



Investigation of intermediate sulfur species during pyrite oxidation in the presence and absence of *Acidithiobacillus ferrooxidans*



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ARTICLE INFO

Article history:

Received 10 June 2016

Received in revised form 22 September 2016

Accepted 3 November 2016

Available online 5 November 2016

Keyword:

Pyrite

Oxidation

Intermediate sulfur species

Acidithiobacillus ferrooxidans

ABSTRACT

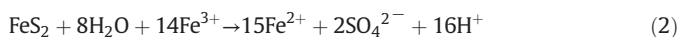
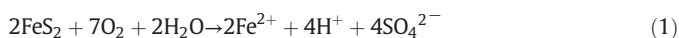
The intermediate sulfur species of pyrite chemical and biological oxidation have been the subject of controversy for some time, especially the question of whether or not elemental sulfur (S^0) and polythionates ($S_nO_6^{2-}$) are formed during the oxidation process. *Acidithiobacillus ferrooxidans* (*A. ferrooxidans*), one of the most common sulfur-oxidizing bacterial strains, has been shown to remarkably accelerate pyrite oxidation. In this study, the intermediate products of pyrite oxidation with and without *A. ferrooxidans* present were compared by employing different analytical techniques; i.e., high performance liquid chromatography (HPLC), X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) with energy dispersive spectrometer (EDS). The HPLC results showed that the concentrations of S^0 , $S_3O_6^{2-}$, $S_4O_6^{2-}$, $S_5O_6^{2-}$ and $S_6O_6^{2-}$ increased during pyrite oxidation process in the presence of *A. ferrooxidans*. Secondary minerals jarosite ($KFe_3(SO_4)_2(OH)_6$) and iron(III) oxide-hydroxide ($FeOOH$) were also detected by XRD and XPS. Without *A. ferrooxidans*, S^0 was also formed and along with $S_3O_6^{2-}$, $S_4O_6^{2-}$ and $S_5O_6^{2-}$ but only at very low concentrations at the end of the experiment. SEM micrographs further revealed that the pyrite was severely eroded by *A. ferrooxidans* and some spheroidal particles covered the surfaces of pyrite residues. These particles are most likely to be $KFe_3(SO_4)_2(OH)_6$ based on EDS analysis. The present study has quantitatively confirmed the presence of intermediate products of S^0 and $S_nO_6^{2-}$ during pyrite oxidation, information that deepens our understanding of the mechanism of pyrite oxidation.

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1. Introduction

Pyrite is one of the most abundant sulfide minerals in the earth's crust. It can be easily oxidized and can generate acid mine drainage (AMD) which has high acidity and high concentrations of toxic heavy metals (Akciil and Koldas, 2006; Lu and Wang, 2012). Therefore, many studies have investigated the mechanism of pyrite oxidation. A widely accepted view is that O_2 and Fe^{3+} are the major oxidants for pyrite oxidation, as shown in Eqs. (1) and (2). Previous studies have also indicated that in the presence of Fe^{3+} , the oxidation rate is several times higher than that in the presence of O_2 alone (Holmes and Crundwell, 2000; Moses et al., 1987). O_2 plays an additional important role in sustaining the oxidation process through the re-oxidation of Fe^{2+} to Fe^{3+} (Eq. (3)). It is this reaction that can be greatly accelerated by some iron-

oxidizing bacteria, such as *Acidithiobacillus ferrooxidans* (*A. ferrooxidans*) and *Leptospirillum ferrooxidans*.



Pyrite oxidation has been divided into chemical and biological oxidation, depending on whether microorganisms are involved in the process or not. In the past several decades, bacteria have been used successfully in metal sulfide leaching. *A. ferrooxidans*, the most common microorganism involved in oxidizing pyrite, has been studied extensively (Devasia and Natarajan, 2010; Liu et al., 2011a; Schippers et al., 1996; Schippers et al., 1999; Vera et al., 2013). However, more studies (Ojumu et al., 2006; Yang et al., 2015; Zhao et al., 2013) have focused on the factors influencing the oxidation rate of pyrite, very little has been known previously about the intermediate sulfur species of pyrite oxidation.

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In an earlier study, thiosulfate ($S_2O_3^{2-}$) was reported to be one of the major products of pyrite oxidation in salt marsh pore waters (Boulegue et al., 1982). Based on molecular orbital theory, Luther (1987) and Moses et al. (1987) demonstrated that the disulfide moiety of FeS_2 is initially transformed to $S_2O_3^{2-}$. In a further experiment, Moses and Herman (1991) found that element sulfur (S^0), SO_3^{2-} , $S_2O_3^{2-}$ and some species of polythionates ($S_nO_6^{2-}$) are generated in the course of pyrite oxidation under dissolved oxygen-saturated conditions, while these $S_nO_6^{2-}$ are absent in Fe^{3+} solutions. In contrast, in closely related experiments, Schippers et al. (1996) found that S^0 , $S_4O_6^{2-}$ and $S_5O_6^{2-}$ are formed after pyrite was oxidized by Fe^{3+} . However, only a very low concentration of S^0 is detectable when pyrite is oxidized in the presence of *A. ferrooxidans*. Based on experimental results, a chemical pathway of “thiosulfate mechanism” and a novel “sulfur chemical cycle” have been proposed to describe pyrite oxidation (Sand et al., 2001; Schippers et al., 1996; Schippers et al., 1999; Schippers and Sand, 1999; Vera et al., 2013). The thiosulfate mechanism involves a process by which the disulfide in the pyrite lattice is oxidized to $S_2O_3^{2-}$, followed by further oxidation resulting in the generation of $S_nO_6^{2-}$, S^0 , and SO_3^{2-} . However, no studies have been published to-date that report on the presence of $S_nO_6^{2-}$ when pyrite is oxidized in the presence of *A. ferrooxidans*. Besides, some studies focused on the surface products of pyrite oxidation by using some surface sensitive techniques. For example, Sasaki et al. (1995), using Raman spectroscopy and X-ray photoelectron spectroscopy (XPS), have confirmed that a S^0 layer was formed on the pyrite surfaces when pyrite was oxidized by Fe^{3+} solution. McGuire et al. (2001) have also found a S^0 passivation layer on the oxidized pyrite surfaces, using near-infrared Raman imaging microscopy. On the other hand, there are numerous studies (Liu et al., 2011b; Mandl et al., 1999; Rodriguez et al., 2003) that have reported that no S^0 was produced during the pyrite oxidation process.

Clearly, the intermediate products of pyrite chemical and biological oxidation are still a matter of controversy. Therefore, the present study is aimed at the elucidation of the uncertainties regarding products both in solution and on the surfaces of pyrite residues when pyrite is oxidized in the presence and in the absence of *A. ferrooxidans*.

2. Materials and methods

2.1. Pyrite ore

The high purity, handpicked pyrite used in this study was obtained from Dabaoshan Mine in Guangdong Province, South China. Before the experiment, the pyrite sample was ground to particles of diameter 39–74 μm . Subsequently, in order to try to remove the oxidation products that covered the pyrite surface, the pyrite was washed twice with boiling HCl (6 mol L^{-1}), three times with acetone, rinsed twice with de-ionized water, and dried in a lyophilizer at $-20^\circ C$ for 48 h. X-ray fluorescence spectroscopy (XRF) was used to analyze the purity of the pyrite. The results are shown in Table 1. The crystalline pyrite was analyzed by powder X-ray diffraction, with results indicating only the presence of pyrite and quartz crystals. In short, the pyrite is 94.81% pure, with the main impurity being quartz (about 2.52%).

Table 1
Chemical composition of pyrite ore analysis by XRF.

Compound formula	(Wt%)	Compound formula	(Wt%)
FeS_2	94.81	MgO	0.41
SiO_2	2.52	BiO_3	0.06
CaO	1.12	TiO_2	0.04
Al_2O_3	0.83	MoO_3	0.21

2.2. Bacterial strain and culture conditions

A strain of *A. ferrooxidans* (Gene-Bank: No. GQ984157) was isolated from an AMD pond in the area of the Dabaoshan Mine in Guangdong province, South China. The bacterium was initially cultured in 9 K medium: $(NH_4)_2SO_4$, 3 g L^{-1} ; K_2HPO_4 , 0.5 g L^{-1} ; $MgSO_4 \cdot 7H_2O$, 0.5 g L^{-1} ; $Ca(NO_3)_2 \cdot 4H_2O$, 0.014 g L^{-1} ; KCl, 0.1 g L^{-1} ; $FeSO_4 \cdot 7H_2O$, 44.5 g L^{-1} . 9 K Fe^{2+} -free culture medium (i.e., 9 K culture medium without $FeSO_4 \cdot 7H_2O$) was also prepared. All the 9 K and 9 K Fe^{2+} -free culture medium used in the experiment were adjusted to pH 2 with 10% H_2SO_4 solution. Next, the *A. ferrooxidans* was successively sub-cultivated in 9 K Fe^{2+} -free culture medium with FeS_2 (2%) as its source. The cells were harvested during the exponential growth phase and filtered through Whatman17 filter paper, centrifuged and washed twice with sterilized 9 K Fe^{2+} -free culture medium to remove residual Fe^{3+} . The cells were re-suspended in the 9 K Fe^{2+} -free culture medium for the following batch experiments. Cell numbers were counted with a hemocytometer.

2.3. Batch experiments

Batch experiments were used to investigate the intermediate sulfur species formed during pyrite oxidation in the presence or absence of *A. ferrooxidans*. The control sample consisted of 3 g FeS_2 in 150 mL 9 K Fe^{2+} -free culture medium. The chemical oxidation sample was similar to the control, but contained an additional 0.16 g $Fe_2(SO_4)_3$ in the 150 mL 9 K Fe^{2+} -free culture medium, resulting in a concentration of Fe^{3+} of approximately 0.3 g L^{-1} . The biological oxidation sample was the same as the chemical oxidation minus the Fe^{3+} in the 9 K Fe^{2+} -free culture medium but inoculated with *A. ferrooxidans*. The numbers of *A. ferrooxidans* were about 5.0×10^7 cells mL^{-1} .

All experiments were conducted in triplicate in 250 mL Erlenmeyer flasks, flasks were closed with hydrophobic cotton plugs, placed in a constant temperature incubator at $30^\circ C$ and shaken at 150 rpm for 30 days.

2.4. Analytical methods

2.4.1. HPLC and IC measurements

$S_nO_6^{2-}$ and S^0 were determined using an Agilent 1200 HPLC instrument equipped with a model G1311A pump, a model G1315D DAD UV-detector, and a Phenomenex Gemin C₁₈ separation column (5.0 μm , 46 $\mu m \times 250$ mm). SO_4^{2-} was measured by ion chromatography (IC) (Dionex ISC90) equipped with an analytical column (Thermo Scientific 4 mm $\times 250$ mm). The sample processing and testing methods were modified from the previous research (Schippers et al., 1996).

Potassium tetrathionate was purchased from Sigma-Aldrich. Other standard substances including sodium thiosulfate, sodium sulfate and elemental sulfur of A.R. grade were purchased from Shanghai Titan Scientific Co., Ltd., China. Tri-, penta-, and hexa-thionate salts were synthesized and supplied by the group of Professor Gao (Pan et al., 2013).

2.4.2. XRD, XPS and SEM-EDX measurements

The crystalline phases of the pyrite ore and pyrite residues were characterized by XRD (Empyrean, Netherlands), employing Cu- K_α radiation, scanning from $2\theta = 10^\circ$ to 80° at a rate of $0.2^\circ/s$. The chemical composition of the products on the pyrite residues' surfaces were analyzed by XPS, using a Thermo Scientific Escalab-250 instrument with a monochromatic Al- K_α source, operating at 15 kV and 25 W, and a spot size of $300 \times 300 \mu m$. The samples were analyzed under high vacuum (2×10^{-9} Torr) at room temperature. SEM (ZEISS, Merlin3700) was used to observe the surface morphology. The composition of the surface products were further analyzed by EDS (Oxford X-Max).

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