

Dynamic corrosion of copper-nickel sulfide by *Acidithiobacillus ferrooxidans*

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Abstract: The dynamic corrosion process of bio-oxidation of copper-nickel sulfide from Karatungk in northern Xinjiang Province of China was studied. The polished wafer of the copper-nickel sulphide was used to carry on a series of oxidation corrosion experiment by *Acidithiobacillus ferrooxidans*. The changes of superficial corrosion appearance and the mineral dynamic corrosion process were discovered by microscope observation. Then, the galvanic cell model was established, and the bio-oxidation activation order of typical copper-nickel sulphide minerals was ascertained as pyrrhotite > pentlandite > chalcocopyrite.

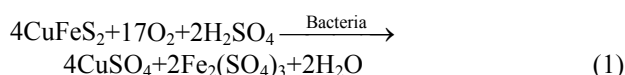
Key words: copper-nickel sulphide; bio-oxidation; dynamic corrosion; galvanic effect

1 Introduction

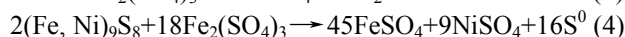
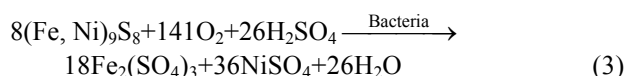
Bio-oxidation is an advanced technique of mineral processing. This method has become the research interest of hydrometallurgy in recent years[1–5]. Previous researches of bio-oxidation were mainly focused on breeding of dominant bacteria[6–8], influence of bio-oxidation, optimization and control of leaching process[9–10] and bio-metallurgical processes of different mineral by bacteria. In fact, the bio-oxidation system involves interface problems such as bacterial/mineral and mineral/mineral[11], so researching the surface morphology changes can help us to reveal oxidation mechanism of bio-oxidation. Chalcocopyrite is the most common copper sulfide in the copper-nickel ores. The oxidation of the secondary copper sulfide was easy but that of the primary copper sulfide was difficult, so secondary copper sulfide (chalcocite, covellite, etc.) was applied in bio-oxidation at present, while the primary copper sulfide (chalcocopyrite) was still treated with pyrometallurgical method[12]. Resource of chalcocopyrite is widely distributed in nature, but it is difficult to treat with bio-oxidation. The purpose of this work is to show the characteristics of dynamic corrosion of the typical copper-nickel sulfide mineral pairs from the microscopic point of view.

The mechanisms in bio-oxidation of chalcocopyrite and the main associated minerals, pentlandite and pyrrhotite, were obtained. Direct and indirect bio-oxidation reactions in bacterial oxidation process of chalcocopyrite, pentlandite and pyrrhotite take place as follows[13–14]:

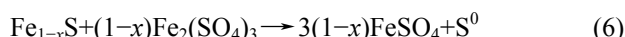
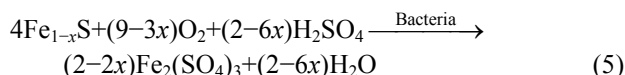
Chalcocopyrite:



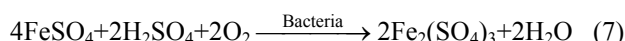
Pentlandite:



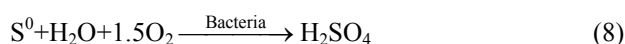
Pyrrhotite:



Oxidation of Fe^{2+} :



Oxidation of S^0 :



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2 Experimental

2.1 Mineral samples

The mineral samples for this research were collected from Karatungk copper-nickel sulfide mineral belt in northern Xinjiang of China. Chalcopyrite (molecular formula CuFeS_2) and pentlandite (molecular formula $(\text{Fe}, \text{Ni})_9\text{S}_8$) were the most important minerals in the copper-nickel sulfide. At the same time, they often co-exist with pyrrhotite (molecular formula Fe_{1-x}S , generally $x=0\pm0.223$, range of corresponding composition $\text{FeS}-\text{Fe}_{11}\text{S}_{12}$)[15].

2.1.1 Mineral testing methods

The mineral species was identified using Leica DMRXP polarized optical microscope by process mineralogy method. EPMA-1600 electron probe micro-analysis (EPMA, SHIMADZU, Institute of Metal Research, Chinese Academy of Sciences) was applied to studying the mineral compositions. The conditions of full spectrum scanning qualitative analysis were as follows: accelerating voltage 15 kV, beam current 10 nA, count time 10 s, beam diameter 20 μm , and analyzer crystals RAP, PBST, PET and LiF. The conditions of spectrum quantitative analysis were as follows: accelerating voltage 15 kV, beam current 10 nA, count time 10 s and beam diameter 20 μm , analyzer crystal of PET for S with FeS_2 as the standard sample, and analyzer crystal of LiF for Co, Fe, Ni with pure Cu as the standard sample, respectively.

2.1.2 Mineral species and compositions

Identification with process mineralogy method shows that the mineral mainly contains metal sulfides of pentlandite (Pe), pyrrhotite (Pyr), chalcopyrite (Cp) and gangue minerals of chrysolite, pyroxene, biotite and plagioclase.

Regions of chalcopyrite, pentlandite and pyrrhotite identified by process mineralogy method were analyzed by electron probe micro-analysis. Fig.1 shows the result of qualitative analysis. There were elements Fe, S, Ni and Co in the region of pentlandite, elements Fe, S, and Cu in the region of chalcopyrite and elements Fe, S, and Ni in the region of pyrrhotite. Table 1 lists the result of quantitative analysis.

2.2 Bacterial sample

Acidithiobacillus ferrooxidans(A.f) were used in experiment. Culture medium was 9K liquid medium ($(\text{NH}_4)_2\text{SO}_4$ 3 g/L, KCl 0.1 g/L, K_2HPO_4 0.5 g/L, $\text{MgSO}_4\cdot 7\text{H}_2\text{O}$ 0.5 g/L, $\text{Ca}(\text{NO}_3)_2$ 0.01 g/L, $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ 44.2 g/L), adjusted to pH 1.80 with 2 mol/L sulfuric acid. Before experiment, activated culture was conducted to bacteria for three times, and the concentration was above 10^8 cell/mL.

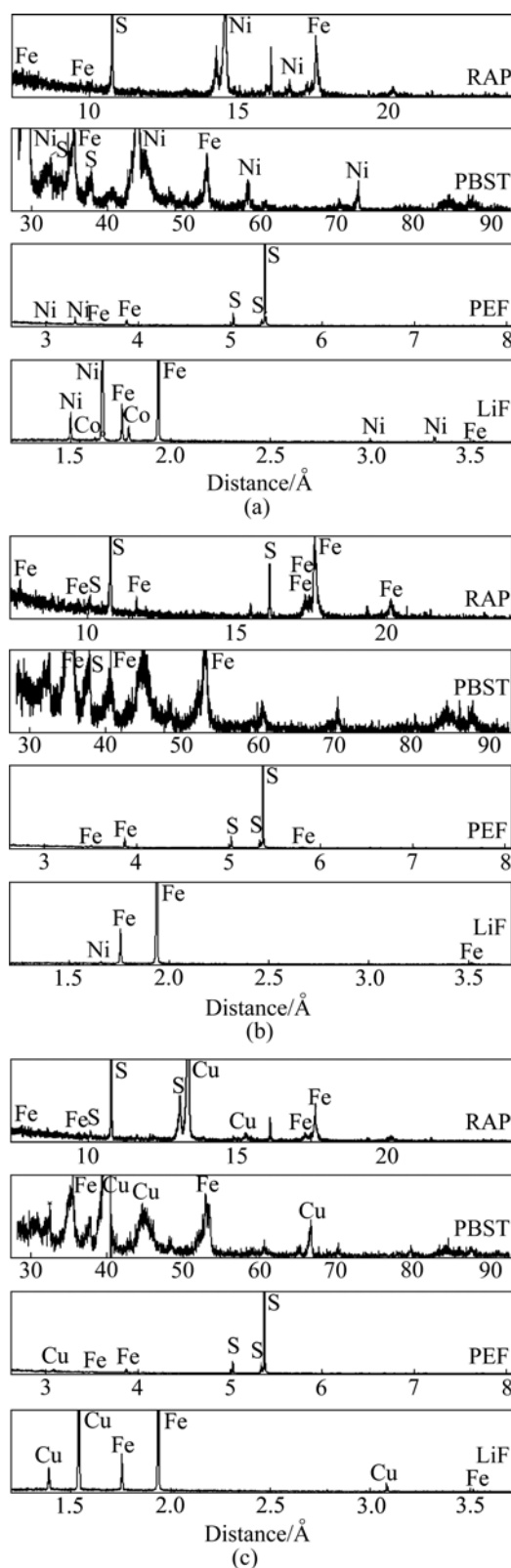


Fig.1 Results of qualitative analysis by EPMA: (a) Pentlandite; (b) Pyrrhotite; (c) Chalcopyrite

This experiment was carried out in a 3 L tank with a mechanic agitator at 950 r/min. When bacteria grow into stationary phase, minerals were added into tank with

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