Effect of Carbon Black on Copper Ore Leaching in Sulfuric Acid Media at 50°C

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Abstract

In this study, we examined the effect of carbon black on the sulfuric acid leaching of a copper ore containing 1.1% Cu occurring as CuFeS₂ (chalcopyrite). Leaching experiments were performed in Erlenmeyer flasks containing 200 mL of the sulfuric acid medium while agitated with a magnetic stirrer at 50°C. The addition of carbon black enhanced the kinetics of chalcopyrite leaching at an initial pH of 1.2. The extraction yield of Cu was 97% in 98 h in the presence of 0.2 g of carbon black, compared with 18% in the absence of carbon black. The acceleration of chalcopyrite dissolution did not occur without direct contact between the ore and the carbon black, suggesting that a galvanic interaction between the two materials plays a role in the improvement of the leaching rate. In the presence of carbon black, the redox potential fell below 600 mV vs. SHE with a decrease in the ratio of Fe(III) to Fe(II), and the leaching rate of chalcopyrite increased markedly. The enhanced kinetics of chalcopyrite leaching in the copper ore could be attributed to dissolution reactions at a low redox potential and to the galvanic interaction between the chalcopyrite and the carbon black.

Key words: Copper ore, Leaching, Carbon black, Galvanic interaction, Low redox potential

1. Introduction

In 2014, 4.0 million metric tons of Cu, which accounted for 37% of world mine production of Cu, were produced via leaching and the SX-EW method. The amount of Cu produced by hydrometallurgical processes has been increasing in recent years. Although CuFeS₂ (chalcopyrite) is one of the most common copper minerals, it is refractory in the ferric sulfate medium which is commonly used for copper ore leaching. The low dissolution rate of Cu from chalcopyrite may be attributed to the formation of passive layers on the chalcopyrite surface, such as an elemental sulfur layer, a Cu-rich polysulfide layer, and layers comprising Fe salt. These layers may prevent the transfer of electrons and ions to the chalcopyrite core, thereby hindering the dissolution of Cu from the chalcopyrite.

To accelerate the kinetics of chalcopyrite leaching in acidic sulfuric media for chemical leaching and bioleaching, the use of several materials have been investigated, including pyrite, nanosized silica, coal, carbon, activated carbon, and carbon black and manganese (IV) oxide. Nakazawa et al. revealed that activated carbon enhances the extraction rate of Cu from chalcopyrite in bioleaching using Acidithiobacillus ferroxidans and in chemical leaching. Liang et al. evaluated the effect of activated carbon on chalcopyrite bioleaching using an extreme thermophile, Acidianus manzaensis YM25, at 65°C and reported that the activated carbon significantly accelerated the chalcopyrite dissolution mainly via a galvanic interaction with chalcopyrite. Okamoto et al. investigated the effects of several different coal samples on copper extraction from a chalcopyrite concentrate in an acidic ferrous sulfate solution at 25°C. The results showed that the use of high rank coals, which contain larger proportions of fixed carbons and less volatile matter, enhance Cu extraction.

Nakazawa investigated the effect of carbon black on the leaching of chalcopyrite flotation concentrate obtained from the Atakama mine in a sulfuric acid medium at 50°C. The extraction yield of Cu was 90% in 94 h in the presence of...
Effect of Carbon Black on Copper Ore Leaching in Sulfuric Acid Media at 50°C

carbon black at pH 0.6, compared to 28% in the absence of carbon black. The acceleration of chalcopyrite dissolution did not occur without the contact between the chalcopyrite and carbon black, suggesting that galvanic interaction between the two materials plays a role in the improvement of the leaching rate. In the presence of carbon black, the ratio of Fe(III) to Fe(II) in the leaching solution decreased below 0.1 in 1 h, whereas it was over 0.1 in the absence of carbon black. The redox potential decreased and remained in the range of 560–570 mV, and the leaching rate of chalcopyrite markedly increased. The enhanced kinetics of chalcopyrite leaching could be attributed to dissolution reactions occurring at the low redox potential and to the galvanic interactions between chalcopyrite and carbon black.

Because of the depletion of high-grade chalcopyrite ores which are easily treated by pyrometallurgical processes following the beneficiation, the development of the hydrometallurgical processes for low-grade chalcopyrite ores has been being sought. In this study, we examined the feasibility of improvement of the leaching of a copper ore containing 1.1% Cu occurring as chalcopyrite with carbon black. In the presence of the carbon black, the extraction rate of Cu from the ore increased at 50°C. The effects of several variables such as the pH, temperature, and the amount of carbon black added on the kinetics of the copper ore leaching in sulfuric acid media were examined.

2. Experimental

The copper ore used in this study was provided by the Huckleberry Mine in Canada. The ore contains 1.1% Cu occurring as chalcopyrite. The ore was crushed and sieved to obtain a size fraction of –500 + 150 μm. For comparison, a leaching test was performed using a chalcopyrite flotation concentrate (–102 μm) (hereafter, referred to simply as chalcopyrite) provided from the Atakama Mine in Chile. X-ray diffraction (XRD) patterns of the samples were obtained using a diffractometer (Regaku Corp., Rint2100) at 40 kV and 20 mA. The results are shown in Fig. 1(a) and (c). For the copper ore, the characteristic peaks of chalcopyrite were observed; quartz, anorthite (CaAl2Si2O8), and birnessite (H3.7K0.23MnO2.7) were also identified. For the chalcopyrite sample, small peaks corresponding to pyrite were observed in addition to the peaks of chalcopyrite. The chemical compositions of the samples are shown in Table 1.

Carbon black powder (hereafter, referred to simply as carbon black) and carbon black granules were used in this study. The carbon black was produced via the continuous thermal decomposition of acetylene gas. The carbon black is a very fine powder and is extremely electrically conductive. Table 2 summarizes the basic characteristics of the carbon black used in this study. The carbon black granules used here were agglomerates of the carbon black with particle size fraction of –712 μm + 500 μm. Both samples were provided by Denki Kagaku Kogyo Co. Ltd.

Leaching experiments were performed using 300-mL Erlenmeyer flasks with 200 mL of a sulfuric acid solution, which was adjusted to a designated pH (referred to as the initial pH) with
sulfuric acid and sodium hydroxide solution, in a constant-temperature oven (Yamato Scientific Co., Ltd., DKM600). After the designated temperature was reached, the samples were added into the flasks. The flasks were sealed with silicon caps, placed on a magnetic stirrer, and stirred at 250 rpm in the constant-temperature oven. At desired intervals, the pH and the redox potential of the leachate were measured. The redox potential was measured using a Pt electrode with an Ag–AgCl (3.3 M KCl) reference electrode, and it was converted and reported with respect to the standard hydrogen electrode (SHE). Next, 4 mL of the solution was collected and centrifuged at 10,000 rpm for 10 min. The supernatant was analyzed for Cu, total Fe (Fe(II) + Fe(III)) and ferrous (Fe(II)). The concentration of Cu was measured with an atomic absorption spectrophotometer (Hitachi Z-5000). The total Fe and Fe(II) were analyzed by the traditional and modified o-phenanthroline method. The volume removed from the flasks during sampling and due to evaporation were replaced by equal volumes of the sulfuric acid solution adjusted to the initial pH. At the end of the leaching experiment, the leachate was filtered, and the residue was recovered and dried at 60°C prior to conducting the XRD measurements.

The ferrous sulfate solution and cupric sulfate solution used in this study were prepared by dissolving reagent-grade FeSO₄·7H₂O, and CuSO₄·9H₂O (Kanto Chemical Co. Inc.) in distilled water, respectively.

3. Results and discussions

3.1 Effect of initial pH on the leaching of the copper ore in the presence of carbon black

To evaluate the effect of the initial pH on the kinetics of copper ore leaching, leaching experiments were conducted by varying the initial pH from 0.6 to 1.2 in the presence of 0.1 g of carbon black at 50°C. The results shown in Fig. 2 indicate that increasing the initial pH from 0.6 to 1.2 improved the copper ore leaching and increased the rate and extent of the Cu extraction from the copper ore. The leaching recovery of Cu was 94% with an initial pH of 1.2, and only 28% with an initial pH of 0.6 over 123 h. Notably, with an initial pH of 1.0, the dissolution rate increased markedly after 71 h.

Although the dissolution rate of Fe during the early stages of the leaching increased with decreasing initial pH values, the dissolution yield of Fe was the same with initial pH values of 0.6, 0.8,
and 1.0 in 123 h (approximately 47%). With an initial pH of 1.2, the dissolution yield of Fe was low (33%).

With an initial pH of 1.2, the redox potential decreased below 600 mV in 6 h and remained approximately 560 mV until increasing after 99 h. With an initial pH of 1.0, the redox potential decreased gradually until 71 h; it further dropped to approximately 560 mV after 99 h. This abrupt decrease in the redox potential was coincident with a rapid dissolution of Cu. For initial pH values of 0.6 and 0.8, the redox potential stayed above 600 mV throughout the leaching test.

The higher the initial pH, the more the pH increased. With an initial pH value of 1.2, the pH rose to 2.0 after 123 h. The XRD pattern of the leaching residue obtained from the experiment conducted at an initial pH of 1.2 are shown in Fig. 1 (b). The peaks which are characteristic of chalcopyrite disappeared, indicating that chalcopyrite in the copper ore was almost completely dissolved.

Based on these results, the subsequent leaching experiments were performed with an initial pH of 1.2.

3.2 Effect of carbon black dosage on copper ore leaching

Fig. 3 shows the results of the leaching experiments conducted with different amounts of added carbon black: 0, 0.05, 0.1, and 0.2 g. The Cu extraction rate increased as the amount of added carbon black increased. The extraction yield of Cu reached 97% in 98 h with 0.2 g of carbon black, whereas it was only 18% in the absence of carbon black.

Fig. 3(b) shows the changes in the concentrations of total Fe ions and Fe(II) as a function of the leaching time in the presence of 0, 0.05, and 0.2 g of carbon black. The dissolution rate of Fe from the copper ore increased as the amount of added carbon black increased. Although the Fe ions dissolved from the copper ore occurred mostly as Fe(II) in the early stages of the leaching, the Fe(III) concentration increased after 71 and 23 h in the presence of 0.05 g and 0.2 g of carbon black, respectively. In the absence of carbon black, some Fe(III) was observed after 23 h.

The redox potential decreased rapidly with increasing amounts of carbon black (Fig. 3(c)). In the absence of carbon black, the redox potential remained at nearly 600 mV for the duration of the experiment. In the presence of carbon black, the redox potential decreased initially but tended to increase after most of the chalcopyrite was dissolved. With the addition of 0.2 g of carbon black, the redox potential dropped below 600 mV in 6 h.

Fig. 3 Effect of carbon black dosage on the leaching of copper ore. (a) Cu extracted (b) Fe concentration (c) Eh
and remained in the range of approximately 560–570 mV until 71 h; it further increased and reached 600 mV after 122 h. In the presence of 0.05 g of carbon black, the redox potential gradually decreased to 560 mV in 98 h and increased thereafter.

### 3.3 Effect of temperature on the copper ore leaching in the presence of carbon black

Joe et al. investigated the effect of temperature on the leaching rate of chalcopyrite in sulfuric acid media and found that elevated temperatures enhance the kinetics of chalcopyrite leaching. It was reported that the Cu extraction from chalcopyrite reached 94% in 11 days at 60°C, whereas it was 83% in 34 days at 40°C in sulfuric acid solutions at pH 0.7.

To examine the effect of temperature on the copper ore leaching in the presence of 0.1 g of the carbon black, leaching experiments were performed at temperatures of 25°C, 40°C, and 50°C. The results are shown in Fig. 4. The extraction yield of Cu in 1 h was approximately 6% for the three experiments. After this time, the leaching rate of the copper ore increased with elevating temperature. At 50°C, 94% of Cu in the sample was dissolved in 123 h, whereas the Cu extraction yields at 25°C and 40°C in 123 h were 10% and 62%, respectively.

At 50°C, the redox potential of the leaching solution decreased below 600 mV in 6 h and remained nearly 560 mV; however, when nearly 80% of the Cu in the sample was dissolved, the redox potential increased to over 570 mV. At 40°C, the redox potential gradually decreased and then remained at approximately 560 mV during the entire remainder of the leaching experiment period. However, the redox potential was approximately 620 mV at 25°C.

The addition of carbon black enhanced the dissolution of Cu from the copper ore at temperatures over 40°C. Therefore, the subsequent leaching experiments were performed at 50°C.

### 3.4 Effect of carbon black and Cu(II) on the oxidation of Fe(II)

In order to investigate the effects of carbon black and Cu(II) on the oxidation of Fe(II), experiments were performed using 200 mL of pH 1.2 ferrous sulfate solutions containing 96 mg/L of Fe(II) with carbon black and/or cupric sulfate solution added. Fig. 5 shows the ratio of the Fe(II) concentration (C) to the initial Fe(II) concentration (C₀, 96 mg/L) as a function of time. In the absence of Cu(II) and carbon black, Fe(II) was not oxidized within 67 h; a similar result was observed in the presence of 0.1 g of carbon black without Cu(II). In the presence of 10.1 mg/L of Cu(II), which corresponds to the Cu concentration measured after 1 h of copper ore leaching (as shown in Fig. 2), nearly 22% of the Fe(II) was oxidized.
Effect of Carbon Black on Copper Ore Leaching in Sulfuric Acid Media at 50°C

oxidized in 67 h regardless of the addition of carbon black, indicating that the Fe(II) was oxidized via catalytic activity of Cu(II) in the presence of dissolved oxygen which acts as an oxidant\textsuperscript{22,23}. Therefore, the Fe(II) released from the copper ore during leaching is oxidized to Fe(III).

3.5 Effect of the contact between chalcopyrite and carbon black

Two leaching experiments were performed using carbon black granular (−720 + 500 μm). One experiment was performed as described in the experimental section. In the other experiment, the leaching test was conducted with 0.2 g of carbon black granular packed into a small bag (30 mm × 30 mm) made from bolting cloth (opening 20 μm, AS One Co. Ltd.) and suspended in the leaching solution containing the copper ore. The opening of the bolting cloth was sufficiently small, so that the copper ore and carbon black were not able to make direct contact with each other. The results of these experiments are compared in Fig. 6. The Cu dissolution was not enhanced in the absence of the contact, suggesting that contact between the chalcopyrite in the copper ore and carbon black is necessary for the acceleration of chalcopyrite leaching.

In the test in which the carbon black was suspended in a bag, the [Fe(III)]/[Fe(II)] ratio gradually decreased and reached 0.8 after 95 h and the redox potential remained above 600 mV. Conversely, the [Fe(III)]/[Fe(II)] ratio in the leaching solution decreased approximately 0.03 in 21 h when the carbon black within contact with the copper ore and the redox potential decreased to approximately 550 mV after 47 h.

As discussed above, the Fe(II) released from the copper ore was catalytically oxidized to Fe(III) in the presence of Cu(II). It is well known that chalcopyrite is passivated in the process of ferric sulfate leaching, resulting in the depression of the dissolution of Cu from chalcopyrite. In this study, chalcopyrite dissolved remarkably well within the first hour. Thereafter, however, the leaching rate was very low and the [Fe(III)]/[Fe(II)] ratio gradually decreased in the absence of direct contact between carbon black and the copper ore. With direct contact, the dissolution rate of Cu increased and the [Fe(III)]/[Fe(II)] ratio in the leachate markedly decreased in the early stages of the leaching, indicating that Fe(III) was consumed during the leaching reaction of the chalcopyrite in the copper ore.

Dixon et al.\textsuperscript{10} developed the ferric sulfate leaching process of chalcopyrite using pyrite.
(called the Galvanox process). In this process, the rapid leaching rate for chalcopyrite is attributed to the galvanic interaction between pyrite and chalcopyrite. Because pyrite is nobler than chalcopyrite, it acts as a cathode, accepting electrons from chalcopyrite and donating them to the ferric ions in the ferric sulfate media. This results in enhanced chalcopyrite leaching kinetics. It was previously reported that the galvanic interaction between chalcopyrite and carbon materials enhances the kinetics of chalcopyrite leaching. Wan et al. found that the dissolution of chalcopyrite/carbon aggregates in ferric sulfate solutions was three times faster than that of chalcopyrite. Further, the results of the study showed that the corrosion current for the anodic reaction on the electrodes of chalcopyrite/carbon aggregate was found to be approximately five times greater than that for chalcopyrite electrodes without carbon addition. The findings suggested that the galvanic coupling between carbon and chalcopyrite eliminates, to some extent, the passivating effect in ferric sulfate solutions.

Because the carbon black used in this study had a high electric conductivity, a galvanic interaction would occur between the chalcopyrite and carbon black when they were in contact with each other. This galvanic interaction could improve the ferric sulfate leaching of chalcopyrite, resulting in a decrease in the \([\text{Fe(III)}]/[\text{Fe(II)}]\) ratio in the early stages of leaching. However, the rest potential of the carbon black was not measured because the massive carbon black sample, which is needed for the preparation of an electric rod from the material, was not obtained. Therefore, further investigation is necessary to understand the galvanic interaction between these two materials.

### 3.6 Effect of carbon black and chalcopyrite on redox potential of leaching solutions

Three experiments were performed with the addition of the carbon black, the copper ore, and a mixture of the copper ore and carbon black. For comparison, a leaching experiment was also conducted with 0.5 g of chalcopyrite and 0.25 g of carbon black with an initial pH of 0.6. These conditions were determined based on the preliminary experiments. The results are shown in Fig. 7. In the presence of carbon black without the copper ore, the solution potential remained above 600 mV. In the leaching test with the chalcopyrite, the redox potential and the ratio of \([\text{Fe(III)}]/[\text{Fe(II)}]\) steeply decreased in the early stages of the leaching; as the dissolution of Cu proceeded, the redox potential increased gradually followed

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![Graph](image.png)

**Fig.7** Effect of carbon black and copper ore on redox potential of leaching solutions. (a) Cu extracted (b) Eh (c) \([\text{Fe(III)}]/[\text{Fe(II)}]\)
by a sharp increase after 72 h at the time at which the extraction yield of Cu was 72%.

In the solo presence of the copper ore, the redox potential decreased gradually to approximately 590 mV in 123 h. However, with the carbon black added to the copper ore, the changes in the redox potential and the ratio of [Fe(III)]/[Fe(II)] over time had the same tendencies as those observed in the chalcopyrite leaching experiment. The redox potential dropped to approximately 570 mV in 22 h and stabilized to around 560 mV; it began to increase after 72 h, reaching 620 mV at 123 h.

Decreasing the [Fe(III)]/[Fe(II)] ratio causes the redox potential to fall in a solution containing Fe(II) and Fe(III). Several studies have previously reported that the extraction rate of Cu from chalcopyrite is enhanced when chemical leaching and bioleaching are conducted at a low redox potential. Hiroyoshi et al. noted that because the redox potential has to be sufficiently low for chalcocite formation and high enough for the subsequent chalcocite oxidation, chalcopyrite leaching kinetics is enhanced according to the following reactions:

\[
\begin{align*}
\text{CuFeS}_2 + 3\text{Cu}^{2+} + 3\text{Fe}^{2+} & \rightarrow 2\text{Cu}_2\text{S} + 4\text{Fe}^{3+} \\
\text{Cu}_2\text{S} + 4\text{Fe}^{3+} & \rightarrow 2\text{Cu}^{2+} + 4\text{Fe}^{2+} + \text{S}_0
\end{align*}
\]

\[
\begin{align*}
\text{CuFeS}_2 + 2\text{Fe}^{3+} & \rightarrow \text{CuS} + 3\text{Fe}^{2+} + \text{S}_0 \\
\text{CuS} + 2\text{Fe}^{3+} & \rightarrow \text{Cu}^{2+} + 2\text{Fe}^{2+} + \text{S}_0
\end{align*}
\]

In the leaching experiments with the copper ore, after the redox potential decreased to the range of 560–570 mV in the presence of carbon black, the dissolution rate of Cu increased remarkably. Thus, the chalcopyrite leaching kinetics could be enhanced according to these hypothesized reactions in addition to galvanic interactions.

As the dissolution of Cu from the copper ore proceeded, the [Fe(III)]/[Fe(II)] ratio increased in the presence of carbon black. Therefore, because of the decrease in the amount of unleached chalcopyrite in the leachate, the oxidation rate of Fe(II) could be faster than the consumption rate of Fe(III). These conditions could lead to the observed increases in the [Fe(III)]/[Fe(II)] ratio and the redox potential.

4. Conclusions

In this study, we examined the effect of carbon black on the leaching of a copper ore containing 1.1% Cu occurring as chalcopyrite in a sulfuric acid medium. The results are summarized as follows:

1. In the presence of carbon black, the leaching kinetics of the chalcopyrite in the copper ore in sulfuric acid media were enhanced at temperatures above 40°C. The extraction yield of Cu was 97% in 98 h in the presence of 0.2 g of carbon black at 50°C, whereas it was 18% in the absence of the carbon black.

2. The acceleration of chalcopyrite leaching did not occur without direct contact between the copper ore and carbon black.

3. In the presence of carbon black, the [Fe(III)]/[Fe(II)] ratio decreased in the early stages of leaching. The redox potential decreased and remained in the range of 560–570 mV during the chalcopyrite dissolution, whereas it was at nearly 600 mV in the absence of carbon black.

4. The enhanced the leaching kinetics of the chalcopyrite in the copper ore may be attributed to dissolution reactions at the low redox potential and to the galvanic interactions between the chalcopyrite and carbon black.

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References

18. H. Nakazawa: (submitted to Hydrometallurgy)