

# Bioleaching behavior and surface property of pyrites in different metallogenic conditions

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**Abstract** The bioleaching behaviors and surface properties of pyrites in two metallogenic conditions by *Sulfobacillus thermosulfidooxidans* were investigated by adsorption tests, zeta-potential measurements and bioleaching experiments. It is found that there were significant differences in the microorganism adsorption capacity, electrokinetic properties and bioleaching behaviors for the two pyrites. The *S. thermosulfidooxidans* adsorption capacity on high temperature hydrothermal (hy\_high\_temp) pyrite is larger than that on sedimentary coal (sed\_coal) pyrite. It may be that more extracellular polymeric substances (EPS) is produced when it is difficult for microorganism to make use of hy\_high\_temp pyrite as source of energy, and get leaching bacteria attached to pyrite by means of EPS. The zeta-potential measurements indicated that zeta-potential value of hy\_high\_temp pyrite was higher than that of sed\_coal pyrite in pH range of 2–10. After interacting with cells, the IEP (Iso-Electric Point) of hy\_high\_temp pyrite shifted obviously to that of bacterial. In contrast, the IEP of sed\_coal pyrite remained unchanged nearly. The bioleaching results showed that hy\_high\_temp pyrite did not dissolve and the leaching extent was only 0.82%, while that of sed\_coal pyrite was 34.59%. Attempts were taken to illustrate the remarkable difference between bioleaching results of two pyrites from a semiconductor energy band theory perspective.

**Key words** pyrite; bioleaching; *S. thermosulfidooxidans*; metallogenic condition; electrokinetic property

## 1 Introduction

Pyrite is the most widely distributed sulfide mineral on the Earth and commonly occurs in coals, hydrothermal veins, contact metamorphic deposits and sedimentary rocks (Chandrababha and Natarajan, 2006). The application of microorganism to accelerate oxidation dissolution of pyrite can facilitate the extraction of inclusive gold, and solubilise base metals such as copper and cobalt. However, the oxidation of pyrite exposed to the environment also generates acid, which results in an environmental problem known as acid mine drainage, whose handling has caused vast sums investments.

The bioleaching of pyrite, especially the mechanism of bacterial leaching of pyrite has been studied extensively over the years (Rossi, 1990; Sand et al.,

1995). The kinetic of dissolution of pyrite has also attracted some researchers' attention (Fowler et al., 2000; Holmes and Crundwell, 1999). However, few literatures report the effect of metallogenic conditions on pyrite bioleaching. At present, only a few theoretical achievements are obtained. Some (Monroy et al. 1993) had proposed that physical property of mineral could play an important role in bioleaching of metal sulfide, such as conductive type. Jack Barrett (1993) considered the Fermi level of minerals as a main factor affecting bioleaching reaction rate. Illumination on pyrite surface was suggested to increase the anodic dissolution of *n*-type pyrite, which implied that the light generated holes react on the surface, and semiconductor properties would influence the kinetics (Mishra and Osseo-Asare, 1992). Springer (1970) found that the Tafel slope of *n*-type and *p*-type pyrite

was the same in the anodic potential region.

The bioleaching behavior and surface property of pyrites in two metallogenic conditions were investigated in this paper. The changes in surface properties of pyrites were observed by the means of adsorption and Zeta-potential measurements. In addition, the effect of metallogenic conditions on bioleaching result and surface property of pyrite was further discussed.

## 2 Materials and methods

### 2.1 Pyrite minerals

Two pyrite samples (about 95%  $\text{FeS}_2$ ) from different metallogenic conditions were used in the present study. Sedimentary coal (sed\_coal) pyrite sample originated from coal seams in Wenshan, Yunnan Province (Tu, 1984). High temperature hydrothermal (hy\_high\_temp) pyrite was obtained from Leiyang, Hunan Province (Xue, 2003). Two hand-picked crystals were dry ground by a porcelain ball mill to the particle size of 38–74  $\mu\text{m}$ , and stored for the experiments. As shown in Fig. 1, the XRD spectrums of two samples were typical for pyrite. The chemical analysis of pyrite samples were listed in Table 1.

### 2.2 Microorganisms and culture media

The following strains of *S. thermosulfidooxidans* obtained from the Key Laboratory of Bio-metallurgy of Ministry of Education, Central South University,

Changsha, China were used for this study. The strains were cultivated aerobically at 53°C in the media, which contained 3.0 g/L  $(\text{NH}_4)_2\text{SO}_4$ , 0.1 g/L KCl, 0.5 g/L  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , 0.5 g/L  $\text{K}_2\text{HPO}_4$  and 0.01 g/L  $\text{Ca}(\text{NO}_3)_2$ . The energy sources was  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (20 g/L).  $\text{H}_2\text{SO}_4$  was used to adjust the pH value. All solutions were sterilized in an autoclave at 121°C for 20 min.

The liquid containing cells were filtrated through Whatman filter paper to remove the suspended solid materials, and the filtrate was centrifuged for 20 min at 9000 rpm. The cells were washed thrice in dilute sulfuric acid (pH 1.6) in order to remove any trapped ions and stored for use.

### 2.3 Semiconductive type tests

The semiconductive type of pyrites was investigated by the semiconductor Seebeck effect. The direction of thermo-electromotive force in *n*-type pyrite is from low to high temperature regions when the semiconductor is heated. The situation was set conversely for *p*-type pyrite.

Two massive samples of pyrite were selected to perform experiments, and then heated by alcohol lamp for about 10 seconds. The positive pole of multimeter was connected to the high temperature area, while the negative pole to the low temperature area. The pyrite was an *n*-type semiconductor if the measured voltage value was positive; otherwise, it was a *p*-type semiconductor.

**Table 1** The chemical composition of pyrites

Sample name	Major element (%)		Trace element ( $\times 10^{-6}$ )			
	Fe	S	Co	Ni	As	Se
Hy_high_temp pyrite	44.94	51.38	190	10	960	4
Sed_coal pyrite	44.43	54.55	40	50	80	1

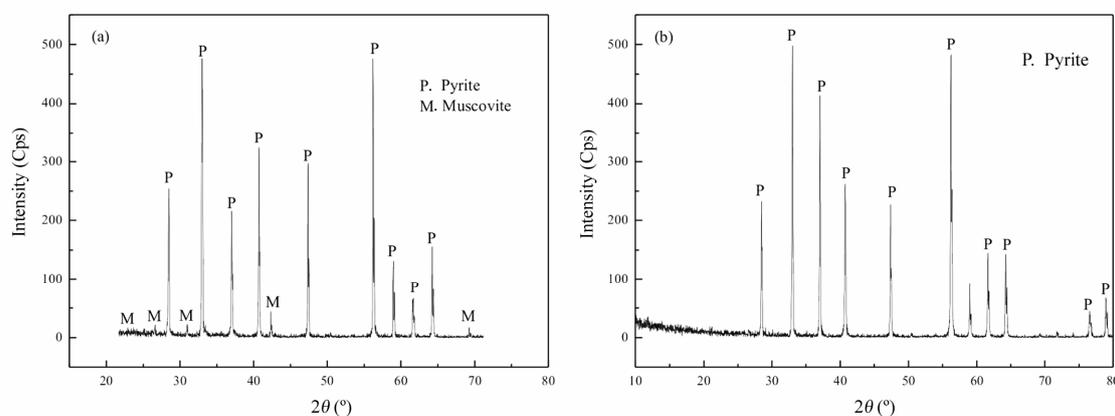


Fig. 1. The XRD analysis of pyrite: (a) hy\_high\_temp pyrite; (b) sed\_coal pyrite.

## 2.4 Adsorption tests

The -0.037 mm pyrite particles were ground by agate mortar for 3 h. 50 mL NaCl (ionic strength  $10^{-3}$  M) solution with 0.2% ground pyrite particles were inoculated with cell suspensions ( $1.0 \times 10^8$  cells/mL). The slurry was agitated on a rotary shaker at 160 rpm. The number of planktonic cells was directly counted with a microscopy. The amount of adsorbed bacterial was calculated by subtracting that of planktonic bacterial from the initial number.

## 2.5 Zeta-potential measurements

Zeta-potential measurements were performed with a JS94H micro-electrophoresis apparatus. 50 mL NaCl solution (ionic strength  $10^{-3}$  M) was used as the base electrolyte in each experiment. The -0.037 mm pyrite particles were ground by agate mortar for 3 h.

The microorganism was frozen at  $-4^\circ\text{C}$  for 48 hours before Zeta-potential measurement of microorganism, which was measured in cell concentration of  $2.0 \times 10^8$  cells/mL. Zeta potential measurement of pyrite was performed in pulp density of 0.2%. When measurements on pyrite samples after interacting with cells were made as pulp density of 0.2% and cell concentration of  $2.0 \times 10^8$  cells/mL, the minerals were pre-conditioned in the presence of the cells for one hour at 250 rpm agitation speed.

## 2.6 Bioleaching experiments

Pyrite samples with a particle size of 38–74  $\mu\text{m}$  were used in the bioleaching experiments, which were carried out in 250 mL Erlenmeyer flasks with 100 mL nutrient media, pulp density of 1% and initial cell concentration of  $1 \times 10^8$  cells/mL. The initial pH was adjusted to 1.6 approximately. In all leaching tests, every flask was sampled by removing 3 mL leaching solution. The redox potential was measured by a platinum electrode combined with an Hg/HgCl<sub>2</sub> reference electrode. The concentration of Fe<sub>total</sub>, pH and redox potential were monitored by regular intervals in the course of bioleaching.

## 3 Results and discussion

### 3.1 Semiconductive type tests

The results of semiconductive type tests are listed in Table 2. The carriers in *n*-type semiconductor are usually free electrons based, while those in *p*-type semiconductor are mostly holes.

## 3.2 Adsorption tests

The attachment of *S. thermosulfidooxidans* cells to pyrites is shown in Fig. 2. The adsorption equilibrium on the pyrite surface was reached quickly, 10 minutes for hy\_high\_temp pyrite and 20 minutes for sed\_coal pyrite, respectively. Meanwhile, the adsorption quantity of *S. thermosulfidooxidans* on hy\_high\_temp pyrite was larger than that on sed\_coal pyrite. But the leaching rate of hy\_high\_temp pyrite was quite low in the following bioleaching results. More extracellular polymeric substances (EPS) is produced when it is difficult for microorganism to make use of hy\_high\_temp pyrite as its source of energy, and let leaching bacteria attached to the pyrite by means of EPS (Gehrke, 1998). The more EPS is produced, the larger adsorption quantity is, which may be able to illustrate the adsorption tests results.

**Table 2** The semiconductive type of pyrites

Origin	Voltage value	Semiconductive type
Leiyang, Hunan Province	Positive	<i>n</i> -type
Wenshan, Yunnan Province	Negative	<i>p</i> -type

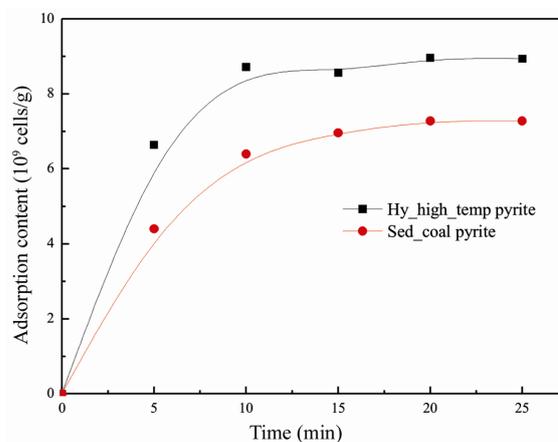
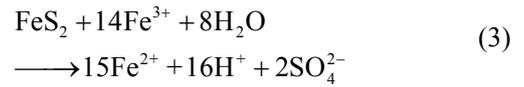
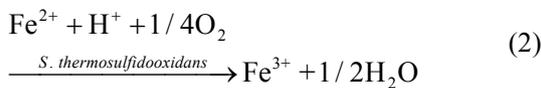
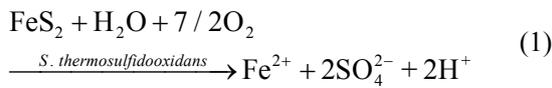


Fig. 2. Adsorption curves of cells of *S. thermosulfidooxidans* grown on Fe<sup>2+</sup> on different pyrites.

### 3.3 Zeta-potential measurements

Zeta-potential of different pyrites as a function of pH is portrayed in Fig. 3. The Iso-Electric Point (IEP) of pyrite is 6.05 for hy\_high\_temp type and 5.55 for sed\_coal one respectively. And zeta-potential value of hy\_high\_temp pyrites is higher than that of Sed\_coal ones in pH 2–10 range, which may be explained by different surface state of two pyrites.

It also could be seen that IEP of hy\_high\_temp pyrite shifted towards to that of bacterial and its zeta potential value decreased with pH below 5 after interacting with cells. In contrast, the IEP of sed\_coal pyrite remained unchanged and its zeta potential value increased in the same case. Combined with the results of adsorption and bioleaching tests, increasing of zeta potential of sed\_coal pyrite is caused by the adsorption of cations generated from bacteria oxidation of mineral. Due to few cations produced by dissolution of pyrite, changing of zeta potential of hy\_high\_temp pyrite is mainly related to the adsorption of cells. The cations are likely to be ferrous or ferric ions and these reactions may are as follow:



### 3.4 Bioleaching experiments

The results in Fig. 4 show the redox potential (vs. SCE) and pH in pyrite bioleaching. As shown in Fig. 4, the pH value of sed\_coal pyrite solution declines with time all the way, while that of hy\_high\_temp pyrite dropped in the first day and remained nearly unchanged later. The decreasing of pH value with time is related to reaction (1) for hy\_high\_temp pyrite and reactions (2) and (3) for sed\_coal pyrite, respectively. The redox potential of sed\_coal sample in bioleaching by *S. thermosulfidooxidans* cells increased sharply in the first three days, and then rose slowly with time. In contrast, the redox potential of hy\_high\_temp pyrite began to increase in first day but decreased in the following days. Fig. 5 is the bioleaching experiments results of two samples. The ultimate leaching extent of Sed\_coal pyrite was 34.59%, while that of Hy\_high\_temp pyrite was only 0.82%.

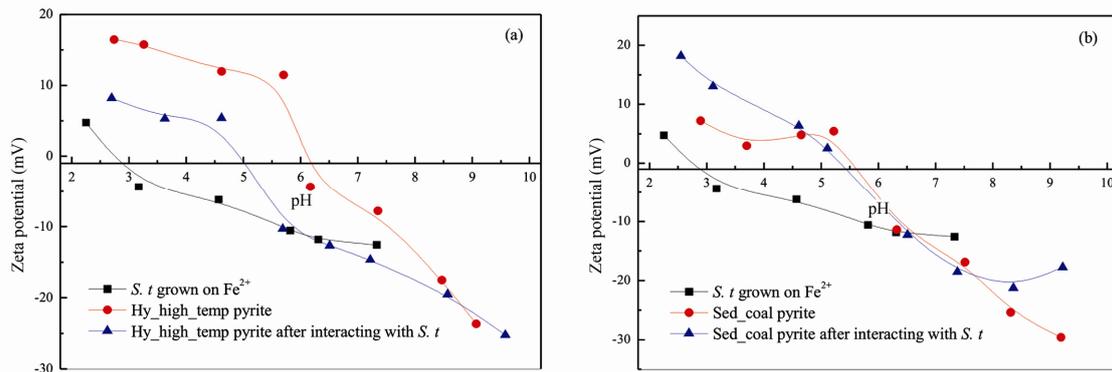


Fig. 3. Zeta-potential of pyrite before and after interacting with *S. thermosulfidooxidans* grown on Fe<sup>2+</sup> as a function of pH. (a) hy\_high\_temp pyrite; (b) sed\_coal pyrite.

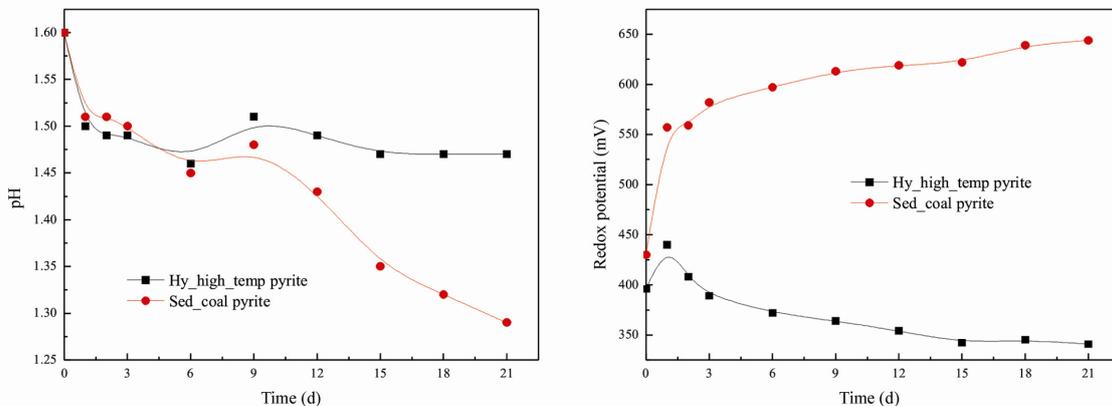


Fig. 4. The redox potential (vs. SCE) and pH as a function of time in pyrite bioleaching.

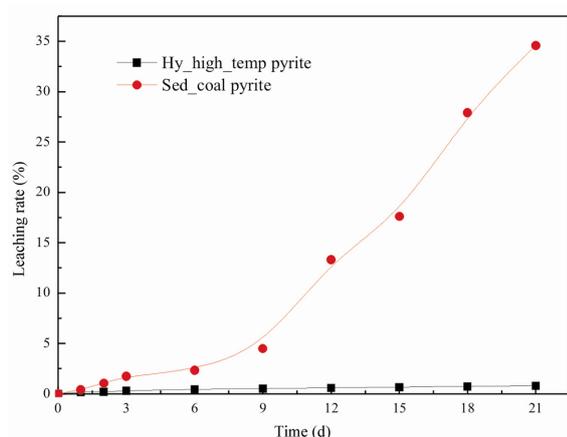


Fig. 5. The leaching rates as a function of time in pyrite bioleaching.

Since jarosite cannot be produced in highly acidic medium, X-ray diffraction pattern of residues bioleached by *S. thermosulfidooxidans* for 21 d shows that all residues remain pyrite and quartz (Fig. 6).

Pyrite is a semiconductor, and has an impact on the dissolution kinetic of pyrite (Crundwell, 1988a, b). The oxidation leaching of pyrite is actually a process of transferring electrons or holes at semiconductor/solution interface (Li and Wang, 2004a), so it is feasible to use semiconductor electrochemistry theory to reveal the mechanism of leaching process of pyrite.

Considering from the perspective of energy band theory, different bioleaching behaviors of different semiconductive type pyrites is related to the semiconductor energy gap. It is demonstrated that the oxidation reaction of semiconductive sulfide mineral mainly proceeds by transferring holes if its energy gap is larger than 0.66 eV (Li and Wang, 2004b). The energy gap of pyrite is  $0.9 \pm 0.1$  eV (Ennaoui et al., 1993), which indicates that the oxidation of pyrite depends on passing on holes. Therefore, the abundant holes in p-pyrite benefit its bioleaching, while hy\_high\_temp pyrite does not dissolved for lack of holes in pyrite.

## 4 Conclusions

Based on the analysis above, it can be drawn that the metallogenic conditions of pyrite play an important role in bioleaching behavior and surface property of pyrite. The experiments in this paper show that hy\_high\_temp pyrite does not almost dissolve and the leaching extent is only 0.82%. Sed\_coal pyrite dissolves partly and the leaching extent is 34.59%. From the point of view of semiconductor energy band theory analysis, hy\_high\_temp pyrite can be hardly oxidized by bacteria alone due to the lack of holes in pyrite. It is different bio-oxidation behaviors that lead to different surface properties and bioleaching behaviors

of pyrite. It is helpful to understand these for solving the environmental problems caused by bio-oxidation of pyrite.

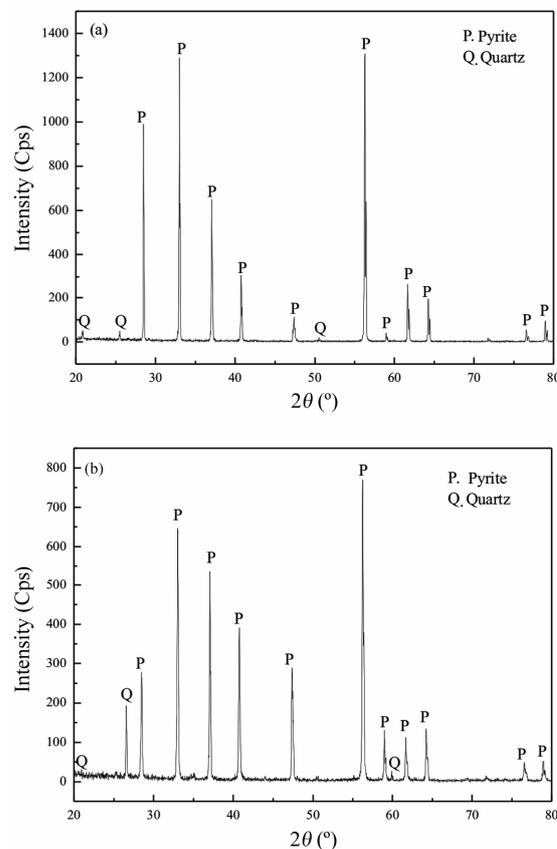


Fig. 6. The XRD analysis of pyrite leaching residues after 21 d by *S. thermosulfidooxidans*. (a) hy\_high\_temp pyrite; (b) sed\_coal pyrite.

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