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Surface analysis of sulfur speciation on pyrite bioleached by extreme thermophile *Acidianus manzaensis* using Raman and XANES spectroscopy

Jin-lan Xia [a,*], Yi Yang [a], Huan He [c], Xiao-juan Zhao [a], Chang-li Liang [a], Lei Zheng [b], Chen-yan Ma [b], Yi-dong Zhao [b], Zhen-yuan Nie [a], Guan-zhou Qiu [a]

[a] *Key Lab of Biometallurgy, School of Minerals Processing and Bioengineering, Central South University, Changsha 410083, China*
[b] *Beijing Synchrotron Radiation Facility, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China*
[c] *Key Lab of Coal Processing and Efficient Utiliazaion Ministry of Education, School Chemical Engineering and Technology, China University of Mining and Technology, Xuzhou 221116, China*

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ABSTRACT

Sulfur speciation on the surface of pyrite leached by extreme thermophile *Acidianus manzaensis* YN-25 was investigated by using scanning electron microscopy (SEM), X-ray diffraction (XRD), Raman spectroscopy and sulfur K-edge X-ray absorption near edge structure spectroscopy (XANES). SEM micrographs showed leaching products with numerous holes were formed into the surface of leached pyrite. XRD spectra indicated that the leach residues were mainly composed of pyrite and jarosite. The sulfur K-edge XANES indicated that elemental sulfur, thiosulfate and/or thiosulfate-like species and jarosite were formed on the mineral surface. Raman spectroscopy further verified the presence of jarosite, elemental sulfur and thiosulfate. Jarosite formed in pyrite leaching appeared much later than in chalcopyrite leaching by the same strain. Jarosite on the mineral surface may account for the passivation of pyrite oxidation, with the passivation effect of elemental sulfur which is less important. In addition, the thiosulfate detected in this study provided novel evidence for surface-bound thiosulfate involved in the stepwise oxidation of pyrite by the extreme thermophile *A. manzaensis*.

1. Introduction

Pyrite usually coexists in base metal sulfide ores and the presence of pyrite can promote the leaching of chalcopyrite (Ahonen et al., 1986). Biooxidation of pyrite can provide energy to the major bioleaching bacteria, promoting the cell growth and the biooxidation of other sulfides minerals. The microorganisms mainly involved in pyrite oxidation are the mesophiles, e.g. *Acidithiobacillus ferrooxidans*, or, at elevated temperatures, the thermophiles, e.g., *Acidithiobacillus caldus*, *Metallosphaera sedula*, and *Acidianus brierleyi* (Schippers et al., 1999; Mikkelsen et al., 2007).

The temperature dependency of pyrite biooxidation rates is well documented (Franzmann et al., 2005; Hita et al., 2009; Wang et al., 2007). At elevated temperatures, jarosite readily forms and deposits onto the surface of pyrite, thus preventing the contact of the microorganisms and hindering the leaching process (Dutrizac, 2008; Blight and Ralph, 2000; Rodríguez et al., 2003).

Besides jarosite, it is reported that sulfur-rich layers may also be formed and inhibit the bioleaching process (Klauber, 2008; Rojas-Chapana et al., 1996; Schippers et al., 1999; Pisapia et al., 2007; Sasaki et al., 1995). However, the major passivation factor and the mechanisms involved in passivating layer formation still seem to be in dispute. Therefore an investigation of the sulfur speciation on the surface of pyrite during oxidation with thermophiles contributes to our understanding of the mechanism of passivating layer formation and to devising ways to restrain it.

The oxidation mechanism of pyrite has been widely investigated, but to our knowledge there is no research about the mechanism in extreme thermophilic leaching systems. The stepwise oxidation of pyrite and the formation of surface-bound thiosulfate have been confirmed (Borda et al., 2003, 2004; Demoisson et al., 2008; Rimstidt and Vaughan, 2003). The subsequent decomposition of surface-bound thiosulfate may occur in different ways depending on the conditions which lead to different pyrite oxidation pathways (Rimstidt and Vaughan, 2003; Druschel and Borda, 2006).

Acidianus manzaensis is a novel extreme thermo-acidophilic Archaea of *Acidianus* genus, firstly isolated from a hot fumarole in Manza, Japan (Yoshida et al., 2006). The strain *A. manzaensis* YN-25 used in this study was recently isolated from an acid hot spring in Tengchong, Yunnan Province in the southwest of China and has potential industrial prospects (He et al., 2008).

In a previous study (He et al., 2009), the surface sulfur species during chalcopyrite leaching by *A. manzaensis* YN-25 was investigated using scanning electron microscopy (SEM), X-ray diffraction (XRD)

* Corresponding author. Tel.: +86 731 88836944.
E-mail address: jlxia@mail.csu.edu.cn (J. Xia).

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and sulfur K-edge X-ray absorption near edge structure spectroscopy (XANES). In this study, we adopted the same methods and Raman spectrometry to investigate the surface sulfur speciation during pyrite leaching with the same strain YN-25.

2. Materials and methods

2.1. Strain and culture conditions

The strain *A. manzaensis* YN-25 (accession number of 16S rDNA in GeneBank: EF522787) was provided by the Key Laboratory of Biometallurgy, Central South University. The basic medium used for cell cultivation was the same as that described by He et al. (2009) and the initial pH of the medium was adjusted to pH 1.5 with 1 M sulfuric acid.

2.2. The preparation of pyrite and standard samples

Pyrite used in the present study was provided by the Institute of Minerals Processing, Central South University. The main components were analyzed by X-ray fluorescence spectroscopy as shown in Table 1. The mineral was finely ground to 95% passing 74 μm, and the mineral powder was washed as described by Klauber et al. (2001) before the leaching experiment.

Polymeric sulfur was prepared by hydrolysis of S_2Cl_2 according to Blight et al. (2009). A 10 mL solution of S_2Cl_2 (97%, Jinshan Tin, Shanghai, China) was slowly injected via a syringe into a stirred 500 mL beaker containing 200 mL distilled H_2O and 0.25 g Triton X100 (Sigma) surfactant. The solid particles formed in the solution were recovered by vacuum filtration through Whatman No. 1 paper after 1 h. The particles were suspended and washed by 2 L distilled H_2O a total of 7 times to remove the residual surfactant. Then the particles were frozen dried and stored in the dark at −20 °C in an airtight container.

Jarosite was prepared following the method described by He et al. (2009) and Ding et al. (2007). *A. manzaensis* YN-25 with a concentration of 3×10^6 cells/mL was inoculated to a 250 mL shake flask containing 200 mL of basal medium (pH 1.5) with additional 30 g/L of $FeSO_4\cdot7H_2O$. The culture was incubated at 65 °C with shaking at 180 rpm, and the jarosite precipitate was collected after 48 h of incubation. The jarosite precipitate was suspended and washed by distilled H_2O for 7 times.

Potassium tetrathionate was purchased from Sigma, and other standard compounds including elemental sulfur, sodium thiosulfate, and sodium sulfite of A.R. grade were purchased from Da Mao Chemical Pharmaceutical Co. Ltd, Tianjin, China.

2.3. Bioleaching experiments

The leaching experiments were carried out with the same conditions and procedures as in the previous study (He et al., 2009), except with 3 g of pyrite instead of chalcopyrite. The leaching characters of total [Fe], pH, Eh (Pt. *vs.* SCE) and cell numbers were monitored. All the samples were frozen with liquid N_2, and then frozen dried and stored at −20 °C in an airtight jar for further analyses.

2.4. SEM, X-ray fluorescence spectroscopy, XRD and XANES studies

All of the instrumental details, calibration and sample preparation were performed as described by He et al. (2009). Pyrite, thiosulfate, sulfite, jarosite, tetrathionate, and elemental sulfur were chosen as standard compounds and ground to a fine powder.

XANES measurements were carried out at 4B7A beam-line (medium X-ray beam-line 2100–6000 eV) using synchrotron radiation from Beijing Synchrotron Radiation Facility, Institute of High Energy Physics, Chinese Academy of Sciences. The normalization of the spectra was performed at 2.50 keV where the variation of the absorption cross-section is small. All the data calculation above was performed in WinXas (3.0) (Ressler, 1998), and the spectra were fitted with the LSFitXAFS (Paktunc, 2004).

2.5. Raman spectroscopic study

Raman spectroscopic study was performed by Raman spectrometer (Jobin Yvon LabRam-010 micro-Raman system, France) equipped with Labspec 4.02 software attached to an integral Olympus BX 41 microscope, with the excitation source of 632 nm (He–Ne laser source) at a low energy level (2 mW). A holographic grating (1800 g mm^{-1}) Peltier-cooled 1024×256 pixels CCD detector was used. Raman spectra were recorded between 100 and 1200 cm^{-1} with a step width of 1 cm^{-1}, and 10 s of collection with two times of accumulation.

3. Results

3.1. Leaching characteristics of pyrite by A. manzaensis YN-25

The leaching characteristics of pyrite in bacteria inoculated and sterile control flasks are shown in Fig. 1a and b, respectively. It shows that the *A. manzaensis* YN-25 has significantly promoted the leaching process, with a final total iron concentration of 3 g· L^{-1}, compared with that of 0.7 g· L^{-1} in the sterile control. During the process, the pH decreased continuously to a value below 1.0. The Eh increased along with the accumulation of Fe^{3+} both in bacterial and sterile systems, with a final value of 450 mV and 300 mV, respectively. Cell numbers decreased sharply after day 12, which might be caused by the low pH at which the bacteria could not thrive.

3.2. Surface morphology and composition analysis of pyrite

The SEM graphs of pyrite in sterile control and bioleaching experiments are shown in Fig. 2a and b,c, respectively. Fig. 2a shows that little leaching product formed in the chemical leaching process and a smooth mineral surface could still be observed after 20 days' leaching. By contrast, the bioleaching experiments led to pronounced changes in the surface morphology. Numerous leaching products were adsorbed over the whole mineral surface (Fig. 2b) and holes in the products are clearly shown in Fig. 2c. These products may hinder the adsorption of bacteria and form a barrier for material exchange between the solid surface and liquid.

The XRD patterns of the original pyrite, residuals in sterile control and bioleaching experiments are shown in Fig. 3a, b and c respectively. The original mineral provided peaks of pyrite and quartz but after 20 days' leaching additional peaks corresponding to jarosite appeared. In the sterile control experiment no obvious change occurred.

3.3. XANES analysis of pyrite surface

Pyrite, thiosulfate, sulfite, jarosite, tetrathionate, and elemental sulfur that may appear in the surface residue were chosen as the references, and their sulfur K-edge XANES spectra are shown in Fig. 4.

Table 1
Chemical analysis of pyrite.

	S	Fe	O	Pb	Si	As	Al	Cu	K	Sn	Mg	Zn
wt.%	45.95	42.48	6.53	2.76	1.95	1.42	0.72	0.24	0.18	0.12	0.1	0.06
Moles/100 g	1.43	0.76	0.41	0.01	0.07	0.02	0.03	0.004	0.005	0.001	0.004	0.001