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Behavior of Fe and S in bioleaching of pentlandite①

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[Abstract] The reaction behavior of Fe and S in bioleaching of pentlandite with *Thiobacillus ferrooxidans* was investigated. The results of leaching experiments and XRD pattern show that pentlandite can not be oxidized easily by 2.8 g/L Fe^{3+} at 35 ℃, and H^+ was released while Fe^{3+} precipitates to form jarosite. Bacteria oxidize the sulfide in the mineral to produce element sulfur, meanwhile, H^+ in the solution is consumed and this process results in pH value increasing about 0.3 everyday in the solution, and this process is supported by SEM morphology and EDS patterns.

[Key words] pentlandite; bioleaching; Fe; S
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1 INTRODUCTION

Oxidizing process by autotrophic bacteria, such as *Thiobacillus ferrooxidans* (Hereinbelow be abbreviated to T.f.), has been widely used to extract valuable metals from sulfide ores. The bioleaching is concerned about a catalytic effect of the organisms. Both direct leaching (bacteria attached to the sulfide minerals) and indirect leaching (Fe^{2+} is oxidized to Fe^{3+} by the bacteria followed by sulfide leaching by the Fe^{3+}) take place in the process. The role of both actions and the reaction behaviors of Fe and S in sulfides, however, might be differred from one mineral to another. On the other hand, recent works[1, 2] have been extended to detailed studies on polymetallic ores. The leaching process for them is relatively complex and often effected by mineral composition in the ores and(or) produced compounds in it. It is therefore very important to identify the reaction behaviors of every special mineral through the study on pure mineral bioleaching, as it was done on the pyrite[3, 4]. In this work, a pentlandite with high purity (95%) is bioleached by T.f. and the behavior of S and Fe in the process is discussed.

2 EXPERIMENTAL

A high grade pentlandite sample, enriched from the polymetallic Ni-Cu ore from Jinchan Mine in Gansu province of China, was used in this study. It contains over 95% of pentlandite in the minerals, and Ni 32.72%, Fe 31.25%, Cu 0.82%, Co 0.41%, S 31.69% and Mg 0.04% in elemental. Its particle size ranges from 0.038 to 0.074 mm.

An iron free leathen medium[5], containing $(NH_4)_2SO_4$ 0.15 g/L, KCl 0.05 g/L, K_2HPO_4 0.05 g/L, $MgSO_4\cdot 7H_2O$ 0.5 g/L, $Ca(NO_3)_2$ 0.01 g/L, was used in all shake flask tests.

The strain of T.f. was provided by Institute of Microbiology, Chinese Academy of Science. The strain was cultured in the leathen medium containing 5% (mass fraction) pentlandite concentrate (industry grade) for a long time to make it adapted to the pulp environment under conditions of temperature 35 ℃ and shake rate of 170 r/min. The cells were harvested by centrifugation and resuspended to a final volume in sterile medium until the leaching experiment started.

The initial densities of cells were approximately 4×10^7/mL in all experiments, determined by direct counting with a microscopy and a Petroff-Hausser counting chamber. The total iron concentration in leachate was determined by spectrophotometer using the phenanthrolene methods[6], and the dissolved nickel was analyzed by atomic adsorption spectrometry (AAS).

3 RESULTS AND DISCUSSION

3.1 Effect of Fe^{3+} on leaching system

In bacterial oxidizing of sulfides the dissolution of minerals is usually resulted from three actions: the direct action of bacteria attached to the mineral surface, the action of the free bacteria in the leaching solution, and the chemical reaction of Fe^{3+} in solution[7]. Sometimes the action of acidic medium which is required for bacteria growth, is not neglected. So it is very important to identify which action is the predominant in the pentlandite bioleaching.

The iron-free leathen medium and density of the pentlandite pulp of 20 g/L was used in all the tests. In the first one the strain of T.f. was inoculated and the pH was controlled at 2.0 by adding sulfuric acid

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solution in the leaching. In the second one the solution contained 2.8 g/L of Fe^{3+} by adding $Fe(SO_4)_3$. In the third test the sulfuric acid was added to keep the pH as same as the solution of $Fe_2(SO_4)_3$. So there were only the action of the acidic solution in the third test, and in the second it was the action of both acidic and Fe^{3+}, and in the first was the combined action of bacteria and acid. The leached Ni in these tests is shown in Fig. 1.

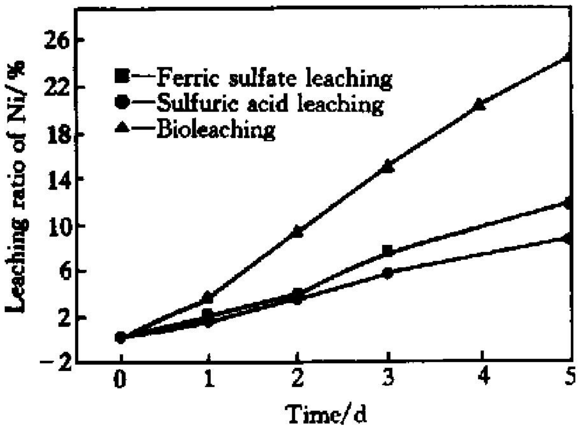

Fig. 1 Leached Ni in bioleaching and chemical leaching by Fe^{3+}

The results indicate that the leached Ni increases a little by chemical reaction of Fe^{3+} ions, and is much lower than that by bioleaching. As shown in Fig. 2, the quantity of Fe^{3+} resulted from bioleaching of pentlandite in the test is very limited, and its action is much lower than that of the initial added Fe^{3+} of 2.8 g/L. It is clear that Fe^{3+} could not oxidize the pentlandite easily. So in the bioleaching of the pentlandite, the contribution of Fe^{3+} could be neglected and the direct action of bacteria is predominant.

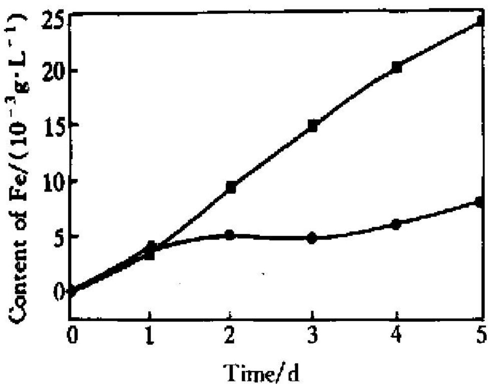

Fig. 2 Concentrations of total Fe in test
■ —Values calculated according to concentrations of dissolved Ni;
● —Measured with spectrophotometer by phenanthrolene methods

There are two kinds of bacteria in bioleaching system—adhered bacteria and free bacteria. The experiment results have indicated that adhered bacteria play a major role in the bioleaching of pentlandite, as mentioned in Ref. [8].

3.2 Precipitation of jarorite

A precipitation was found in the bioleaching process, and it was identified as jarosite by XRD (Fig. 3). The reaction of jarosite precipitation can be described as

$$4Fe^{2+} + 4H^+ + O_2 \xrightarrow{\text{Bacteria}} 4Fe^{3+} + 2H_2O \qquad (1)$$

$$3Fe^{3+} + 2SO_4^{2-} + R^+ \longrightarrow RFe_3(SO_4)_2(OH)_6 + 6H^+ \qquad (2)$$

where $R^+ = NH_4^+$, K^+.

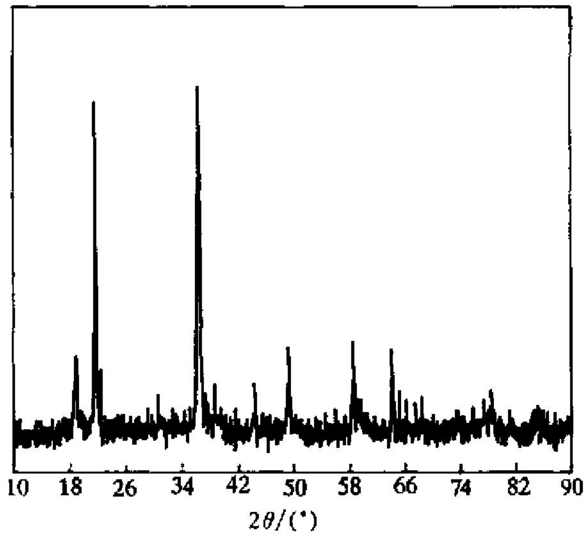

Fig. 3 XRD pattern of precipitation produced in bioleaching

The concentration of total iron in leathates was monitored and shown in Fig. 2. It can be seen that the actual concentration of iron (Fe^{3+} and Fe^{2+}) is much lower than the calculated value throughout the run, so it is doubtless that almost all iron released from pentlandite deposited as jarosite in the bioleaching. According to the reaction (1) and (2), there is H^+ released into the liquid in the procedure of jarosite formed. This is favor to keep pH at the value required for bioleaching.

It was reported that jarosite could retard the bioleaching rate by covering the surface of the mineral particle[9]. The scanning electron micrograph shows that, after a leaching of 6 d, there are some white specks on the surface of the mineral, as shown in Fig. 4. The EDS pattern of the white speck (Fig. 5) shows that its elemental composition is identical with jarosite mainly precipitated as single particles. The layer of jarosite on the mineral surface does not observed by SEM.

On the other hand, precipitation of jarosite may be resulted in consumption of NH_4^+ and K^+, i.e. the lack of nutrient, which is necessary to the growth of the bacteria.

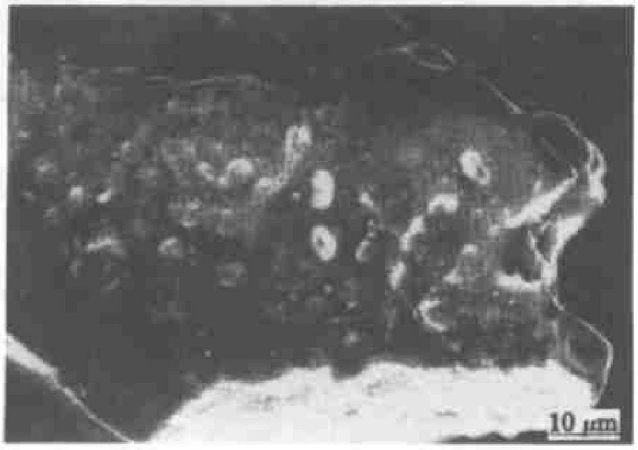

Fig. 4 SEM morphology of mineral surface after bioleaching for 6 d

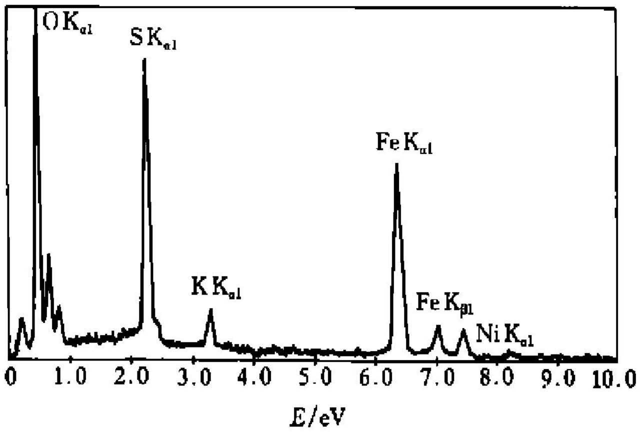

Fig. 5 EDS pattern of white speck on surface of mineral after bioleaching for 6 d

3.3 Behavior of S

During the bioleaching of pentlandite pH increased, it need to add sulfuric acid to keep pH at the same level. The consumption of acid in the tests is listed in Table 1.

Table 1 pH values comparison between sulfuric acid leaching and bioleaching

Time /d	Sulfuric acid leaching		Bioleaching	
	Initial pH	Adjusted pH	Initial pH	Adjusted pH
1	1.63	1.59	2.52	2.19
2	1.64	1.58	2.59	2.21
3	1.64	1.60	2.59	2.18

A little acid is consumed in the acidic leaching, because a few of alkaline gangue mineral contained in the pentlandite sample was used. However, from Table 1, it is shown that the acid consumption is relatively high in the beginning period of the bioleaching. This fact means more acid consumed in bioleaching process and suggests that only a part of sulfide be oxidized to sulfate. Elemental sulfur is therefore formed as

$$2S^{-1} + \frac{1}{2}O_2 + 2H^+ \xrightarrow{\text{Bactericа}} 2S^0 + H_2O \qquad (3)$$

$$2S^0 + 3O_2 + 2H_2O \xrightarrow{\text{Bacteria}} 2SO_4^{2-} + 4H^+ \qquad (4)$$

The bacteria adhered to the surface of the mineral get the energy required for their growth only by oxidizing the sulfide and do not oxidize Fe^{2+}, similar to the bioleaching of pyrite[10]. However, these bacteria oxidize the sulfide to the element sulfur only, but not to the sulfate as usual. Therefore, most of the element sulfurs are accumulated in the capsule of the adhere bacteria, and only a small part are released into the solution and oxidized to sulfate by the free bacteria, as occured in the bioleaching of pyrite[11]. The H^+ produced in reaction (2) and (4) can not meet the acid consumption in reaction (3), thus lead to the increase of pH in the solution. In Fig. 4, the other surface area except the specks of jarosite is covered with a layer containing a great deal of sulfur (Fig. 6), which may be the remains of adhered bacteria.

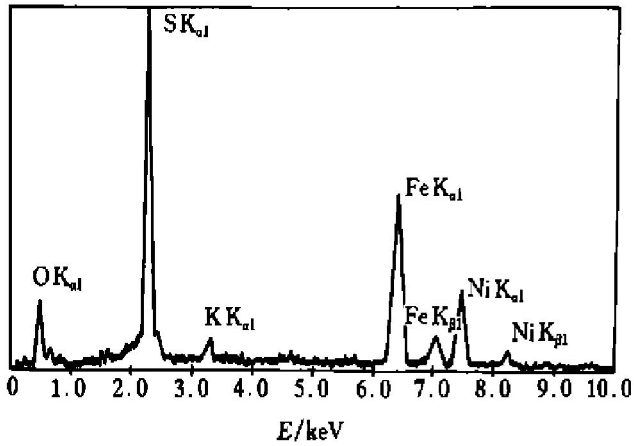

Fig. 6 EDS pattern of surface of mineral after bioleaching for 6 d

Though sulfur leads to the pH increasement in the solution, it is the more important energy resource than Fe^{2+} to the free bacteria, because there is more energy released when sulfur is oxidized[12]. In fact the number density of bacteria was 10^9/mL in the mineral pulp. But in the medium that Fe^{2+} acted as energy resource, the number was 10^7/mL at best.

4 CONCLUSION

In the bioleaching of pentlandite with *Thiobacillus ferrooxidans*, the chemical action of Fe^{3+} has a little contribution to the mineral dissolution. In the bioleaching, a lot of Fe^{3+} in leachates are deposited as jarosite while H^+, which is helpful to the bioleaching, is released. Sulfide in the mineral is oxidized by bacteria and produces elemental sulfur, which becomes the major energy resource of free bacteria in the solution. Because more H^+ are consumed in this process than released when Fe^{3+} are deposited, the pH value in the solution rises at the first phase of the bioleaching.

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