than with ferrous addition alone. As shown in Figs. 7 and 8, ferrous ions suppressed chalcopyrite leaching when concentrations of extracted cupric ions were low. These results indicate that cupric ions play an important role in the ferrous-promoted chalcopyrite leaching and that copper extraction is not enhanced with ferrous ions alone.

Generally, it has been accepted that chalcopyrite oxidation with ferric ions (Eq. (4)) can be decomposed into the following half-cell reactions:

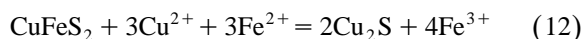


According to this model, it may be expected that copper extraction is suppressed by cupric and ferrous ions because these ions are the products of the anodic and cathodic reactions. The driving force of chalcopyrite leaching in the model is the difference between chalcopyrite potential and solution redox potential that is determined by the concentration ratio of oxidant ferric ions to reductant ferrous ions,

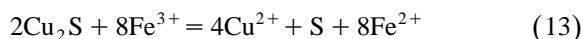
and the potential difference was reduced with decreasing the solution potential as shown in Fig. 11. Therefore, it may also be predicted that a lower solution potential should cause slow copper extraction. However, these predictions conflict with the observed results.

If we use the model expressed by Eqs. (10) and (11), the only way to avoid the conflict is to assume the passivation of chalcopyrite in a higher potential region. In the case of metals like iron, the anodic dissolution rate and current increase with increasing potential but suddenly decrease at a passivation potential, due to the formation of a passive layer such as metal oxides on the metal surface. Warren et al. [10] reported the passivation of the anodic dissolution of chalcopyrite in sulfuric acid solution. However, the passive behavior of chalcopyrite is not similar to that of the typical passivating metals, i.e., the anodic current due to Eq. (10) does not decrease at a certain potential and the passive region can be recognized as a region where the current is independent from the potential [10]. Therefore, the passivation does not explain the drastic decrease in copper extraction at higher potentials shown in Fig. 5.

To interpret the enhancement of chalcopyrite leaching by ferrous and cupric ions, we propose the following two-step reaction model. In the presence of enough cupric and ferrous ions, chalcopyrite is reduced by ferrous ions to Cu_2S according to



Then the intermediate Cu_2S , which is more amenable to leaching than chalcopyrite, is oxidized by ferric ions as follows:



Summing up Eqs. (12) and (13) gives Eq. (4) as the overall reaction. Even when the concentrations of ferrous or cupric ions are not enough, the overall reaction of chalcopyrite leaching is given by Eq. (4). In this case, however, Cu_2S does not form and chalcopyrite is directly oxidized by ferric ions according to Eqs. (10) and (11), and copper extraction rate is slower than that with ferrous and cupric ions. Thermodynamic aspect of the model was discussed elsewhere [9,11] and it was shown that the criterion

of enhanced copper extraction by ferrous and cupric ions can be expressed as:

$$E_c > E > E_{ox} \quad (14)$$

where E_c is the critical potential of Cu_2S formation and E_{ox} is the oxidation potential of Cu_2S . At 298 K and 1 atm, these potentials are given by

$$E_c = 0.681 + 0.059 \log \frac{(a_{\text{Cu}^{2+}})^{0.75}}{(a_{\text{Fe}^{2+}})^{0.25}} \quad (15)$$

$$E_{ox} = 0.561 + 0.059 \log (a_{\text{Cu}^{2+}})^{0.5} \quad (16)$$

where a_i is the activities of species i .

There are several reports of the effect of ferrous ions on chalcopyrite oxidation by ferric ions in sulfuric acid solution, which apparently show conflicting results. Based on the proposed model, these conflicts are discussed below.

Dutrizac et al. [6] and Hirato et al. [7] reported that ferrous ions suppress chalcopyrite oxidation with ferric ions (Eq. (4)). Here leaching experiments were performed with a chalcopyrite crystal mounted in resin. In these studies, the amount of extracted copper was reported in mole units but the volume of solutions is not detailed, so the concentration of cupric ions accumulated in solution is not clear. In such an experimental system, however, the concentration of cupric ions accumulated in the solutions would be low, because the surface area of the chalcopyrite exposed to solution is small (5.8 cm^2 in the experiments by Dutrizac et al. and $0.3\text{--}0.5 \text{ cm}^2$ in the experiments by Hirato et al.). Following to the proposed model, enhanced copper extraction by ferrous ions occurs only when enough cupric ions are present, because intermediate Cu_2S does not form without cupric ions. Direct oxidation of chalcopyrite (Eq. (4)), i.e. the reaction not involving the intermediate Cu_2S , is suppressed by ferrous ions, because ferrous ions are the product of the reaction. Therefore, in the Dutrizac et al. [6] and by Hirato et al. [7] studies, low cupric ion concentrations would cause a suppression of copper extraction by ferrous ions.

Kametani et al. [8] investigated the effect of solution potential on the leaching of chalcopyrite concentrate at 323 to 363 K in 1 mol dm^{-3} sulfuric acid solutions containing ferrous and ferric ions using a

chalcopyrite concentrate (mean diameter: $6.6 \mu\text{m}$). During the experiments, potassium perchlorate was titrated to reproduce the ferric ions consumed by the chalcopyrite oxidation (Eq. (4)) and to maintain a constant solution potential. They reported that the leaching rate increased with increasing potential but that it suddenly decreased above a critical potential (about 670 mV vs. SHE). This may be interpreted as follows: below the critical potential, intermediate Cu_2S is formed according to the chalcopyrite reduction shown in Eq. (12) because the chalcopyrite concentrate used has a large specific surface area and high concentrations of extracted cupric ions are present in the solutions. In this potential region, the leaching rate increases with increasing potential, because the concentration of ferric ions, which is needed to oxidize Cu_2S , increases with increasing the potential in Kametani's experimental system. At higher potentials, intermediate Cu_2S does not form and the result is a decrease in the leaching rate above the critical potential.

In the presence of dissolved oxygen, ferrous ions promote chalcopyrite leaching [2–5]. The present study shows that, even under anaerobic conditions, chalcopyrite oxidation due to ferric ions is enhanced by ferrous ions in the presence of high concentrations of cupric ions. These results indicate that ferrous and cupric ions are important in interpreting the leaching behavior of chalcopyrite and when trying to establish optimum conditions for copper recovery in dump leaching.

5. Conclusions

This paper investigates the effects of ferrous ions on chalcopyrite oxidation with ferric ions by leaching experiments in nitrogen. In the presence of high concentrations of cupric ions, the chalcopyrite oxidation was enhanced by high concentrations of ferrous ions and copper extraction was mainly controlled by the ferrous to ferric ion concentration ratio. When cupric ion concentrations were low, however, ferrous ions suppressed the chalcopyrite oxidation. These results imply that ferrous promoted chalcopyrite leaching is an electrochemical phenomenon where ferrous ions act as reductant and cupric ions play an important role.

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