

Chalcopyrite Bioleaching by *A. Ferrooxidans* and Surface Passivation

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Abstract—Based on the fact that the primary copper sulfide bioleaching has long leaching time and low leaching rate and has not been used in industry, through selective breeding, domesticated species leaching good using the scanning electron microscopy. The chalcopyrite bioleaching by *A. ferrooxidans* was studied. Understanding of passivation phenomenon of chalcopyrite surface and the types of passivation layer formed. The mechanism of chalcopyrite reaction and passivation reasons was analyzed. Study on chalcopyrite bioleaching by *A. ferrooxidans*, Ferrous sulfate Pretreatment and Sulfate Pretreatment, The results show that chalcopyrite surface has Obvious bacteria and a mixture of jarosite flock parcel layer when chalcopyrite bioleaching by *A. ferrooxidans*. When impregnated iron sulfate and ferrous sulfate, leaching of chalcopyrite does not improve the basic problem of delay, but causing obstruction.

Keywords- *A. ferrooxidans*; Chalcopyrite; Bioleaching; Passivation

I. INTRODUCTION

Chalcopyrite is the main part of copper resources and the most widespread copper ore in industry. It is a common type of copper ore in all kinds of copper deposits and also a kind of ore extracted the most in copper extraction. According to the current consumption of copper and characteristic of copper resource in our country, we should make full use of chalcopyrite bioleaching which have advantages such as shorter and simpler process, easier operation, less investment, less energy consumption, low cost and environment- friendly. It is suitable to deal with complex copper resources in low grade. At present, wet process of chalcopyrite mainly are ferric sulfate leaching, chloride leaching, bioleaching and reduction leaching etc. Bioleaching is the research hotspots in recent years, but the speed of chalcopyrite leaching is slow and the rate is low, therefore, the study progress relatively lags behind. Many researchers believe that the main reason hinder chalcopyrite bioleaching is the forming of the passive layer such as sulfur layer, sulfide layer and jarosite layer etc in mineral surface. Passive layer hinder the spread of bacteria,

nutrients, reactants and products, thus it hinder the further dissolve of chalcopyrite, the leaching rate declines significantly after a period. This influence in bioleaching processing is called “passivation phenomenon”^[5,6]. This paper studies the leaching by *A. ferrooxidans* directly, ferric sulfate pre-leaching and ferrous sulfate pre-leaching to get oxidation of chalcopyrite and looks for possible solid-state products of the reaction layer to confirm the real reasons caused the passivation.

II. TEST MATERIALS AND METHODS

A. Microbial strains and the medium

The microorganism *Acidithiobacillus ferrooxidans* used in experiment comes from DEERNI Mine Area water samples. The culture medium for cultivating bacteria is 9K medium, its basic compositions are as follows: mineral base salt ($\text{g} \cdot \text{L}^{-1}$) (NH_4)₂SO₄, 3.0, KCl, 0.1, K₂HPO₄, 0.5, MgSO₄, 7H₂O, 0.5, Ca (NO₃)₂, 0.01. All the culture mediums are used 30 minutes after sterilization at 121°C.

B. Pure chalcopyrite

The mineral used in experiment comes from a deposit in which Chalcopyrite is the dominant copper mineral in Yunnan. Ore blocks are gained by crushing, hand picking, table separation, magnetic separation, gravity concentration and preserved in ground glass stopper bottle for bacteria domestication under the normal temperature. Pure minerals are preserved in ground glass stopper bottle under normal temperature, and partly are fine grinded for detection of bacteria leaching effect and study on mechanism. the results of analysis Composition of pure Chalcopyrite mineral by diffraction of X-ray (X'pert pro MPD) and fluorescence spectrum are in Fig 1, elemental analysis results are in table 1.

TABLE 1 RESULTS OF CHEMICAL ANALYSIS OF CHALCOPYRITE

Elements	Cu	Fe	S
Content (%)	32.14	29.94	30.04

Jiangxi Province Educational Science planning project (10YB147), Jiangxi Social Science Planning project (09YJ233), and Department of Education projects in Jiangxi Province (GJJ11135 and GJJ08277).

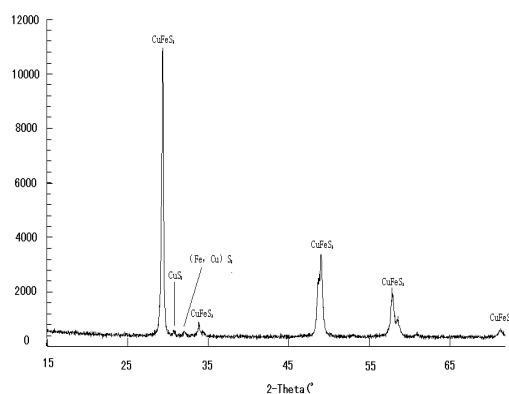


Fig 1 X-ray diffraction patterns of pure chalcopyrite

From analysis results of table 1 and figure 1 we know that purity of chalcopyrite used in test reached 98.87%, and the percentage composition of copper, iron, Sulfur are respectively 32.14%, 30.04% 29.94%. The results show that: chalcopyrite is natural mineral with good crystallization.

C. Ore leaching test

Add 40 mL sterile distilled water and 5mL 9K inoculums in a 100ml triangular flask, and then add 1g pure powder of chalcopyrite, the pH value was adjusted to 1.9 ~ 2.0 with 1mol.L-1 sulphuric acid. Inoculate 5 mL bacteria in logarithmic growth (concentration of bacterial is 108 / mL), then put the inoculums inoculated on a rotary shaker (220 r/min) (DHZ-C) at 28 °C for cultivation for 24 days. By analysis the number of cell in leaching, pH, Eh, concentration of ions of iron and copper, we can monitor the characteristics of chalcopyrite bioleaching. The concentrations of metal ions are analyzed by atomic absorption spectrometer (GGX - 9) and the numbers of cell are analyzed by micro-metering. Leaching experiments are done in three parallel groups, and another acidic medium is as comparison of it.

D. Observation and microanalysis of mineral surface with SEM

After leaching, we collect the mineral powder sample to observe with scanning electron microscope SEM and do the microanalysis of the mineral surface.

E. Analysis of mineral surface with SEM Analysis of mineral composition with XRD

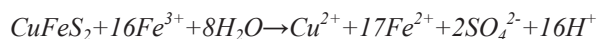
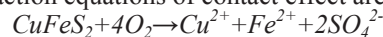
After leaching, analysis the mineral composition of chalcopyrite by X-ray diffraction after drying treatment. The scanning mode is 2θ, the range is from 10 to 85 and the step is 0.02.

III. RESULTS AND DISCUSSION

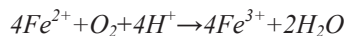
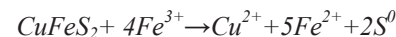
A. Research of leaching pure chalcopyrite minerals by *A. ferrooxidans*

Role of *A. ferrooxidans* in copper sulfide bioleaching: it is generally considered to oxidize Fe^{2+} into Fe^{3+} and that the iron bacteria's get energy from it to grow, at the same time provide sufficient oxidant for chalcopyrite leaching. Also somebody thinks *A. ferrooxidans* can leach ore directly. Chalcopyrite

bioleaching have contact effect, indirect effect or both. The reaction equations of contact effect are as follows:



The reaction equations of indirect effect are as follows:

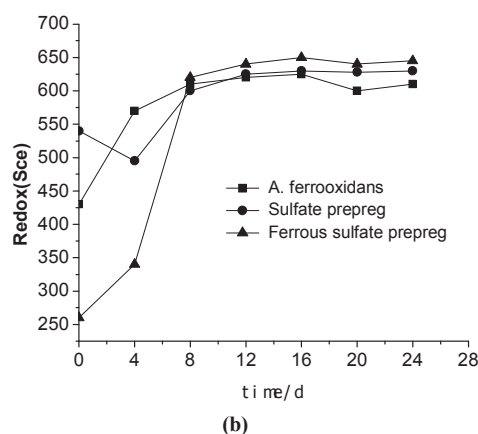
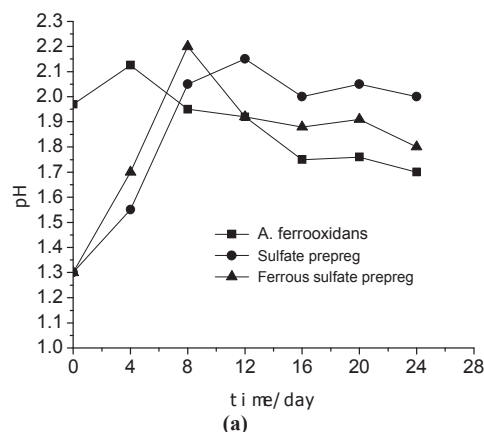


Both effects include both contact effect and indirect effect.

B. Behavioral analysis in leaching by *A. ferrooxidans* alone, ferric sulphate pre-leaching and ferrous sulphate pre-leaching

Figure 2 shows the pH, Redox potential, trend of concentration of metal ions in leaching system by *A. ferrooxidans* alone leaching and ferric sulfate pre-leaching and ferrous sulfate pre-leaching.

From figure 2, we know that in chalcopyrite leaching by *A. ferrooxidans* pH value is on the rise in the former four days, and then gradually descend to 1.70 meters. The potential of liquid reaches 570mv in the first four days (SCE) and then stand stably at 610mv (SCE); The concentration of copper iron in liquid grows fast early, gradually slow late, but still shows ascendant trend. The concentration of iron ion rises relatively fast, but stands basically stably at about 1.75 g · L⁻¹ four days later.



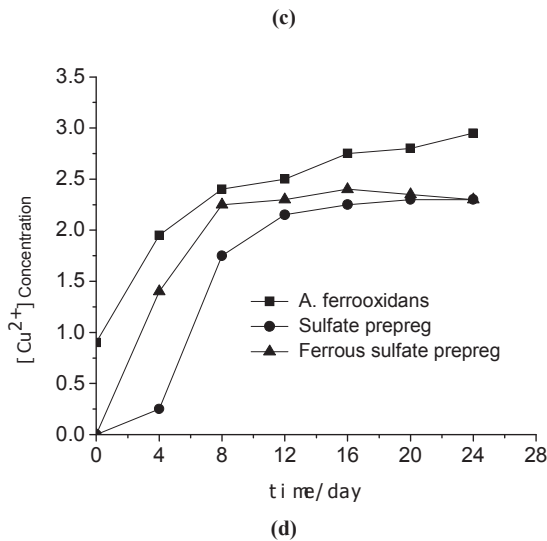
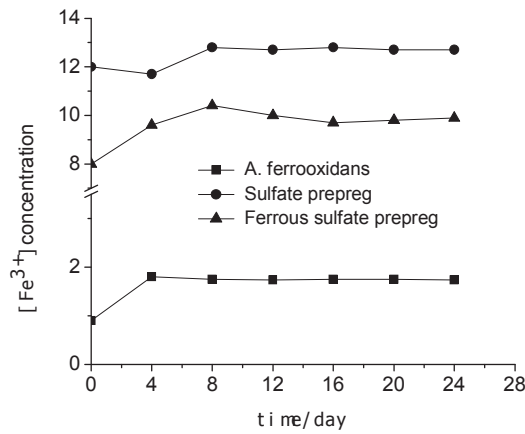
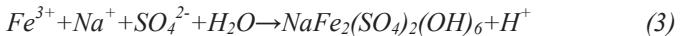
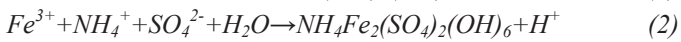


Figure 2 Variations of the parameters of leaching at different conditions (a) : pH, (b) : redox potential, (c) : Variation of concentration of iron ion . (d) : Variation of concentration of copper ion

At first-phase of leaching by *A. ferrooxidans*, the leaching rate lifts quickly in effect of both H^+ ions and *A. ferrooxidans*. Fe^{2+} ions released in mineral dissolution are turned into Fe^{3+} ions by catalytic oxidation by of bacteria, the potential of liquid rises rapidly. At the medium-term of leaching, the concentration of Fe^{3+} ions Cu^{2+} ions in liquid continue to increase on the basis before, but when the pH value and the concentration of Fe^{3+} ions of liquid rise to a certain degree, a part of Fe^{3+} precipitate in certain form, its reactions are (1), (2) and (3), release of H^+ prompted soaking liquid pH value falls. Leaching later period, mineral surface properties change on leaching block is more significant, soaking liquid Cu^{2+} ions in grew very slowly, while chalcopyrite dissolve Fe^{2+} , released by bacteria oxidized to Fe^{3+} directly after precipitation down.



After *A. ferrooxidans* is inoculated into the group of ferric sulfate pre-leaching, the pH value of liquid maintains at 2.0 or so, Redox Properties of liquid raises to 600mv (SCE) 4 days later. The concentration of copper ion of liquid grows slowly

and concentration of iron ion of liquid does not grow basically ; After *A. ferrooxidans* is inoculated into the group of ferrous sulfate pre-leaching, the pH value of liquid has certain raise and then gradually decline to 1.85 or so. Redox Properties of liquid rapidly raises to 620mv (SCE) 4 days later. The concentration of copper ion of liquid grows slowly and concentration of iron ion of liquid does not grow basically.

C. Analysis composition and surface in leaching by *A. ferrooxidans* alone , ferric sulphate pre-leaching and ferrous sulphate pre-leaching

The SEM electron micrograph of residue in chalcopyrite leaching by *A. ferrooxidans* alone, ferric sulfate pre-leaching and ferrous sulfate pre-leaching is shown in figure 3. The X-ray diffraction photograph of residue in chalcopyrite leaching is shown in figure 4.

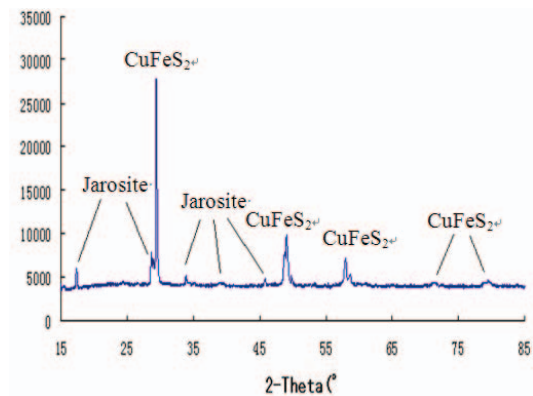
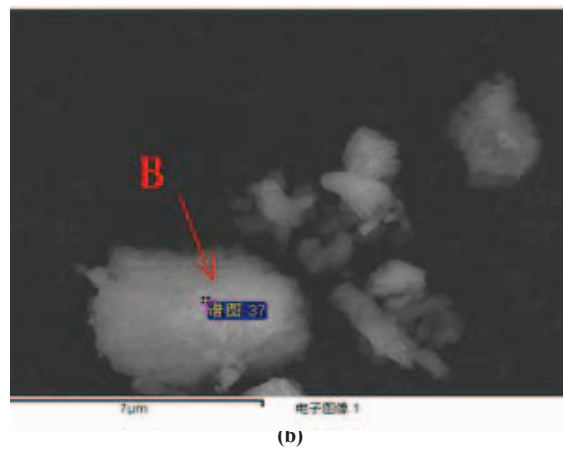
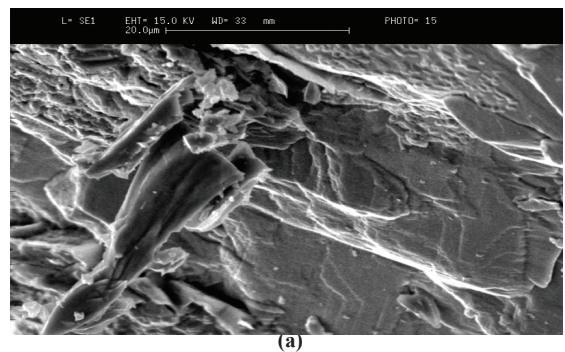
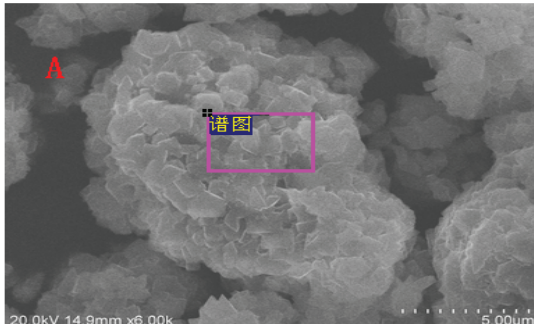
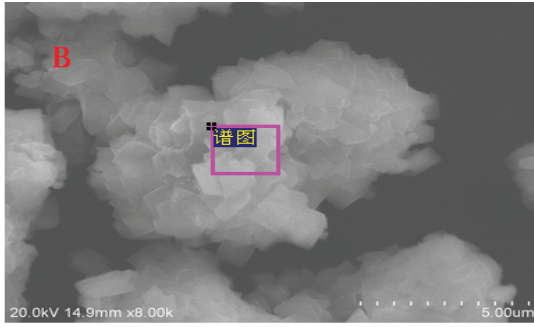


Fig 4 X-ray diffraction patterns of Residue





(c)



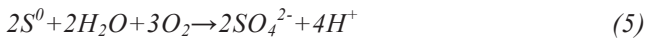
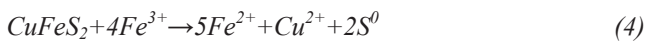
(d)

Figure 3 SEM electron micrograph of leaching residue under different conditions

(a) : pure chalcopyrite, (b) : SEM electron micrograph of residue in leaching by *A. ferrooxidans*, (c) SEM electron micrograph of residue in ferric sulphate pre-leaching, (d) SEM electron micrograph of residue in ferrous sulphate pre-leaching.

Leaching by *A. ferrooxidans* that the mineral surface is enwrapped with flocculent substance and may be this flocculent substance hindered the leaching of chalcopyrite. From the test of covers by energy spectrum, we know that its main compositions are C, O, a small amount of S, K, Fe, Cu elements and etc.

The X-ray diffraction photograph of residue in chalcopyrite leaching shows the crest line of chalcopyrite obvious, but there still exist the crest line of other substances obvious, it should be some kinds of jarosite by contrasting cards and leaching process. The jarosite is compact in texture, which has important influence on the slow of leaching rate; it directly reduced concentration of Fe^{3+} that has important role in oxidation. The passivation of Chalcopyrite is partly on account of ferric hydrate settles on the mineral surface in bioleaching process, it is mainly jarosite. The formulas of the reaction are (4), (5) and (6):



From analysis the X-ray diffraction photograph of residue in leaching by *A. ferrooxidans*, we haven't found object unknown, the mineral surface is neat and without foreign bodies, the test of SEM and the analysis on compositions of mineral surface by energy spectrum also gives the effective evidence. The Mineral surface is not wrapped with flocculent obviously like leaching by *a. ferrooxidans*, the content of S on Mineral surface seems to be superfluous, but not obvious, and

there is no corrosion phenomenon on mineral surface. The result of Analysis shows that there is a layer difficult to destroy for *a. ferrooxidans* formed on the surfaces of mineral, which hinders the dissolution of mineral; just like leaching by sulphuric. But it is more likely the dissolution of minerals to decide the degree of reaction.

By analysis the X-ray diffraction of residue, the SEM electron micrograph of surface and energy spectrum of composition in leaching by ferric sulfate pre-leaching, ferrous sulfate pre-leaching and *A. ferrooxidans*, we know that the surface of mineral is covered with flocculent stuff similar to leaching directly by *A. ferrooxidans*, and the elements are basically the same.

IV. CONCLUSION

The experiment shows that the ferric sulfate pre-leaching and ferrous sulfate pre-leaching do not improve leaching by *A. ferrooxidans* basically. The mineral surface is enwrapped with flocculent substance that hindered the leaching of chalcopyrite after inoculation of *A. ferrooxidans*. The analysis of composition shows that it might be the bacterial residues and crystal of jarosite. Contrast to ferric sulphate leaching with bacteria, the effect of leaching by *a. ferrooxidans* directly is basically the same. I think that leaching by *a. ferrooxidans* may have contact function, but later it turns into indirect function, the main reason of passivation of leaching later should be the forming of the flocculent on the surface of minerals. There exists obvious passivation in the leaching by *A. ferrooxidans*, can see the possible passive film, some kinds of jarosite attached, in the residue. The ferric sulfate pre-leaching and ferrous sulfate pre-leaching do not improve the blocking problem basically and caused some trouble instead.

ACKNOWLEDGMENT

The study was supported by Jiangxi Province Educational Science planning issues (10YB147), and also by Department of Education projects in Jiangxi Province (GJJ11135 and GJJ08277), both of which are gratefully acknowledged. We highly appreciate Jiangxi University of Science and Technology for providing fund for this research work.

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