Leaching of Chalcopyrite under Bacteria–Mineral Contact/Noncontact Leaching Model

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Abstract: Bacteria–mineral contact and noncontact leaching models coexist in the bioleaching process. In the present paper, dialysis bags were used to study the bioleaching process by separating the bacteria from the mineral, and the reasons for chalcopyrite surface passivation were discussed. The results show that the copper leaching efficiency of the bacteria–mineral contact model was higher than that of the bacteria–mineral noncontact model. Scanning electron microscopy (SEM), X-ray diffraction (XRD), and Fourier-transform infrared (FTIR) were used to discover that the leaching process led to the formation of a sulfur film to inhibit the diffusion of reactive ions. In addition, the deposited jarosite on chalcopyrite surface was crystallized by the hydrolysis of the excess Fe$^{3+}$ ions. The depositions passivated the chalcopyrite leaching process. The crystallized jarosite in the bacteria EPS layer belonged to bacteria–mineral contact leaching system, while that in the sulfur films belonged to the bacteria–mineral noncontact system.

Keywords: chalcopyrite; bacteria leaching; passivation; jarosite

1. Introduction

Chalcopyrite (CuFeS$_2$) is one of the most widespread and refractory copper-containing minerals [1]. The main technologies to extract copper are pyrometallurgical processes; however, the byproduct, i.e., sulfur dioxide, leads to serious environmental pollution. Currently, researchers are focusing on developing new environmentally friendly metallurgy technologies and, since bio-metallurgy is renowned for low cost and pollution [2,3], it has already become a research hotspot. There are two widely received bioleaching mechanisms, i.e., direct action and indirect action, providing theoretical support for research on sulfuric mineral bio-metallurgy [4]. On the other hand, further research has shown that these mechanisms cannot explain several complex chemical, electrochemical, and biochemical phenomena. Tributsch found that an extracellular polymeric substance (EPS) is produced as the bacteria are adsorbed onto the ore surface [5]. Fe(III) and H$^+$ are accumulated on the contact surface of the ore/solution by EPS to hasten ore decomposition. This conclusion was rather different from the previously characterized “direct action”. Crundwell [6] developed Tributsch’s theory and summarized other research results, eventually establishing the indirect leaching mechanism, indirect contact leaching mechanism, and direct contact leaching mechanism. This mechanism has been already authorized in the bio-metallurgy academic community. In recent years, bio-metallurgy technology developed rapidly and was applied in the smelting process of arsenic-bearing refractory gold ore and secondary copper sulfide [7]. For chalcopyrite bioleaching technology, the development is slow due to the following reasons: the high lattice energy of chalcopyrite [8], its difficulty to be oxidized in the bioleaching process, and the passivation layer produced by the insoluble substance that inhibits the further diffusion of bacteria and reactant [9–15].
Parker reported that jarosite deposition has an important role in the decrease in copper leaching efficiency [16]. Dutrizac promoted that a dense sulfur layer covered the surface of chalcopyrite which would inhibit leaching [17]. Ghahremaninez promoted that leaching of \( \text{Cu}_{1-x} \text{Fe}_{1-y} \text{S}_2 \) \((x < y)\) was the main reason for the observation of electrochemistry [18,19]. Altogether, the widely accepted view is that jarosite deposition leads to chalcopyrite passivation [20,21].

Fe\(^{3+}\) ion concentration, pH, and monovalent cation concentration have an effect on the generation of the jarosite deposition. Rapid crystallization of jarosite is produced by bacteria, hastening the Fe\(^{3+}\) ion supply [22–27]. However, the location of crystallization and mechanism of generation remain unclear. It is very important to study the passivation mechanism of chalcopyrite, especially to ascertain whether jarosite crystallizes on the ore surface or in the EPS layer of bacteria absorbed onto ore surface. In this paper, the chalcopyrite bioleaching processes are divided into two parts by bag filters so as to separate bacteria from ore. The aim was to study the leaching mechanism under different conditions including the bacterium–mineral contact and noncontact leaching models. The leaching residue was analyzed by several experimental methods, such as scanning electron microscopy (SEM), X-ray diffraction (XRD), and Fourier-transform infrared (FTIR) in order to discuss the reason for chalcopyrite surface passivation.

2. Materials and Methods

2.1. Leaching Bacteria

The bioleaching bacterial strains were composed of \textit{Acidithiobacillus ferrooxidans}, \textit{Acidi-thiobacillus thiooxidans}, and \textit{Leptospirillum ferriphilum}. They were provided by the Northeastern University bio-metallurgical laboratory. The strains have good antitoxic characteristic and oxidative ability of sulfur and ferrous ions, and they grow in a pH range of 1.0–2.5 and a temperature range of 25–44 °C [28,29].

2.2. Microorganism Culture

The culture medium used for this experiment was 9 K [28,29]. The composition of the medium is as follows: 3.0 g/L (NH\(_4\))\(_2\)SO\(_4\); 0.1 g/L KCl; 0.5 g/L K\(_2\)HPO\(_4\); 0.5 g/L MgSO\(_4\) 7H\(_2\)O; 0.01 g/L Ca(NO\(_3\))\(_2\); 44.3 g/L FeSO\(_4\) 7H\(_2\)O. All chemical reagents used were of analytical grade.

2.3. Mineral Sample

The mineral sample was obtained from a certain copper mine in Hubei province of China. The elementary composition of the sample is listed in Table 1. It can be seen that the mineral sample contained Cu 13.82%, Fe 37.50%, and S 39.76%. The particle size distribution is listed in Table 2. It can be seen that the proportions of particles with size >75 \(\mu\)m, 75–45 \(\mu\)m, 45–37 \(\mu\)m, and <37 \(\mu\)m were 1.12%, 9.53%, 20.16%, and 69.19%, respectively. The X-ray diffraction pattern is shown in Figure 1. The main metallic minerals in the mineral sample were chalcopyrite and pyrite.

Table 1. The main element contents of mineral samples.

| Element | Cu   | Fe   | S    | SiO\(_2\) | CaO  | Al\(_2\)O\(_3\) | MgO |
|---------|------|------|------|-----------|------|----------------|-----|
| Content, % | 13.82 | 37.50 | 39.76 | 2.72      | 0.79 | 0.40           | 0.15|

Table 2. Particle size distribution of mineral samples.

| Particle Size | >75 \(\mu\)m | 75–45 \(\mu\)m | 45–37 \(\mu\)m | <37 \(\mu\)m |
|---------------|-------------|---------------|----------------|------------|
| Content, %    | 1.12        | 9.53          | 20.16          | 69.19      |
The chalcopyrite samples were divided into two groups for bioleaching. Each group consisted of five parallel samples, as the leaching process needed to be observed and studied under different periods. In the first group, each sample had 10 g of chalcopyrite wrapped with a dialysis bag, which was added to a 500 mL shaking flask containing 180 mL of 9 K culture medium. The dialysis bag was made up of polyvinylidene fluoride with a cutoff relative molecular mass of 8000, preventing bacteria from contacting the mineral but allowing ions to dialyze and diffuse freely. Therefore, the first group test could simulate the leaching behavior of the noncontact bacteria–mineral model, while the second group test could simulate the leaching behavior of the contact bacteria–mineral model. Each sample in the second group had 10 g of chalcopyrite directly added to a 500 mL shaking flask also containing 180 mL of 9 K culture medium. Then, 20 mL of bacterial solution with $3.2 \times 10^8$ cells/mL was injected into each of the 10 flasks mentioned above. The initial pH was adjusted to 1.4 with H$_2$SO$_4$. The flasks were put into a constant-temperature shaker incubator and shaken at 170 rpm at 44°C. The experiment was supplemented with distilled water instead of volatilized water.

2.5. Measurement

A PHS-25 acidometer made by Shanghai digital electronics holding (group) co., LTD was used to measure the solution pH. A platinum plate as a working electrode and a saturated calomel electrode as reference were used to measure redox potential. A Leica DM2500 biological microscope and XB-K-25 hemacytometer were used to count the number of free bacteria in pulp. The total count on the ore surface was measured by ninhydrin colorimetry [30]. The copper concentration was measured using a TAS-990 atomic absorption spectrophotometer, manufactured by PERSEE Company in Beijing. The atomic absorption method is based on the characteristic spectral line of the element to be measured emitted by the hollow cathode lamp. The sample vapor is absorbed by the ground-state atom of the element to be measured in the vapor, and the content of the element to be measured in the sample is determined by the weakening degree of the characteristic spectral line. The leaching residue was observed using an SSX-550 SEM/energy-dispersive spectrometer (EDS) made by the Japanese Shimadzu Company. The phase of leaching residue was measured in the sample is determined by the weakening degree of the characteristic spectral line. IR analysis of leaching residue was performed in a 400–4000 cm$^{-1}$ scanning range by a Vertex70 Fourier-transform infrared spectrometer of the Germany BRUKER Company. Leaching residue was bonded to the metal platform with a conductive adhesive.
3. Results and Discussion

3.1. pH and Potential Change

Figures 2 and 3 show the variations of pH and potential in the process of bioleaching. During the bioleaching process of sulfide minerals, these changes are caused by the transfer of hydrogen ions and electrons. It can be seen from Figure 2 that pH increased at the beginning of the reaction, and then subsequently decreased. Furthermore, the pH remained relatively constant in a range of 1.2–1.75, which is suitable for bacterial survival. Equations (1) and (2) represent the oxidation reaction of sulfide minerals in the bacteria–mineral contact leaching model. Fe$^{3+}$ as an oxidant comes from two aspects; one is dissociative Fe$^{3+}$ in the solution, whereas the other occurs in EPS layer of bacteria. The solution pH increases when Fe$^{2+}$ is oxidized to Fe$^{3+}$ by the bacteria, according to the reaction shown in Equation (3). However, the pH decreases slowly due to sulfur being oxidized by the bacteria, as shown in Equation (4), and Fe$^{3+}$ being hydrolyzed, as shown in Equation (5). In the bacteria–mineral noncontact leaching model, the bacteria were isolated from the ore using a dialysis bag, preventing them from being adsorbed onto the ore surface. The chalcopyrite was oxidized only by dissociative Fe$^{3+}$ in the solution. The standard electrode potential of Fe$^{3+}$/Fe$^{2+}$ was 0.771 V vs. SHE which is less than the 0.808 V vs. SHE necessary for the production of S$^{6+}$ [31,32]. Therefore, S$^{2-}$ in the chalcopyrite was oxidized only to S$^0$, as detected on the ore surface. Fe$^{2+}$ oxidized to Fe$^{3+}$ after passing through the dialysis bag and reacting with bacteria, leading to a pH increase. Moreover, S$^0$ on the ore surface could not be oxidized by Fe$^{3+}$. Thus, the bacteria–mineral noncontact leaching model appeared to have a higher increase in pH than the corresponding contact leaching model. On day 9 of the bioleaching process, the pH reached 1.74, before subsequently decreasing due to Fe$^{3+}$ hydrolysis, as can be seen in Equation (5). Pulp potential increased rapidly, and then remained relatively constant. Moreover, the potential of the bacteria–mineral noncontact leaching system rose higher than that of the bacteria–mineral contact leaching system. This was due to the sulfur film formed in the bacteria–mineral noncontact leaching system after the ores were oxidized by Fe$^{3+}$, which in turn obstructed the leaching of ores. Furthermore, the bacteria outside the dialysis bag could oxidize Fe$^{2+}$ into Fe$^{3+}$, which led to the increase in [Fe$^{3+}$]/[Fe$^{2+}$] in the solution, and oxidation reduction potential rose quickly. In the bacteria–mineral contact leaching system, the sulfur film, however, obstructed the leaching of ore to lesser extent due to the existence of Acidithiobacillus thiooxidans. Thus, the sulfide ores could be oxidized continuously [33].

\[
\begin{align*}
\text{CuFeS}_2 + 4\text{Fe}^{3+} & \xrightarrow{\text{chemical}} \text{Cu}^{2+} + 5\text{Fe}^{2+} + 2\text{S}^0. \\
\text{Fe}_2\text{S}_2 + 2\text{Fe}^{3+} & \xrightarrow{\text{chemical}} 3\text{Fe}^{2+} + 2\text{S}^0. \\
4\text{Fe}^{2+} + 4\text{H}^+ + \text{O}_2 & \xrightarrow{\text{biological}} 4\text{Fe}^{3+} + 2\text{H}_2\text{O}. \\
2\text{S}^0 + 3\text{O}_2 + 2\text{H}_2\text{O} & \xrightarrow{\text{biological}} 2\text{H}_2\text{SO}_4. \\
3\text{Fe}^{3+} + 2\text{SO}_4^{2-} + 6\text{H}_2\text{O} + \text{M}^+ & \rightarrow \text{MFe}_3(\text{SO}_4)_2(\text{OH})_6 + 6\text{H}^+. 
\end{align*}
\]

(M = K$^+$, NH$_4^+$, H$_3$O$^+$)
3. Results and Discussion

3.1. pH and Potential Change
Figures 2 and 3 show the variations of pH and potential in the process of bioleaching. During the bioleaching process of sulfide minerals, these changes are caused by the transitive Fe3+/Fe2+ redox reaction. During the bacteria–mineral contact leaching system, the bacterial concentration is the sum of the adsorbed count and free count. According to Figure 4, leaching from 3 days to 15 days followed the bacterial growth logarithmic phase. Bacterial concentration reached $6 \times 10^8$ cells/mL on the 15th day, before approaching the stationary phase. During the whole bioleaching process, the bacterial concentration remained relatively stable. There was no obvious decline phase, indicating that the bacteria adapted very well to the leaching system, and the energy provided by the oxidation of sulfide ore could support the bacteria. In the bacteria–mineral noncontact leaching system, the bacterial concentration increased slowly and reached $2.1 \times 10^8$ cells/mL on the 15th day, which was one-third that of the bacteria–mineral contact leaching system. After 15 days, bacterial growth started to decline. The bacterial concentration decreased rapidly and reached $8.2 \times 10^7$ cells/mL at the end of the bioleaching process, which shows that Fe$^{3+}$ had no obvious effect on the oxidation of chalcopyrite in the bacteria–mineral noncontact leaching system. It was so hard for chalcopyrite to decompose persistently that some bacteria struggled to survive. This led to the occurrence of a decline phase and the decrease in bacterial concentration.

3.2. Bacterial Concentration Change
The change in bacterial concentration during the process of bioleaching is shown in Figure 4. In the bacteria–mineral contact leaching system, the bacterial concentration is the sum of the adsorbed count and free count. According to Figure 4, leaching from 3 days to 15 days followed the bacterial growth logarithmic phase. Bacterial concentration reached $6 \times 10^8$ cells/mL on the 15th day, before approaching the stationary phase. During the whole bioleaching process, the bacterial concentration remained relatively stable. There was no obvious decline phase, indicating that the bacteria adapted very well to the leaching system, and the energy provided by the oxidation of sulfide ore could support the bacteria. In the bacteria–mineral noncontact leaching system, the bacterial concentration increased slowly and reached $2.1 \times 10^8$ cells/mL on the 15th day, which was one-third that of the bacteria–mineral contact leaching system. After 15 days, bacterial growth started to decline. The bacterial concentration decreased rapidly and reached $8.2 \times 10^7$ cells/mL at the end of the bioleaching process, which shows that Fe$^{3+}$ had no obvious effect on the oxidation of chalcopyrite in the bacteria–mineral noncontact leaching system. It was so hard for chalcopyrite to decompose persistently that some bacteria struggled to survive. This led to the occurrence of a decline phase and the decrease in bacterial concentration.
dized only by dissociative Fe$^{3+}$ in the leaching solution, as shown in Equations (1) and (2),

\[ \text{Fe}^{2+} + \text{S}^0 + \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}^{3+} + \text{SO}_4^{2-} + 2\text{H}^+ \]  
\[ \text{Fe}^{2+} + \text{S}_0 + \text{H}_2\text{O} \rightarrow \text{Fe}^{3+} + \text{HS}^- + 2\text{H}^+ \]  

pyrite surface. In the bacteria–mineral noncontact leaching system, chalcopyrite was oxi-

sulfur by

earlier stage of chalcopyrite bioleaching, the ox idation rate of ore was faster than that of

efficiency was higher than that of the bacter ia–mineral noncontact leaching system. This

formed on chalcopyrite surface by bacteria, and ore was oxidized by Fe$^{3+}$ enriched in EPS.

bacteria–mineral contact leaching system. According to the first mode, an EPS layer was

was bioleached for 30 days under two differen t leaching conditions. As shown in Figure

Thiobacillus thiooxidans

Thiobacillus ferrooxidans

microbe-mineral uncontact leaching model

microbe-mineral contact leaching model

microbe-mineral uncontact leaching model

microbe-mineral contact leaching model

Time/d

Copper Leaching efficiency/%

0 3 6 9 12 15 18 21 24 27 30

7.4 7.6 7.8 8.0 8.2 8.4 8.6 8.8 9.0

7.4 7.6 7.8 8.0 8.2 8.4 8.6 8.8 9.0

Figure 4. Bacterial concentration changes with bioleaching time.

3.3. Copper Leaching Efficiency

The copper leaching efficiency during the bioleaching process is shown in Figure 5. As

seen from Figure 5, the percentage of leached copper reached 61.67% on the 30th day during

the bacteria–mineral contact leaching system, while that of the bacteria–mineral noncontact

leaching system reached only 21.86%. In the bacteria–mineral noncontact-leaching system,

both the copper leaching rate and the efficiency were very low as a function of the oxidation

of dissociative Fe$^{3+}$. In the bacteria–mineral contact leaching system, the bacteria–EPS–ore

system was formed when bacteria were adsorbed on the chalcopryte surface. Fe$^{3+}$ was

accumulated in the EPS layer, subsequently oxidizing the ore. The efficiency was higher

than that of the bacteria–mineral noncontact leaching system. This shows that bacterial

adsorption has an important influence on chalcopryte bioleaching.

Figure 5. Copper leaching efficiency with bioleaching time.

3.4. Discussion

3.4.1. XRD Analysis of Leaching Residue

Figure 6 presents the XRD spectrum of several bioleaching residues after chalcopyrite

was bioleached for 30 days under two different leaching conditions. As shown in Figure 6,

the residue composition of the bacteria–mineral contact leaching system was essentially the

same as that of the bacteria–mineral noncontact leaching system, including chalcopyrite,

pyrite, elementary sulfur, and jarosite. There were two kinds of leaching mode in the

bacteria–mineral contact leaching system. According to the first mode, an EPS layer was

formed on chalcopryte surface by bacteria, and ore was oxidized by Fe$^{3+}$ enriched in EPS.

In the second mode, bacteria, such as *Thiobacillus ferrooxidans*, were adsorbed onto the

ore surface and supported by HS$^-$, $S^0$, and $S_2O_3^{2-}$ released by ore decomposition [35,34].

In the earlier stage of chalcopryte bioleaching, the oxidation rate of ore was faster than

that of sulfur by *Thiobacillus thiooxidans*. Therefore, elementary sulfur accumulated on the
chalcopryrite surface. In the bacteria–mineral noncontact leaching system, chalcopryrite was oxidized only by dissociative Fe$^{3+}$ in the leaching solution, as shown in Equations (1) and (2), such that the sulfur formed could not be oxidized and accumulate on the ore surface. As bioleaching proceeded in the bacteria–mineral contact leaching system, the further oxidation of ore by Acidithiobacillus ferrooxidans was inhibited by sulfur accumulated on the chalcopryrite surface, resulting in a rise in pH in the EPS layer and the hydrolysis of redundant Fe$^{3+}$. In addition, the jarosite crystal was separated out from the active matter in the EPS layer as a nucleation center. In the bacteria–mineral noncontact leaching system, the chalcopryrite surface was passivated due to the formation of elementary sulfur; thus, chalcopryrite could not effectively be further oxidized by Fe$^{3+}$. As redundant Fe$^{3+}$ content increased, Fe$^{3+}$ was hydrolyzed, and the jarosite crystal was separated out on the chalcopryrite surface. Thus, there was no further increase in the leaching efficiency. Figure 3 shows the XRD spectra of bioleaching residue after bioleaching.

![XRD spectra of the leaching residue after 30 days.](image)

**Figure 6.** XRD spectra of the leaching residue after 30 days.

### 3.4.2. SEM Analysis of Leaching Residue

SEM micrographs of leaching residue at different leaching times are shown in Figures 7 and 8. As shown in Figure 7a, most of the elliptic eroded pits and cracks can be found on the surface of several residues after leaching for 10 days due to bacterial adsorption in the bacteria–mineral contact leaching system. Passivation did not occur due to a slippery ore surface, but fine jarosite crystals existed in the pits. After leaching for 20 days, the pits increased, and the cracks started to broaden and deepen, which clearly indicates that the ores were severely corroded. The ore surface remained sleek, and no jarosite crystal was found on the outer surface of the ore. The jarosite was produced only in the pits. The jarosite appeared only in the eroded area of the ore surface, as shown in Figure 7b. At 20 days through 30 days, since bacteria constantly produced Fe$^{3+}$, jarosite crystal in the corrosion pits grew, eventually covering the whole chalcopryrite surface, especially where there was no reaction. This led to the thorough passivation of the chalcopryrite surface, as seen in Figure 7a. Figure 8 shows that bacteria were not adsorbed onto the chalcopryrite surface because of the isolation of the bag filter. Chalcopryrite was oxidized by dissociative Fe$^{3+}$. Elementary sulfur occurred on the chalcopryrite surface after leaching for 10 days. The energy spectrum shows that the crystal floc around sulfur is jarosite, as seen in Figure 8a. Along with the steady oxidation by bacteria, both the Fe$^{3+}$ concentration and its redox potential increased, resulting in the chemical deposition of jarosite and severe passivation on the chalcopryrite surface. Finally, the copper bioleaching process stopped, as shown in Figure 8b,c.
3.4.3. FTIR Analysis of Leaching Residue

Figure 9 shows the FTIR spectra of both kinds of leaching residue after leaching for 30 days. The adsorption peaks at 515 and 474 cm\(^{-1}\) were attributed to the stretching vibration of the FeO\(_6\) octahedron [35], that at 630 cm\(^{-1}\) was attributed to the \(\upsilon_4\) stretching vibration of SO\(_4^{2-}\), that at 1020 cm\(^{-1}\) was attributed to the \(\gamma_1\) bending vibration of SO\(_4^{2-}\), those at 1090 and 1193 cm\(^{-1}\) were attributed to the \(\gamma_3\) bending vibration of SO\(_4^{2-}\) [36], that at 1663 cm\(^{-1}\) was attributed to the \(\delta_2\) bending vibration of the FeO\(_6\) octahedron [35].
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![FTIR spectra of leaching residue](image)

Figure 9. Fourier-transform infrared (FTIR) spectra of leaching residue.

3.4.4. Model of Bioleaching Process

Although bacteria–mineral contact and noncontact leaching coexist in chalcopyrite bioleaching, bacteria–mineral contact leaching represents the main mode. In Figure 10, a mechanism model is presented for the chalcopyrite bioleaching process and jarosite production. In the initial phase, bacteria are adsorbed onto the mineral surface owing to its chemotaxis, as shown in Figure 10a. A substantial amount of Fe\(^{3+}\) exists in the EPS layer, which is reduced to Fe\(^{2+}\) due to the oxidation of ore. Then, Fe\(^{2+}\) is oxidized to Fe\(^{3+}\), which is accompanied extensive H\(^+\) consumption, as seen in Figure 10b,c. Chalcopyrite is oxidized, and Fe and Cu are liberated. The sulfur in the reduced state is oxidized to S\(^0\), and a sulfur film is formed on the chalcopyrite surface, thereby inhibiting the leaching of chalcopyrite. The copper leaching rate decreases and pH increases in the EPS layer. The remaining Fe\(^{3+}\) hydrolyzes and forms jarosite, as shown in Figure 10d. In the EPS layer, active matter is used as the nucleation center of jarosite. Fe\(^{2+}\) is oxidized by free bacteria, thereby increasing the Fe\(^{3+}\) concentration and redox potential. During the anaphase, the jarosite sediment is increased, thereby inhibiting the copper leaching process with the rise in Fe\(^{3+}\) concentration. Thus, passivation of the bacteria–mineral contact and noncontact leaching systems depends on the accumulation of sulfur on the chalcopyrite surface. In the passivation process, the formation of a sulfur film has an inhibitory effect on the rapid diffusion of reaction ions, thus decreasing the leaching rate of chalcopyrite. However, jarosite is the main reason for chalcopyrite passivation.
Figure 10. Schematic diagram of chalcopyrite bioleaching and jarosite formation. (a) Adsorption bacteria on chalcopyrite surface, (b) Microenvironment between bacteria, EPS and minerals, (c) Fe$^{2+}$ was oxidized to Fe$^{3+}$ on the cell wall of bacteria, and consuming H$^+$, (d) Jarosite crystal precipitation.

4. Conclusions

(1) The bacteria–mineral contact and noncontact leaching systems coexisted in the chalcopyrite bioleaching process. In the bacteria–mineral contact leaching system, the bacteria oxidized elemental sulfur on the surface of chalcopyrite and enriched Fe$^{3+}$ in the EPS layer, which hastened copper leaching. In the bacteria–mineral noncontact leaching system, dissociative Fe$^{3+}$ oxidized chalcopyrite, and it was regenerated by the bacteria.

(2) In the chalcopyrite bioleaching process, the formation of sulfur was found in both the bacteria–mineral contact and the bacteria–mineral noncontact leaching systems. In the bacteria–mineral contact leaching system, the oxidation rate of ore was faster than that of sulfur by *Thiobacillus thiooxidans*. Sulfur was deposited on the chalcopyrite surface. In the bacteria–mineral noncontact leaching system, the oxidation of S$^{2-}$ and S$^{1-}$ to S$^{0}$ induced by Fe$^{3+}$ could not generate S$^{4+}$ and S$^{6+}$ with a higher valence state, consequently inhibiting further copper leaching.

(3) A layer of sulfur was produced and consequently inhibited the rapid diffusion of reaction ions. The redundant Fe$^{3+}$ was hydrolyzed and formed jarosite. In the bacteria–mineral contact leaching system, jarosite was separated out from the active matter in the EPS layer as a nucleation center. In the bacteria–mineral noncontact leaching system, the jarosite crystallized on the sulfur layer of the chalcopyrite surface.

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