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Bioleaching of marmatite in high concentration of iron①

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[Abstract] Bioleaching of marmatite with a culture of *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans* in high concentration of iron was studied, the results show that the zinc leaching rate of the mixed culture is faster than that of the sole *Thiobacillus ferrooxidans*, the increasing iron concentration in leaching solution enhances the zinc leaching rate. The SEM analysis indicates that the chemical leaching residues is covered with porous solid layer of elemental sulfur, while elemental sulfur is not found in the bacterial leaching residues. The primary role of bacteria in bioleaching of sphalerite is to oxidize the chemical leaching products of ferrous ion and elemental sulfur, thus the indirect mechanism prevails in the bioleaching of marmatite.

[Key words] bioleaching; marmatite; bacteria
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1 INTRODUCTION

Presently more than 80% zinc metal in the world was produced by hydrometallurgical process. The conventional zinc hydrometallurgical process includes roast, leach, purification, electrowinning and casting etc, with near one hundred years development, the process has been achieved automatization and macro-scale equipments, and the general recovery ratio of metals is elevated to a high level. However, the zinc hydrometallurgical process has defects of long flowsheet and complicated procedure; the sulfur dioxide and other hazardous substance such as arsenide and antimonide released from roast have serious pollution on environment. To simplify the flowsheet and reduce pollution, direct leaching of sphalerite has been widely researched.

In 1981, the pressure oxidative leaching of sphalerite concentrate was firstly used in Trail, Canada. The pressure leaching canceled the roast process, and the leaching products were zinc sulfate and elemental sulfur, without emitted fume. However, it was not widely used because of its high demand on equipment and its economical viability. Other studies on direct leaching of sphalerite such as simultaneous leaching of zinc sulfide and manganese dioxide, leaching of zinc sulfide in ferric media, leaching of zinc sulfide with strong sulfuric acid etc, have been carried out in recent years[1~3].

Another method of direct leaching of sphalerite is bioleaching, which is characterized by simple techniques, low cost and good selectivity; it shows more advantages on treating low-grade zinc sulfide ore and bulk concentrates[4, 5]. However, the zinc leaching rate of bioleaching is slow. Many works have been done to improve the bacterial leaching rate, such as electro-bioleaching and catalyzed bioleaching, which have been on pilot experiment[6, 7]. If bioleaching is carried out in high concentration of iron, the leaching rate will be improved by an indirect mechanism. The ferric ion is an effective oxidizing agent, and it can be regenerated through bio-oxidation of ferrous ion[8~10].

Here bioleaching of low-grade zinc sulfide ore and marmatite concentrate was studied, and the mechanism of bioleaching of sphalerite at high concentrate of iron was discussed.

2 MATERIALS AND METHODS

2.1 Characterization of ore

The chemical compositions of the ore containing marmatite and marmatite concentrate are given in Table 1 and Table 2, respectively. The mineralogical analysis shows that the major metal sulfides in the ore are marmatite, pyrrhotite and pyrite, the gangues are dolomite, calcite and quartz. The major metal sulfide in the concentrate is marmatite, besides there are portion of pyrrhotite and pyrite. The ore samples were ground to less than 0.074 mm. The marmatite concentrate was washed with a 0.5 mol/L solution of Na_2S to removed flotation agents.

Table 1 Chemical components of ore(%)

Zn	Pb	Cu	Fe	Ca	S	SiO_2	Ag
2.24	0.20	0.067	11.50	4.23	9.84	55.06	16.82*

* —g/t

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Table 2 Chemical components of marmatite concentrate(%)

Zn	Pb	Fe	Cu	S	Ag
45	0.16	13.56	0.54	31.50	44.49*

* —g/t

2.2 Bioleaching

Two pure strains of *Thiobacillus ferrooxidans* (Tf1, Tf2) and two corresponding mixed cultures of *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans* (Mix1, Mix2) were used in the bioleaching experiments.

Bioleaching of marmatite concentrate were carried out in shake flasks containing ore sample and iron-free 9K nutrient medium. Before inoculating bacterial medium, the pH was adjusted to a level of 2.0 with 5 mol/L sulfuric acid. In bioleaching of marmatite concentrate, the amount of ferric sulfate($Fe_2(SO_4)_3 \cdot xH_2O$) was 65 g/L, and the original number of bacteria was kept nearly 10^7 cell/ml. In the sterile control, 2 ml 4% thymol in methyl alcohol solution was added instead of the bacterial inoculum. The flasks were incubated at 30 ℃ in an incubator shaker(170 r/min).

Periodically, if pH > 2.0, it was adjusted to 2.0 with sulfuric acid, and the water lost by evaporation was compensated by the addition of deionized water; 50 ml supernatant liquid sample was drawn from the flasks to determine the concentration of zinc and iron, and 50 ml samples were replaced with an equal volume of iron-free 9 K nutrient medium.

2.3 Analytical methods

The total concentration of zinc and iron was determined by Atomic Absorption Spectrophotometry. The ferrous ion content was determined by titration with potassium dichromate (0.002 mol/L $K_2Cr_2O_7$), with barium diphenylamine sulphonate as indicator (0.2% water solution), and the content of ferric ion was calculated by difference.

3 RESULTS AND DISCUSSION

3.1 Effect of bacterial strains on bioleaching

The effect of bacteria on bioleaching is shown in Fig. 1. From Fig. 1 it can be seen that the zinc extraction rate of mixed cultures was higher than that of pure *T. ferrooxidans*. In the eighth day the zinc extraction of the mixed culture was about 100%, and that of *T. ferrooxidans* was about 80%. The curves did not pass through the origin because about 17% zinc released during pH adjustment, of sterile control the zinc extraction was kept at this value.

There are two slopes for the curves of bioleaching, of which the critical point is on the fifth day. Before

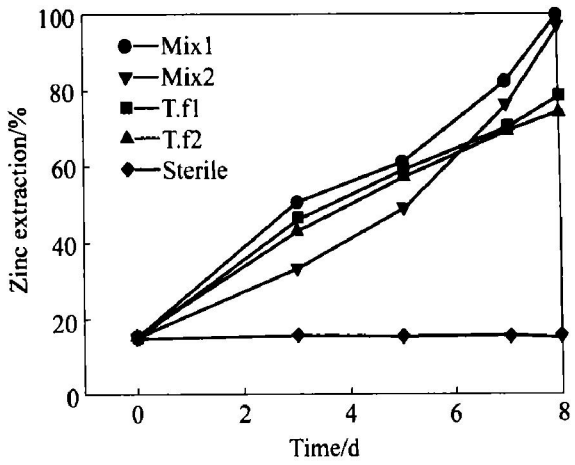

Fig. 1 Effect of bacteria on bioleaching of zinc sulfide ore

the fifth day, there were similar high leaching rates for Mix1, Tf1 and Tf2. the rise in zinc leaching could attribute to the chemical leaching by ferric ion, and the oxidation of ferrous ion to ferric ion by *T. ferrooxidans*. It was observed previously that in Mix2 medium *T. ferrooxidans* was less in numbers than *T. thiooxidans*, so its oxidizing rate of ferrous ion lagged behind the other bacterial mediums at the beginning, thus before the sixth day its leaching rate was the slowest.

After the fifth day, there were higher rise in zinc leaching of the mixed culture, while the rise in zinc leaching of *T. ferrooxidans* were small. Obviously, the second large increase of zinc leaching rate of the mixed culture was attributed to the cooperative action of the two bacterial stains. Elemental sulfur was the solid product of chemical leaching. With its accumulation on the surface of mineral particle, the solid sulfur began to baffle the bioleaching. In the mixed culture, the sulfur oxidizing capacity of *T. thiooxidans* was greater, so the sulfur product could be dissolved in time and the bioleaching was not baffled. However, the sulfur oxidizing capacity of *T. ferrooxidans* is weak, and the solid sulfur could not be eliminated quickly enough, then the transfer of reactant inward and reaction products outward from the reaction interface was interfered, so the leaching rate slowed down.

The reactions during bioleaching of marmatite concentrate can be illustrated as:

$$ZnS + 2O_2 \xrightarrow{Bact.} Zn^{2+} + SO_4^{2-} \quad (1)$$

$$2FeS + 3O_2 + 2H_2O \xrightarrow{Bact.} 2Fe^{2+} + 2SO_4^{2-} + 4H^+ + 4e \quad (2)$$

$$2FeS_2 + 7O_2 + 2H_2O \xrightarrow{Bact.} 2Fe^{2+} + 4SO_4^{2-} + 4H^+ \quad (3)$$

$$2S^0 + 3O_2 + 2H_2O \xrightarrow{Bact.} 4H^+ + 2SO_4^{2-} \quad (4)$$

$$4Fe^{2+} + O_2 + 4H^+ \xrightarrow{Bact.} 4Fe^{3+} + 2H_2O \quad (5)$$

$$ZnS + 2Fe^{3+} \longrightarrow Zn^{2+} + 2Fe^{2+} + S^0 \quad (6)$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \longrightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (7)$$

In zinc sulfide ore, pyrrhotite can be dissolved by acid or bacterial behavior, of which the reactions can be illustrated as

$$Fe_{1-x}S + 2H^+ \longrightarrow (1-3x)Fe^{2+} + 2xFe^{3+} + H_2S \quad (7)$$

$$Fe_{1-x}S + O_2 + 4H^+ \xrightarrow{Bact.} (2-6x)Fe^{2+} + 4xFe^{3+} + 2S + 2H_2O \quad (8)$$

With the dissolution of pyrite and pyrrhotite, iron was released to the leach solution. From Fig. 2 it can be seen that the increase of iron concentration corresponded to the increase of zinc leaching in Fig. 1. The increase of iron concentration accelerated the zinc leaching rate. In the mixed culture, the iron concentration reached 5 g/L approximately after the eighth day, while that of *T. ferrooxidans* was fixed at the level of about 2.8 g/L, and in the sterile sample the iron concentration was 1.7 g/L. The pH of bacterial leaching solutions, especially for the mixed culture, decreased with the increase of leaching time. The final pH of the leach solution of Mix1 and Mix2 were 1.51 and 1.80 respectively. The decreased pH was due to two reasons, firstly, the elemental sulfur was oxidized to sulfuric acid by bacteria, secondly, the ferric ion precipitated as the form of jarosite according to the equation as:

$$3Fe^{3+} + K^+ + 2HSO_4^- + 6H_2O \longrightarrow KFe_3(SO_4)_2(OH)_6 + 8H^+ \quad (9)$$

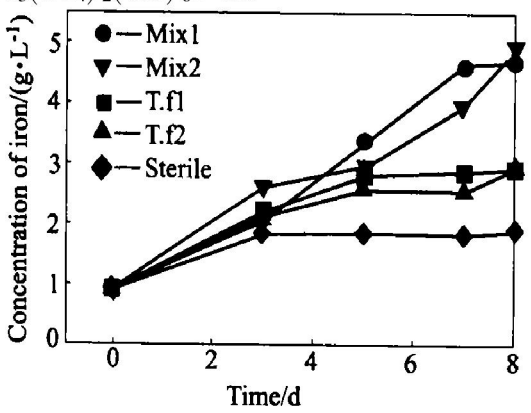

Fig. 2 Variation of iron concentration in bioleaching of zinc sulfide ore

3.2 Simultaneously leaching of marmatite concentrate by Fe^{3+} and bacteria

The bioleaching of marmatite concentrate at high original concentration of Fe^{3+} (about 15 g/L) is shown in Fig. 3, where a sterile control of chemical leaching by Fe^{3+} is presented as contrast. The inoculum was a mixed culture of the two strains of bacteria.

In the presence of bacteria, the zinc leaching rate was almost twice that of absence of bacteria. In Fig. 4 the variation of ferric ion and ferrous ion during the

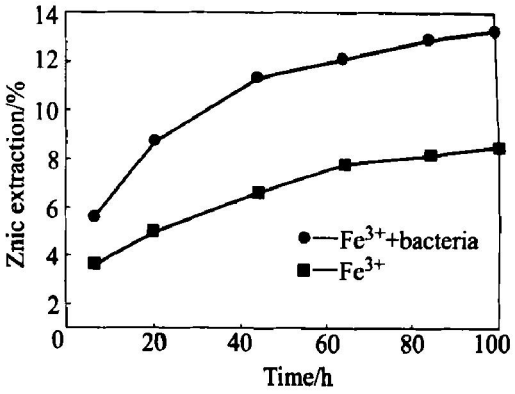

Fig. 3 Leaching of marmatite concentrate by Fe^{3+} in presence and absence of bacteria

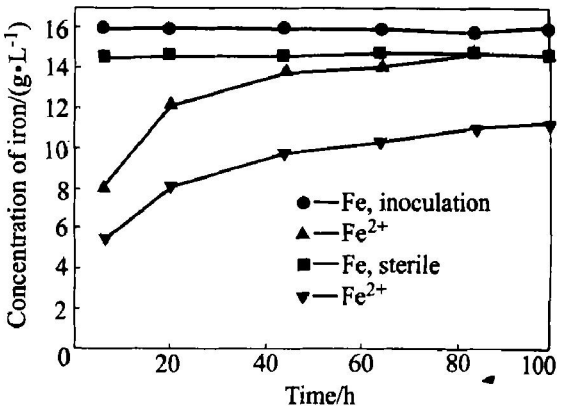

Fig. 4 Variation of iron during ferric leaching of marmatite in presence and absence of bacteria

leaching of marmatite concentrate is shown. In the presence or absence of bacteria, the total iron concentration are about 16 and 14.5 g/L respectively. During bioleaching, the iron was more adapt to release, following the increase of zinc leaching. The ferrous ion concentration of inoculation and sterile control was 14.6 and 11.1 g/L respectively in 100 h, which indicated that there was more ferric ion involved in the chemical leaching of marmatite concentrate in the presence of bacteria.

The leaching residues of marmatite concentrate were examined by SEM. The typical results are shown in Fig. 5.

It can be seen from Fig. 5 that the chemical leaching particle without bacteria was covered with solid elemental sulfur, while elemental sulfur was not found in the bacterial leaching residue. There were corrosion cavities on the surface of the mineral surface of bioleaching.

The sulfur was the product of chemical leaching of marmatite by ferric ion, though it attached on the mineral particle surface as a porous layer, it could still baffle zinc leaching without enough agitation, such as the shake flasks. In the sterile chemical leaching, the transfer ferric ion into the reaction interface was baffled by

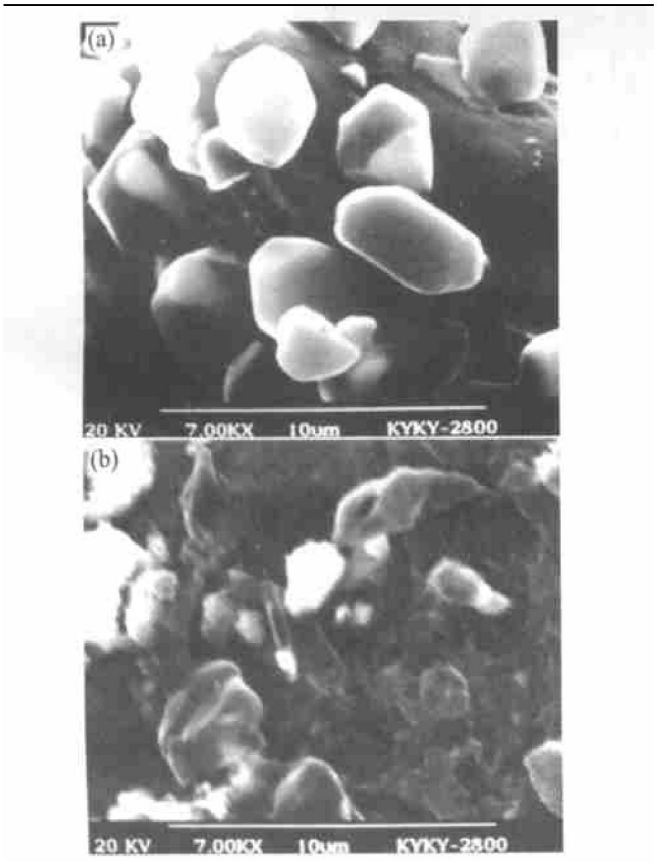

Fig. 5 SEM photographs of ferric leaching residues in presence and absence of bacteria
(a) —Sterile; (b) —Inoculation

the elemental sulfur in some extent, so were the reaction products of ferrous ion and zinc ion. Therefore, the zinc leaching was limited and the concentration of ferrous ion in chemical leach solution was lower.

In the presence of bacteria, the elemental sulfur was oxidized to sulfuric acid and the ferric ion could reach the reaction interface freely, bacteria may also have a direct attack on mineral. With the simultaneously leaching of ferric ion and bacteria, the zinc leaching rate was improved.

4 CONCLUSIONS

1) The leaching capacity of the mixed culture of *T. ferrooxidans* and *T. thiooxidans* on marmatite was better than that of the sole *T. ferrooxidans*. The cooperative action of the two bacterial strains enhanced the leaching rate of zinc.

2) In bioleaching of zinc sulfide ore, the high concentration of iron released from dissolved pyrrhotite and pyrite accelerate the leaching rate of zinc.

3) There were porous layer of solid elemental sulfur on the mineral surface in chemical leaching, which baffled the transfer of reactant and reaction products, and decreased the leaching rate.

4) The primarily role of the bacterial in bioleaching of marmatite was to oxidize the chemical leaching products of ferrous ion and elemental sulfur, thus the indirect mechanism prevailed in the bioleaching of marmatite.

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