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# Submicro-battery effect and selective bio-oxidation model of gold-bearing arsenopyrite by *Thiobacillus ferrooxidans*<sup>①</sup>

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**[Abstract]** Through the study by electronic probe it was found that many new cracks and holes appear on the surface of gold-bearing arsenopyrite crystal oxidized by *Thiobacillus ferrooxidans*, which are along with some directions. Then the selective bio-oxidation model of gold-bearing arsenopyrite was set up. The selective bio-oxidation resulting from the submicro-battery effect of gold-bearing arsenopyrite mineral pairs naturally forms in the gold-bearing arsenopyrite crystal. *Thiobacillus ferrooxidans* has priority to oxidize the place of gold-rich and oxidizes selected along with the crystal border, crystal face and crack. The bacteria oxidation process of gold-bearing arsenopyrite is divided into three stages: the first stage is the surface oxidation, the second stage is restraining oxidation and the third stage is the filament oxidation, bacteria oxidize along with cracks of arsenopyrite.

**[Key words]** selective bio-oxidation model; submicro-battery effect; gold-bearing arsenopyrite; *Thiobacillus ferrooxidans*

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## 1 INTRODUCTION

There are many kinds of sulphide minerals, such as arsenopyrite, pyrite, chalcopyrite, sphalerite, galena, pyrrhotite, stibnite, tetrahedrite etc. in refractory gold ore containing arsenic. The arsenopyrite has some peculiar characteristics: 1) arsenopyrite is the most important gold containing sulphide mineral, the sequence according to the percentage of gold in minerals is (from high to low) arsenopyrite, pyrite, pyrrhotite, marcasite, then pentlandite; 2) arsenopyrite is the most main mineral in the high-arsenic concentrated ore; 3) arsenopyrite is the highest arsenic mineral, its As content (mass fraction) is high up to 46.01%; (4) compared with the other elements, As is the most harmful one for *Thiobacillus ferrooxidans*, arsenopyrite played a very important role during the process of bio-oxidation for refractory gold ore. Its bio-oxidation degree affects directly the effect of the gold extraction. Definitely, it is necessary to study furtherly the bio-oxidation model of gold-bearing arsenopyrite.

## 2 EXPERIMENTAL

### 2.1 Crystal chemistry of arsenopyrite

Arsenopyrite (FeAsS) is classified as the subgroup of sulphide minerals with isolated structure, cobaltitene (CoAsS)-arsenopyrite (FeAsS) group, arsenopyrite subgroup. The bond strength of joined atoms in the atomic group structure is bigger than that joined out the group,

[AsS] is in the single linear order. Arsenopyrite is the monoclinic system,  $a = 0.953 \text{ nm}$ ,  $b = 0.566 \text{ nm}$ ,  $c = 0.643 \text{ nm}$ ,  $\beta = 90^\circ$ ,  $z = 8$  (or triclinic system,  $a = 0.574 \text{ nm}$ ,  $b = 0.567 \text{ nm}$ ,  $c = 0.578 \text{ nm}$ ,  $\beta = 112^\circ 10'$ ,  $\alpha \approx \gamma \approx 90^\circ$ ). Arsenopyrite belongs to heterodesmic bond type, S—As is connected with the covalent bond and constituted the As—S pair. Interatomic distances are As—S 0.230 nm, Fe—As 0.233 nm and Fe—S 0.223 nm. The crystal structure of arsenopyrite is a type of derived structure of NaCl pattern, As—S pairs are dumbbell states, iron as  $\text{Fe}^{2+}$ , arsenic and sulfur as  $\text{As}^-$  and  $\text{S}^-$  separately<sup>[1]</sup>. Its chemical composition, theoretically, is Fe 34.30%, As 46.01%, S 19.69%. There are the composition variation of As and S, from  $\text{FeAs}_{0.9}\text{S}_{1.1}$  to  $\text{FeAs}_{1.1}\text{S}_{0.9}$ . Fe and Co usually form isomorphous replacement incompletely. In addition, some arsenopyrites contain Au, Ag, Cu, Pb, etc.

### 2.2 Characteristic of sample

Samples are choosed from the natural gold-bearing arsenopyrites occurred in a high arsenic gold mine. Arsenopyrites with the strong metallic luster and high reflectance rate is tin-white colour and anisotropism. The idiomorphs of crystals are well developed, most of which are idiomorphic and hypidiomorphic crystals and the others are allotriomorphic crystals. The (101) and (230) crystal faces developed well, generally as columnar, needle-like and diamond-shaped crystals, twin crystal of arsenopyrite occurring by chance. The crystal size is often  $5.0 \times 0.8 \sim 1.0 \times 0.2 \text{ mm}$ , its aggregate as radiate

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and dissemination.

The gold-leaching ratio of the concentrated gold ore is only 2.8% by the direct process of the cyanide leaching. Gold minerals mainly exist in the arsenopyrite crystals and next in the pyrite crystals. 75% of gold minerals is in the arsenopyrite crystals as the submicro-gold<sup>[2]</sup>, which chiefly crystallize in the border of arsenopyrite crystals, where are gold-rich bands(places).

### 2.3 Experimental condition

A tamed strain of *Thiobacillus ferrooxidans*, named SH-T, was used in the experiment, cell population of the culture was amounted to  $8.87 \times 10^9$  cell / ml, and the redox potential was 590 mV. The experiment was conducted in a 250 ml flask with 100 ml culture in it. The flask was continuously shaken on a HZQ-C type shaker at 130 r/min and kept at 36 °C. The polishing arsenopyrite sample was immersed into the culture and then the preliminary pH value was adjusted to 2.0. The located site of the sample was observed, recorded and photographed every 12 h under the microscope for comparison. The whole experiment lasts 84 h.

### 2.4 Electronic probe study

After a period of bio-oxidation by SH-T culture the surface of the sample was polished to remove oxidized product, then the sample was used for electronic probe examination. The morphologies feature of the sample surface are shown in Fig. 1.

## 3 RESULTS AND DISCUSSION

### 3.1 Test results

Bio-oxidation test of arsenopyrite sample indicates that the whole oxidation may be divided into three stages:

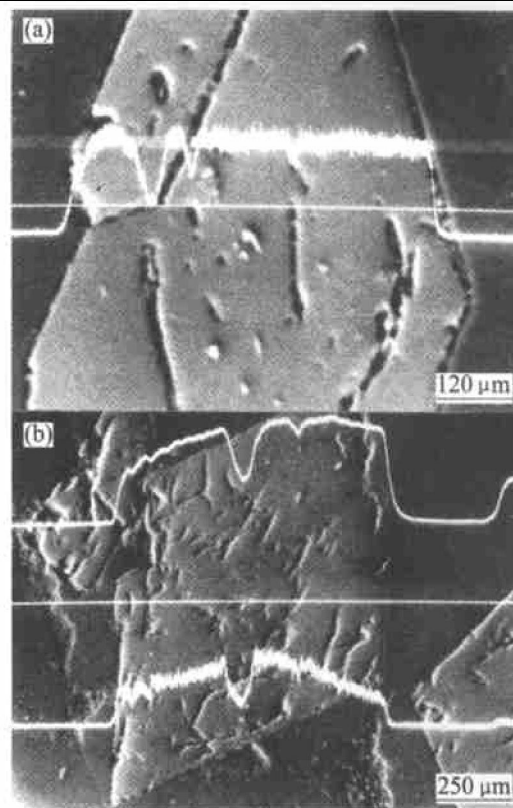
#### 1) The first stage(0~ 24 h)

Large area of oxidation occurred on the surface and the sample metallic luster lost. Rusty or colourful semi-metallic luster appeared. Zonal structure was produced by the corrosion effect of bio-oxidation on the surfaces, especially, of the complicated composition of arsenopyrite.

#### 2) The second stage(24~ 72 h)

Semi-metallic luster and zonal structure disappeared and earthy luster appeared, which means that there was an oxidized membrane formed on the crystal surfaces. With the development of bio-oxidation the thickness of oxidized product increased up to 20 nm.

#### 3) The last stage(72~ 84 h)



**Fig. 1** Microscopic characteristic of gold-bearing arsenopyrite oxidized by

*Thiobacillus ferrooxidans*

(a) —Thin long cracks; (b) —Thick short cracks

The whole crystal surface was covered by the oxidation membrane. Bio-oxidation was limited and large area of surface oxidation tended to terminate, then bio-oxidation began to proceed in the direction of vertical to the cracks and disintegration section of arsenopyrite crystal. Bio-oxidation went into linear oxidation period.

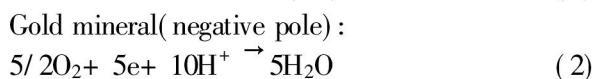
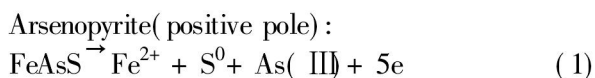
The microscopic feature of arsenopyrite surfaces was examined by electronic probe after the bio-oxidation test terminated. Results demonstrate that a lot of cracks are in the form of crossing or network, occurring on arsenopyrite surfaces. The cracks are much denser, most distributed along the face of crystal, which means that bio-oxidation of arsenopyrite has directive and selective feature.

### 3.2 Discussion

The property of gold-bearing arsenopyrite has been the hot problem for the mineralogists, who widely study not only the natural arsenopyrites but also the synthetic ones in order to find the regular pattern. At present there are mainly several view points of gold occurrence of arsenopyrite as: visible gold, submicro-gold, colloid gold and crystal lattice gold<sup>[3]</sup>. In spite of disputes, the most of scholars have accepted the gold occurrence of arsenopyrite as the submicro-gold. Through many studies it

is shown that the gold grains are uneven. The gold grains are dense at submicro-gold in the border and up to 0.148% ~ 0.28%, contrarily, the core is poor gold area<sup>[4]</sup>. Xin et al<sup>[5]</sup> made a synthetic test of gold-bearing arsenopyrite. It was shown that the gold grains were also unevenly distributed. Au varies directly with As. The amount of gold is high in the As-rich area, even as high as 1.7% in the border. There is not nearly any gold in the core, called as Au-poor area. Definitely, the test result is identical with the natural gold-bearing arsenopyrite. Gold minerals are mainly sedimentary and crystallize along the crystal face, cleavage face and fracture in the border and crystal defect<sup>[6~10]</sup>.

As we known, the gold grains of less than 0.1  $\mu\text{m}$  are called submicro-gold<sup>[3]</sup>. The gold grains are distributed in border of the arsenopyrite at the submicro-grain gold state. These small gold grains are wrapped up the arsenopyrite crystal. Indeed, quite a lot of gold/arsenopyrite mineral pairs are naturally formed, there are almost no mineral pairs in the core. Due to high ionization potential, high electronegativity and high oxidation-reduction potential, gold is wholly inert on the chemistry, it undoubtedly belongs to quite stable mineral. Compared with gold, the arsenopyrites show the strong chemical activity, which easily conduct oxidation and corrosion. During the process of the bacteria oxidation, the host mineral-arsenopyrite and guest mineral-gold naturally form a kind of distinctive relationship, i. e. submicro-battery relationship (Fig. 2). The active arsenopyrite is always the positive pole of submicro-battery, and the inert gold the negative pole. During the bacteria oxidation the positive pole-arsenopyrite is unceaselessly oxidized, in which Fe, As, S are dissolved and the crystal is gradually broken. Meanwhile the negative pole-gold is protected. Along with the continuous oxidation and corrosion of arsenopyrite, the gold wrapped up in the arsenopyrite is exposed finally. Because gold grains are at the submicro-gold state, such battery effect is also micro-phenomenon and unobserved with naked eyes, which is called submicro-battery by authors, its oxidation-reduction reactions are as:



After the study on surfaces appearance of arsenopyrite oxidized using the electronic probe, it shows that many new cracks, crevices and holes appear. From the direction of the cracks, they almost parallel to the crystal face direction (Fig. 1). The cracks form on the networks textures indicating that the crystal face direction of

arsenopyrite was quite weak. Under the effect of submicro-battery the arsenopyrite is easily oxidized, i. e. *Thiobacillus ferrooxidans* selectedly oxidizes along the direction of gold, compared with it, the core of arsenopyrite is oxidized slowly, which shows that *Thiobacillus ferrooxidans* oxidized the gold-bearing arsenopyrite selectedly. Fig. 2 is bio-

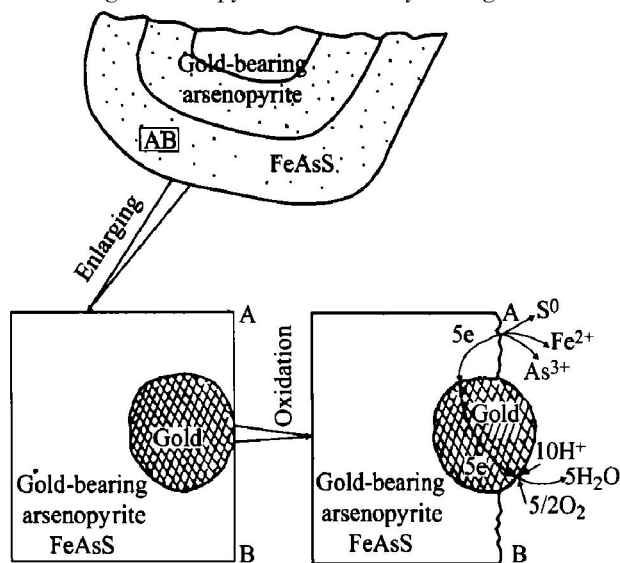


Fig. 2 Bio-oxidation model of gold-bearing arsenopyrite

oxidation model of submicro-battery.

Because of the submicro-battery effect, *Thiobacillus ferrooxidans* gave priority to spontaneous oxidation for the gold-rich place, mainly in the border of arsenopyrite. On the other hand, it oxidized slowly at the place of gold-poor. For this reason such bacteria (*Thiobacillus ferrooxidans*) possesses the distinctive characteristic of following gold during oxidation of the gold-bearing arsenopyrite, which improves the effect of the bio-oxidation. Therefore the bio-oxidation may be better than the roast oxidation and add-pressure oxidation. Undoubtedly, the submicro-battery of gold/arsenopyrite can play an inestimable role on speeding up the bio-oxidation and raise the dearsenication ratio of the refractory gold ore. The gold grains mainly distribute in the border of arsenopyrite and the core is gold-poor area. Therefore, it can be inferred that gold-bearing arsenopyrite does not need to be oxidized wholly.

## 4 CONCLUSIONS

1) The bacteria oxidation process of gold-bearing arsenopyrite is divided into three stages. The first stage: the arsenopyrite is oxidized mainly on the crystal surfaces. The second stage: the gold-bearing arsenopyrites are oxidized strongly with *Thiobacillus ferrooxidans*. and

covered the oxidized membrane on the crystal surfaces, which restrained the further oxidation of arsenopyrite. The third stage, bacteria oxidize along with cracks of arsenopyrite.

2) Many new cracks and holes formed on the surfaces of gold-bearing arsenopyrite oxidized with *Thiobacillus ferrooxidans*. These cracks were along with certain direction, which shows that *Thiobacillus ferrooxidans* oxidized selectedly arsenopyrite.

3) The distribution of submicro-gold in the arsenopyrite crystals was uneven. The mineral pairs of gold/arsenopyrite naturally form the relationship of submicro-battery. When *Thiobacillus ferrooxidans* oxidized gold-bearing arsenopyrite, it oxidizing the place of gold-rich firstly. Definitely, *Thiobacillus ferrooxidans* oxidized selectedly along with the crystal border, crystal face and crack of gold-bearing arsenopyrite.

4) It can be inferred that gold-bearing arsenopyrite does not need to be oxidized wholly. On the theory, *Thiobacillus ferrooxidans* just oxidized effectively the gold-rich place in the arsenopyrite and the recovery ratio of gold is reached.

#### [ REFERENCES ]

- [ 1 ] ZHAO Shao-rong, TAN Jing, CHEN Sheng-ping. The feature of the crystal boundary and the formation for arsenopyrite twin[ J ]. Journal of Mineralogy and Petrology, 1997, 17(1): 1-6.
- [ 2 ] YANG Hong-ying. Study on the Bacterial Oxidation Process of Sulfide in the Refractory Gold Ore [ D ]. Shenyang: Northeastern University, 2001.
- [ 3 ] ZHANG Zhen-ru. Study on Gold Deposit [ M ]. Changsha: Central South University of Technology Press, 1989. 81-92.
- [ 4 ] WANG Yu-ming, CHEN Ke-rong. Study on enrichment for submicro Au in arsenopyrite, pyrite and other minerals [ J ]. Journal of Mineralogy and Petrology. 1996, 16(3): 20-26.
- [ 5 ] Xin Wu, Francois D B. Hydrothermal synthesis of gold-bearing arsenopyrite [ J ]. Economic Geology, 1989, 84(7): 2029-2032.
- [ 6 ] HE Yi-xing, HU Da-qiang, YAO Jie. Arsenopyrite and its effect on gold mineralization in Qiqiu No. 1 gold deposit, Xinjiang [ J ]. Acta Mineralogica Sinica. 1993, 13(3): 277-281.
- [ 7 ] ZHANG Zhen-ru, WANG Qing-duo, LIAO Feng-xian, et al. Studies on manner of occurrence of submicro-gold in arsenopyrite [ J ]. Journal of Guilin College of Geology. 1991, 11(2): 150-153.
- [ 8 ] WANG Yu-ming, JI Shou-yuan, CHEN Ke-rong. A further study on the existing states of submicro-gold in pyrite and arsenopyrite [ J ]. Acta Mineralogica Sinica, 1994, 14(1): 83-87.
- [ 9 ] MAO Shu-he. EMPA study of occurrence of ultramicro gold in ore [ J ]. Acta Mineralogica Sinica, 1990, 10(1): 66-74.
- [ 10 ] Wells J D, Mullens T E. Gold-bearing arsenian pyrite determined by microprobe analysis, Cortez and Carlin gold mines [ J ]. Econ Geol, 1973, 68: 187-201.

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