[Article ID] 1003- 6326(2002)01- 0142- 05

Bioleaching of refractory gold ore (Ⅱ)①

——Mechanism on bioleaching of arsenopyrite by *Thiobacillus ferrooxidans*

MIN Xiao-bo(闵小波)[1], CHAI Li-yuan(柴立元)[1], CHEN Wei-liang(陈为亮)[1], ZHANG Chuan-fu(张传福)[1], ZHONG Hai-yun(钟海云)[1], KUANG Zhong(邝 中)[2]
(1. Department of Metallurgical Science & Engineering, Central South University, Changsha 410083, China;
2. Guangxi Guanghe Industry Co. Lt. Hechi, China, 547000)

[Abstract] The variation of main parameters was examined in bioleaching arsenopyrite, such as arsenic concentration, solution pH value, potential and biomass. Solution pH value decreased slightly and few *T ferrooxidans* adhered to the surface of arsenopyrite. The surface properties of arsenopyrite and leached products were determined by using modern measurement techniques including SEM, EDS and XRD. The corrosion characteristic of arsenopyrite surface is of uniformity, and arsenic in arsenopyrite was preferential to be dissolved. Element sulfur, jarosite and scorodite are the primary products in bioleaching arsenopyrite. It can be drown from above that arsenopyrite is oxidized mainly through the indirect role of *T ferrooxidans*. A band model for bioleaching arsenopyrite was built, by which illustrated the bioleaching process theoretically. The model shows that the holes, which are provided by ferric ion, inject into the valence band of arsenopyrite to result in the dissolution of arsenopyrite.

[Key words] mechanism; arsenopyrite bioleaching; *Thiobacillus ferrooxidans*
[CLC number] TF 18 **[Document code]** A

1 INTRODUCTION

Bioleaching processes have been used extensively to recover base metals (mainly copper) and uranium from low-grade ores and more recently for the extraction of gold in pilot plants. Recovery of gold from refractory ores requires the ore to undergo a pretreatment to liberate the gold from the host mineral in which gold are finely disseminated such as arsenopyrite (FeAsS) and pyrite (FeS_2)[1,2]. In order to optimize the bioleaching pretreatment process, it seems to be very important to understand the mechanism of biooxidation.

Generally, two mechanisms are known to be responsible for the bioleaching of sulfide ores, namely, indirect and direct mechanisms (Eqns.(1) and (2) respectively)[3,4]. The indirect mechanism operates by the chemical action of acidic ferric sulfate produced by the bacterial metabolism. In this mechanism, adhesion of the bacteria to the mineral surfaces is not required. The direct mechanism, on the other hand, involves the enzymatic attack of the mineral by the bacteria, for which intimate contact and hence adhesion are required.

$$4FeAsS + 2Fe_2(SO_4)_3 + 6H_2O + 9O_2 \xrightarrow{\text{Chemical}} 4H_3AsO_4 + 8FeSO_4 + 2S^0 \quad (1)$$

$$2FeAsS + 2H_2O + 7O_2 + H_2SO_4 \xrightarrow{\text{Bacteria}} 2H_3AsO_4 + Fe_2(SO_4)_3 \quad (2)$$

Despite extensive studies on the growth[5~7] and applications[8] of *Thiobacillus ferrooxidans* have been carried out by many researchers, it is not well understood that which mechanism (direct or indirect) is predominant in arsenopyrite and pyrite bioleaching. Previous investigation[9] has indicated that the dissolution of pyrite in presence of *Thiobacillus ferrooxidans* is the result of direct oxidation mechanism. This study is aimed at clarifying the mechanism of arsenopyrite biooxidation through investigation of the behavior of arsenopyrite bioleaching, including physicochemical composition of leachate, the evolution of corrosion patterns, and the nature of surface-oxidized chemical species.

2 EXPERIMENTAL

The arsenopyrite used for this experiment was prepared from large pure natural crystals originating from Chinese Geology Museum. Iron, sulfur and arsenic contents were, respectively, of 30.03%, 17.05% and 46.16% (mass fraction). After washing with a 6 mol/L HCl solution, the arsenopyrite crystals were carefully dry-ground in a tungsten mill and wet-sieved in order to obtain a particle fraction of 45~ 74 μm.

The results of arsenic concentration in solution versus time in arsenopyrite bioleaching are shown in Fig. 1. Initially, arsenic solubilization was obvious,

① [Received date] 2001- 04- 25; [Accepted date] 2001- 06- 20

which was due to the effect of ferric iron in solution on the arsenopyrite. And then arsenic contents tended to approach a plateau, since the bacterial growth was in the lag phase, and bacteria regenerated ferric iron slowly. With the strengthening of bacterial activity, the solubilization of arsenic became significant. The third step was dominated by the differences between the soluble arsenic concentration and the total arsenic concentration, which shows that arsenic precipitation produced in reactor. Because of this, the oxidation of arsenopyrite is inhibited.

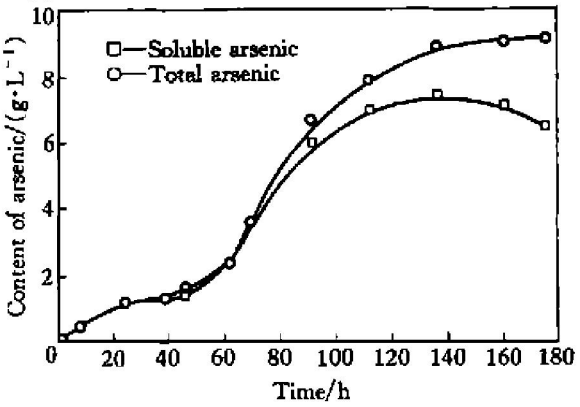

Fig. 1 Evolution of arsenic ion contents in arsenopyrite bioleaching

Fig. 2 is a plot of the ferrous iron contents in solution vs time in arsenopyrite bioleaching. For a start, ferrous iron solubilization resulted from the chemical solubilization of arsenopyrite in nutrient medium (about 0.8 g/L). With the beginning of the exponential growth phase, bacteria oxidized the ferrous ions, and the ferrous iron concentration tended to decrease. After 140 h, the ferrous iron concentration increased slightly.

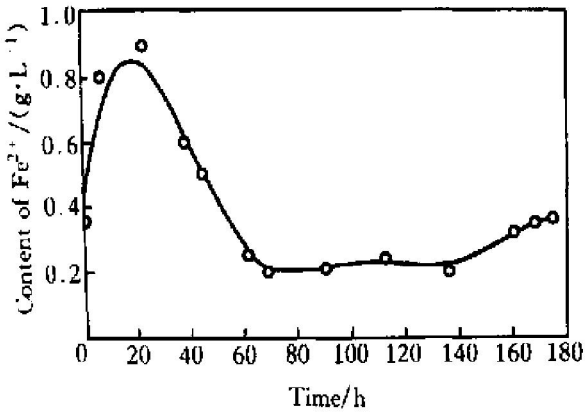

Fig. 2 Ferrous iron concentration in solution vs time in arsenopyrite bioleaching

2.1 Evolution of pH value

The evolution of pH in arsenopyrite bioleaching is given in Fig. 3. During the whole bioleaching process, solution pH value changed slightly, from initial value 2.06 to final value 2.01. Little evolution of solution pH had something to do with the oxidation of ferrous ion to ferric ion and the formation of the precipitation.

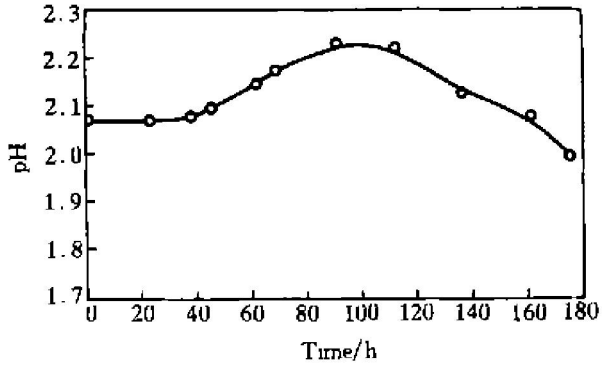

Fig. 3 Evolution of pH in arsenopyrite bioleaching

2.2 Evolution of solution potential

The Evolution of solution potential is presented in Fig. 4. From 0 to 50 h, the solution potential decreased from 490 mV to 435 mV, which resulted from the generation of ferrous ion in solution. After 50 h, it increased and reached a stable value 550 mV.

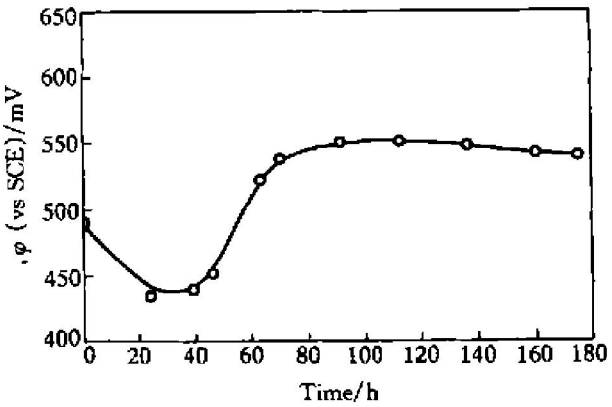

Fig. 4 Evolution of solution potential in arsenopyrite bioleaching

2.3 Evolution of bacterial population

Fig. 5 shows bacterial population growth in ar-

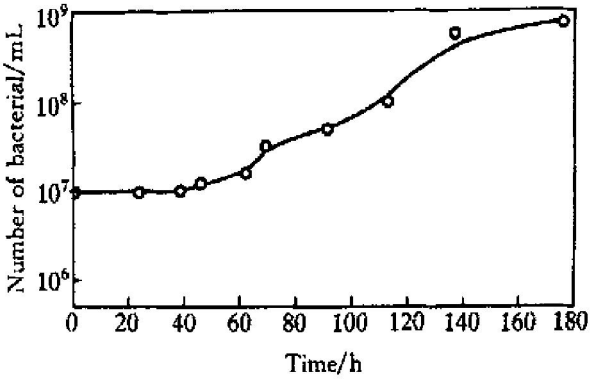

Fig. 5 Bacterial population growth in arsenopyrite bioleaching

senopyrite bioleaching. The number of bacteria in the liquid medium didn't decrease. This result shows that few inoculated bacteria adhered to the surface of arsenopyrite. The number of bacteria in the nutrient medium increased with the exponential growth phase and reached a stable value 8×10^8/mL at the end of bioleaching.

2.4 SEM, EDS and XRD analysis of arsenopyrite

SEM photographs which show evolution of the surface of the arsenopyrite in the bioleaching process, are shown in Fig. 6. A clean surface and no corrosion pattern are detectable by SEM examination at high magnification initially (Fig. 6(a)). At 20 h, the first patterns of corrosion are evident from the appearance of some along longitudinal cracks (Fig. 6(b)). At 80 h, deep pores, which pass through the arsenopyrite layer, are evident and the corrosion feature can be called uniform corrosion. At the end of bioleaching, the surface of the arsenopyrite is completely covered by a coarse pellicular phase (Fig. 6(d)).

The results of energy dispersive spectra analysis of arsenopyrite surface in bioleaching were given in Fig. 7 and Table 1. According to the variation of stoichiometric composition of arsenopyrite, it can be determined that the preferential oxidation composition in arsenopyrite is arsenic. Fig. 8 shows the X-ray diffractogram of arsenopyrite powders after bioleaching. Bacterial leaching led to the concurrent precipitation of two minerals: scorodite ($FeAsO_4$), jarosite [$KFe_3(SO_4)_2(OH)_6$] and element sulfur could be detectable.

Table 1 EDS analysis results of arsenopyrite surface during bioleaching

No.	Composition	Mass fraction/%	Mole fraction/%	Stoichiometric composition
a	As	50.50	37.48	$FeAs_{1.19}S_{0.99}$
	Fe	31.60	31.46	
	S	17.91	31.06	
b	As	40.44	28.55	$FeAs_{0.79}S_{0.98}$
	Fe	38.16	36.07	
	S	21.40	35.38	
c	As	44.32	31.65	$FeAs_{0.95}S_{1.05}$
	Fe	34.75	33.26	
	S	20.93	35.09	

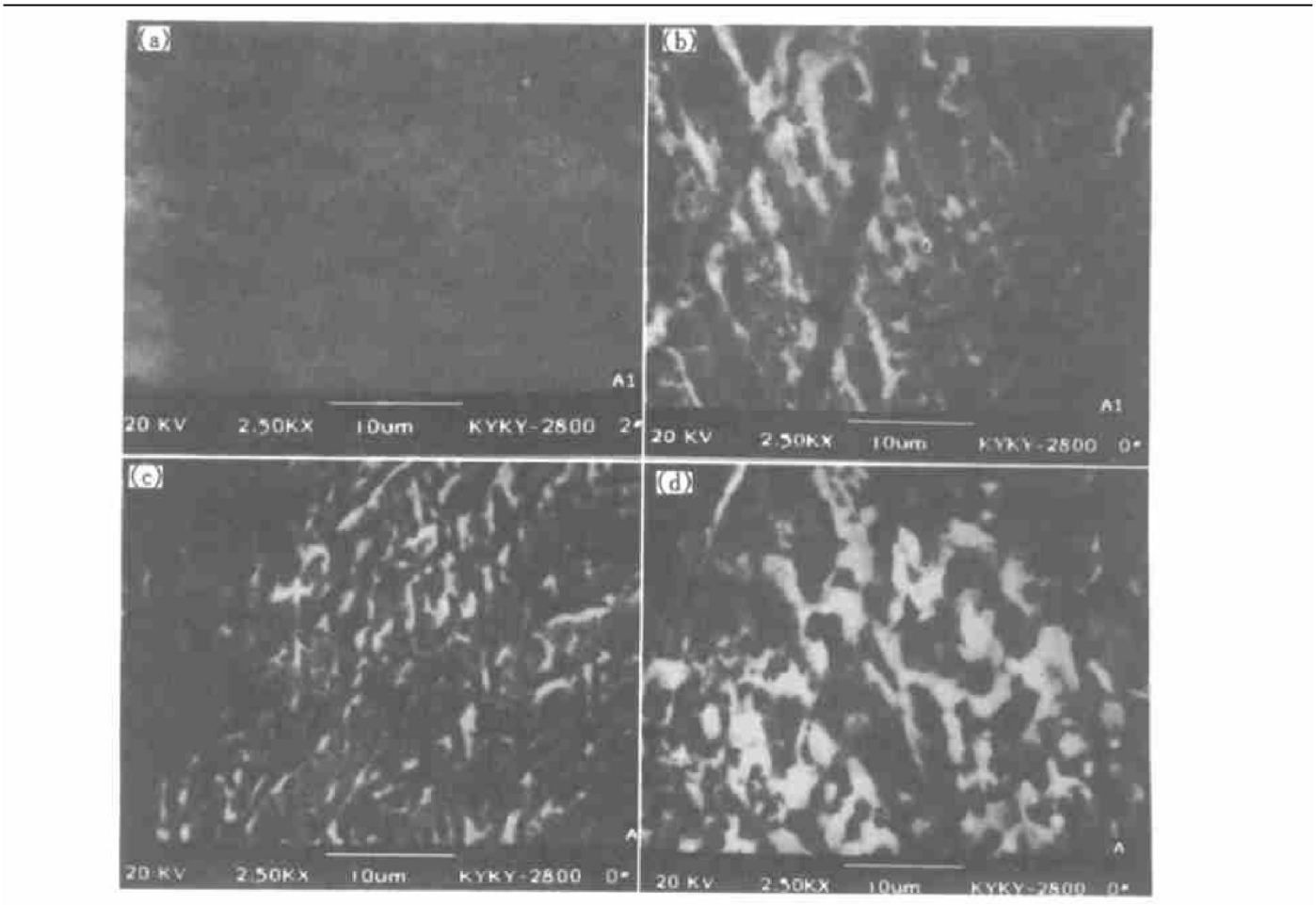

Fig. 6 SEM photographs of surface of arsenopyrite in bioleaching process
(a) —Initial arsenopyrite surface; (b) —Massive arsenopyrite surface attacked for 20 h; (c) —Massive arsenopyrite surface attacked for 80 h; (d) —Massive arsenopyrite surface attacked for 160 h

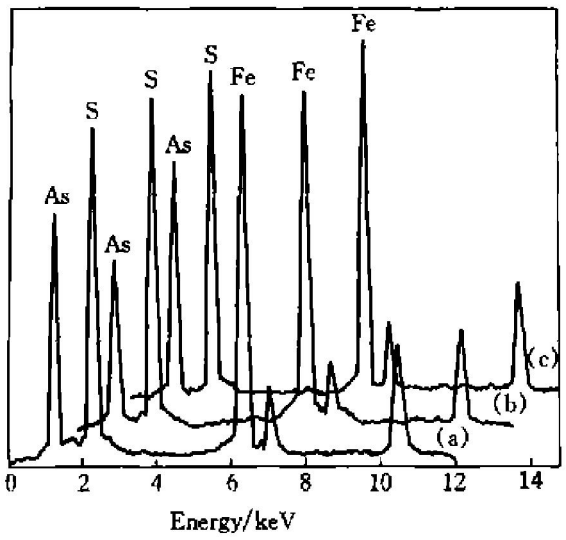

Fig. 7 EDS analysis of arsenopyrite surface during bioleaching
(a) —Initial arsenopyrite surface;
(b) —Massive arsenopyrite surface attacked for 20 h;
(c) —Massive arsenopyrite surface attacked for 80 h

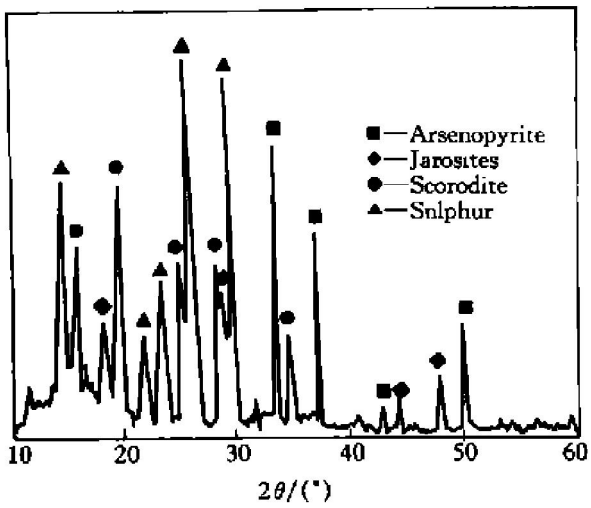

Fig. 8 X-ray spectrum of arsenopyrite powder after bioleaching

3 MECHANISM OF ARSENOPYRITE BIOLEACHING

The characteristics of arsenopyrite bioleaching are listed in Table 2. On the base of these bioleaching characteristics, the mechanism of arsenopyrite bioleaching could be ascertained. As noted above, the mechanisms of bioleaching could be divided into two kinds: direct and indirect mechanism. Which mechanism is the most important in arsenopyrite bioleaching? Previous article[9] illustrated the direct oxidation mechanism of pyrite bioleaching in detail. Assuming the direct oxidation was the most important in arsenopyrite bioleaching. Then at first, most bacteria must adhere on arsenopyrite surface initially, but experimental result showed that only a few bacteria did; second, the direct oxidation of arsenopyrite by bacteria didn't produce element sulfur, because bacteria must be sure to oxidize the element sulfur to sulfate acid further; third, it is impossible that arsenic in arsenopyrite was oxidized preferentially under direct bacterial oxidation role, since arsenic was toxic to bacterial growth; finally, SEM observation showed that the corrosion pattern of bioleaching arsenopyrite was uniform, which was related to the chemical indirect oxidation role of ferric iron. Through the discussion above, it can be concluded that the indirect oxidation mechanism is the most important in bioleaching arsenopyrite. The main role of bacteria is regeneration of ferric ion in order to oxidize the arsenopyrite.

Detail calculating method to build the band model was reported in previous article[9]. Table 3 lists the basic parameters for arsenopyrite band model. According to these parameters and equation, the band model can be set up (Fig. 9).

Indirect mechanism is the most important in arsenopyrite bioleaching. In arsenopyrite/solution band model (Fig. 9), since the energy level of Fe^{3+}/Fe^{2+}

Table 2 Characteristics of arsenopyrite and pyrite[9] bioleaching

Characteristics	Arsenopyrite	Pyrite
Leaching rate	Arsenic 0.11/(g·L^{-1}·h^{-1})	Iron 0.029/(g·L^{-1}·h^{-1})
Evolution of pH	Change slightly, from 2.06 to 2.01	Decreasing markedly, from 2.0 to 1.35
Evolution of potential	Increasing to stable value 550 mV	Increasing to a stable value 600 mV
Bacteria growth	Few bacteria adhering on arsenopyrite surface, final biomass 8×10^8/mL	Bacteria adhering on pyrite surface, final biomass 10^9/mL
Corrosion feature	Uniform corrosion	Selective corrosion
Preferential oxidation	Arsenic in arsenopyrite	Sulfur in pyrite
Element sulfur	Element sulfur produced	No element sulfur produced
Precipitation	Scorodite and jarosite	Jarosite

Table 3 Basic parameters for arsenopyrite band model (eV)

Element	X_p	W	Material	X	χ	E_g [10, 11]	E_c	E_v
S	2.58	5.74	FeS2	5.29	4.84	0.9	- 0.34	- 1.24
Fe	1.83	4.39	FeAsS	5.05	4.85	0.4	- 0.35	- 0.75
As	2.18	5.02						

Notes: X_p—Pauling electronegativity, W—Work function, X—Semiconductor electronegativity, χ—Electron affinity, E_g—Band gap, E_c—Energy of the bottom of conduction band, E_v—Energy of the top of valence band.

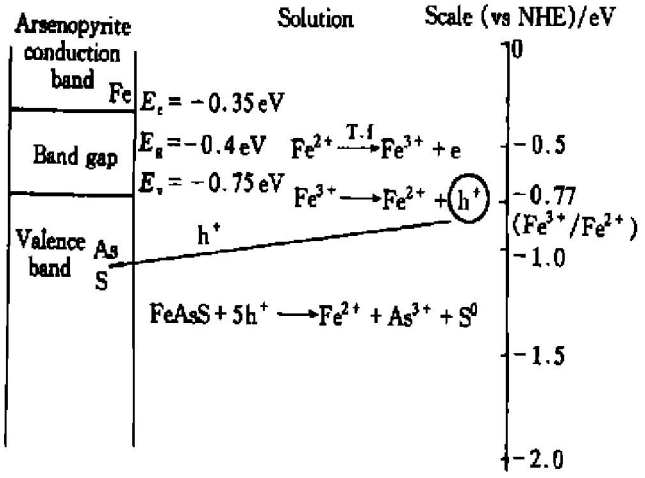

Fig. 9 Band model of arsenopyrite bioleaching in indirect oxidation mechanism

couple is near to the top of valence band of arsenopyrite, hole exchange with the valence band was the preferred pathway. As a result, arsenopyrite lost its electron and was oxidized by ferric ion.

4 CONCLUSION

With respect to arsenopyrite bioleaching process, Element sulfur is produced and solution pH value changed slightly. Few *T ferrooxidans* adhere to the surface of arsenopyrite. The indirect oxidation makes the preferential oxidation of the arsenic in arsenopyrite, and the main precipitates are scorodite and jarosite. The corrosion pattern shows the feature of uniform corrosion, after indirect oxidation by ferric iron. The model shows that the holes, which are provided by ferric ion, inject into the valence band of arsenopyrite to result in the dissolution of arsenopyrite. Based on these results, it can be found that arsenopyrite is oxidized mainly through the indirect role of *T ferrooxidans*. i. e. the indirect oxidation mechanism is the most important in bioleaching pyrite.

[REFERENCES]

[1] Brieriey L. Bacterial oxidation [J]. Engineering and Mining Journal, 1995, 196(5): 42- 44.

[2] Fraser K S, Walton R H, Wells J A. Processing of refractory gold ores [J]. Mineral Engineering, 1991(4): 1029- 1041.

[3] Barrett J, Hughes M N. Mechanism of the bacterial oxidation of arsenopyrite-pyrite mixtures: the identification of plant control [J]. Minerals Engineering, 1993, 6(8-10): 969- 975.

[4] Karavako G I, Rossi G, Agate A D, et al. Biogeotechnology of Metals Manual [M]. Moscow, 1988. 13.

[5] Chai L Y, Wei W, Okido M. Studies on effect of Cu (Ⅱ) on growth of *Thiobacillus ferrooxidans* using series piezoelectric quartz crystal [J]. Minerals Engineering, 2000, 13(8- 9): 969- 972.

[6] MIN Xiao-bo, CHAI Li-yuan, ZHONG Hai-yun, et al. Kinetic parameters for growth of *T Ferrooxidans* [J]. The Chinese Journal of Nonferrous Metals, (in Chinese), 2000, 10(3): 443- 447.

[7] ZHANG Chuan-fu, MIN Xiao-bo, CHAI Li-yuan, et al. Influencing factors of lag phase in growth of *T Ferrooxidans* [J]. Journal of Central South University of Technology, (in Chinese), 1999, 30(5): 492- 496.

[8] van Aswegen P C. Developments and innovations in bacterial oxidation of refractory ores [J]. Minerals and Metallurgical Processing, 1991, 8(4): 188- 191.

[9] MIN Xiao-bo, CHAI Li-yuan, CHEN Wei-liang, et al. Study on bioleaching of refractory gold ore (Ⅰ)—Mechanism on bioleaching of pyrite by *Thiobacillus ferrooxidans* [J]. Transactions of Nonferrous Metals Society of China, 2001, 11(5):

[10] Crundwell F K. The influence of the electronic structure of solids on the anodic dissolution and leaching of semiconducting sulphide minerals [J]. Hydrometallurgy, 1988, 21: 155- 190.

[11] Tributsch H, Bennett J C. Semiconductor-electrochemical aspect of bacterial leaching (Ⅰ)—Oxidation of metal sulfides with large energy gap [J]. J Chem Tech Biotechnol, 1981, (31): 565- 577.

(Edited by LONG Huai-zhong)