Catalytic Effects of Red Mud and Acidithiobacillus ferrooxidans on Biodissolution of Pyrite

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Abstract: The catalytic effect of red mud on biodissolution of pyrite was studied with Acidithiobacillus ferrooxidans in this study. Dissolution and results showed that red mud could significantly promote pyrite biodissolution. The bacterial group with 4g/L red mud had best dissolution effect. The iron extraction rate in the group was 47.9% higher than the control group. Red mud in sterile group could inhibit pyrite dissolution. The iron extraction rate in the group with 8.0g/L red mud was 75.4% lower than the control group. The biodissolution results indicated that red mud could accelerate pyrite dissolution by promoting electron transfer in biodissolution system and enhancing the growth of A. ferrooxidans.

1. Introduction
Mining activities have created lots of economic benefits, however they also produced large number of tailings which caused severe environmental problems. According to incomplete statistics, the content of tailings in China has exceeded 10 billion tons at present, and is increasing by several hundred million tons every year1. These huge piles of tailings will not only occupy a large amount of land, but also some sulfide minerals will be oxidized by air or bacteria, and then washed by rainwater, which will cause serious environmental problems, such as acid mine drainage (AMD)2,3. AMD will pollute groundwater and surface water, destroy the ecological environment, and cause serious human health problems4. Therefore, control and governance of AMD formed in the process of mining is imminent.

Pyrite is the main contributor to AMD5. When microbial oxidation and dissolution of pyrite occur in the mining area, a large number of iron ions and acids are released into the environment to form AMD6. However, there are few studies on the oxidation dissolution of pyrite causing AMD. Therefore, it is of great significance for the management and control of AMD to actively carry out related studies on the biodissolution of pyrite and explore effective measures to inhibit the biodissolution of pyrite.

2. Materials and Methods

2.1 Minerals
Pyrite samples were obtained from a mining area in Hunan Province, China. Chemical analysis showed that the pyrite sample contained (w/w) 44.68% Fe, 45.44% S. XRD result indicated that pyrite used in the study were of high purity.
2.2 Microorganisms and Biodissolution Experiments

The Acidithiobacillus ferrooxidans ATCC 23270 used in this study was obtained from the Key Lab of Biohydrometallurgy of the Ministry of Education, Central South University, Changsha, China. The pH of the medium was adjusted to 2.0 with H₂SO₄. A. ferrooxidans was pre-activated in a shaker containing 9 K medium at 30 ℃ and 170 rpm with 20 g/L chalcopyrite and then cultured in the same environment. The 9K medium contained (NH₄)₂SO₄ (3 g/L), KCl (0.1 g/L), K₂HPO₄ (0.5 g/L), MgSO₄•7H₂O (0.5 g/L), and Ca(NO₃)₂ (0.01 g/L).

2.3 Analysis Methods

The methods used in chalcopyrite biodissolution to monitor the variations in pH, redox potential, and the concentrations of copper ions and iron ions in the solutions are based on a previously reported study. The pH and ORP values in the dissolution solution were measured with a pH meter (PHS-3C) and a platinum electrode potentiometer (vs Ag/AgCl, BPH-221). The copper and iron concentrations were analyzed by Dicyclohexanoneoxaly dihydrazone (BCO) spectrophotometry and o-phenanthroline spectrophotometry. The cell concentration was measured using a 40× optical microscope (CX31).

3. Results and Discussion

The total iron ion concentration, iron dissolution rate, ferrous ion concentration, pH and REDOX potential in the process of chemical dissolution of pyrite are shown in Figure 1. After dissolution, when red mud concentration was 0.0g/L, 1.0 g/L, 2.0 g/L, 4.0 g/L and 8.0 g/L, total iron concentration of the sterile group was 1.38 ± 0.05g/L, 1.16± 0.05g/L, 1.24± 0.04g/L, 1.17± 0.04g/L and 0.34± 0.05g/L, respectively. As shown in figure 1a, b, c, except for the component added with 8.0g/L red mud, the variation trends of total iron ion concentration, iron dissolution rate and ferrous ion concentration in other components were basically the same: In the first two days of the dissolution test, the total iron ion concentration, iron dissolution rate and ferrous ion concentration increased rapidly, and the growth rate slowed down but still maintained an increasing trend after two days. The total iron ion concentration, iron dissolution rate and ferrous ion concentration of the sterile group with 8.0g/L red mud showed a slight increase in the first 2 days of the reaction and then a slow decrease in the second to tenth day of the reaction, and a slight increase in the 10th to 14th day of the reaction. The total iron ion concentration, iron dissolution rate and ferrous ion concentration of the system were negatively correlated with the concentration of red mud added to the system in the sterile group. Combined with the pH and REDOX potential of the reaction system in Figure 1d and e, the reason why red mud inhibited the dissolution of pyrite in the sterile group was that the addition of red mud increased the pH of the system and inhibited the electron transfer ability of the system.

$$4\text{FeS}_2 + 15\text{O}_2 + 2\text{H}_2\text{O} \xrightarrow{\text{Af}} 2\text{Fe}_2(\text{SO}_4)_3 + 2\text{H}_2\text{SO}_4$$  \hspace{1cm} (3-1)
$$\text{FeS}_2 + 7\text{Fe}_3(\text{SO}_4)_2 + 8\text{H}_2\text{O} \rightarrow 15\text{FeSO}_4 + 2\text{H}_2\text{SO}_4$$  \hspace{1cm} (3-2)
$$\text{K}^+ + 3\text{Fe}^{3+} + 2\text{SO}_4^{2-} + 6\text{H}_2\text{O} \rightarrow \text{KFe}_3(\text{SO}_4)_2(\text{HO})_6 + 6\text{H}^+$$  \hspace{1cm} (3-3)

The variation trend of pH in the sterile system is shown in Figure 1d. The pH of the sterile groups with low concentration red mud remained basically unchanged during the whole reaction process, indicating that the low concentration red mud had little effect on pH. The pH of 4.0g/L and 8.0g/L sterile groups rose rapidly in the first 2 days of the reaction, and then decreased slowly, because the red mud itself was composed of iron, calcium, aluminum and other compounds and solid silica residue, with strong alkalinity and high salinity. The main reactions involved in the biodissolution of pyrite are shown in Eqs 1~3⁹. In the middle stage, due to the chemical dissolution of pyrite to produce H⁺ (Eq.2), the pH of the system decreased.
Fig. 1. Changes in of dissolved copper concentration (a), copper dissolution rate (b), total iron concentration (c), ferrous concentration (d), pH (e), and redox potential (f), during chalcopyrite dissolution under sterile conditions.

The changes of total iron ion concentration, iron dissolution rate, ferrous ion concentration, pH, REDOX potential and bacterial concentration in the biodissolution process of pyrite are shown in Fig.2. Total iron ion concentration in all bacterial groups achieve the rapid increase in the first 10 days, and then, total iron ion concentration growth declining gradually flatten out in about 10 days. On the one hand it may be because of the formation of pyrite surface passivation layer (Fig 2a). On the other hand, at the tenth day of the experiment, the concentration of *A. ferrooxidans* in the dissolution environment all showed a downward trend and had decreased to a relatively low level compared with the maximum value When the concentration of red mud was 0.0g/L, 1.0 g/L, 2.0 g/L, 4.0 g/L and 8.0 g/L, the final total iron concentrations of the bacterial group were 4.26 ± 0.05g/L, 5.24± 0.05g/L,
5.87± 0.04g/L, 6.30± 0.04g/L and 5.69± 0.05g/L, respectively, and the dissolution rates were 47.6%, 57.2%, 62.7%, 64.4% and 53.7%, respectively (Fig. 2b). The total leaching iron concentration of red mud treatment group was significantly higher than that of blank control group without red mud treatment, and the optimal concentration of red mud treatment group was 4.0 g/L. Under this condition, the total leaching iron concentration of red mud treatment group was 47.9% higher than that of bacterial blank group, and 356.5% higher than that of chemical blank group, indicating that red mud can significantly promote the biological dissolution of pyrite. When high concentration of red mud is added, the promoting effect of red mud on pyrite dissolution is weakened. On the one hand a high concentration of red mud dissolved itself and chalcopyrite dissolution formed the competition, weaken the promoting effect of red mud, on the other hand, high concentrations of red mud making passivation objects such as jarosite in minerals that form quickly, passivation layer of the impact of the dissolution of pyrite.

In the first ten days of the experiment, a large number of ferrous ions were released into the dissolution environment with the dissolution of red mud. However, at this time the concentration of cells in the dissolution environment was higher and the reaction rate was faster. The ferrous ions in the dissolution environment were rapidly oxidized into ferric ions (Eq.1). The dissolution rate of pyrite slowed down after about 10 days (Fig.2ab), which may be due to the formation of passivating materials such as jarosite on the surface of pyrite, which hindered the dissolution of pyrite. At this time, the production rate of ferric ions slowed down, and the dissolution of red mud and the chemical dissolution of pyrite led to the large accumulation of ferrous ions in the solution (Figure 2c).

The pH variation trend of pyrite bacterial dissolution system is shown in Figure 2d. In the early stage of reaction, the pH of the groups with more than 2.0g/L of red mud rose rapidly. Due to the high alkalization of red mud itself, a large amount of acid was consumed in dissolution. Subsequently, the pH of the bioleaching system falls rapidly, indicating acid production, which is caused by the oxidation of elemental sulfur by A.f to sulfuric acid and jarosite to acid production (Eq 1 and 3).

Fig. 2e shows that the change trend of the REDOX potential (ORP) of each group of the biodissolution system is basically the same during the whole dissolution. After the REDOX potential in the bacterial system was relatively stable, the REDOX potential in the solution was positively correlated with the concentration of red mud added, indicating that red mud could enhance the REDOX capacity of the system.

Fig.2f indicates the concentration of Acidithiobacillus ferrooxidans cells in the biodissolution system of pyrite. The concentration of cells in each group increased to the maximum and then began to decline, due to the accumulation of toxic substances and the consumption of nutrients. In the whole process of dissolution, the concentration of free cells in the biological dissolution system with red mud was higher than that in the biodissolution system without red mud treatment, indicating that red mud had a promoting effect on the growth of A.f. The maximum cell concentration of the group with 4.0g/L red mud was higher than that of the group with 8.0g/L red mud during the whole dissolution process, because the dissolution of high concentration of red mud consumed H+, leading to the high pH of solution and affecting the growth of A.f.

According to the above results, it can be concluded that the addition of red mud significantly promote the biodissolution of pyrite, resulting in the release of more iron ions. The addition of red mud promot the dissolution of pyrite by promoting the growth of A.f and electron transfer in the dissolution system.
Fig. 2. Changes in (a) dissolved copper concentration, (b) copper dissolution rate, (c) total iron concentration, (d) ferrous concentration, (e) pH, and (f) redox potential, during biodissolution of chalcopyrite by A. ferrooxidans.

The results in Figure 2c show that the variation trend of the concentration of ferrous ions in each group is basically the same. Before 10 days, the concentration of ferrous ions in all components increased at a slow rate. After 10 days of the experiment, the concentration of ferrous ions in the dissolution environment increased rapidly, reached the peak at about 12 days and then decreased again at 18 days.
4. Conclusion

1) Red mud can significantly promote the biodissolution of pyrite with \textit{A. ferrooxidans} and release more iron ions, which also indicates that under the influence of red mud, pyrite will lead to the increase of acid mine drainage release.

2) Red mud can promote the growth of \textit{A. ferrooxidans} which is conducive to the oxidation and reduction of pyrite.

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