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Surface characterization of arsenopyrite during chemical and biological oxidation

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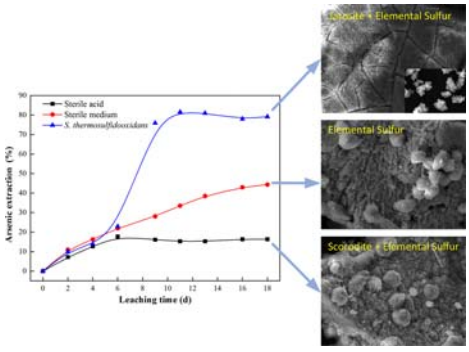
HIGHLIGHTS

- The chemical and biological oxidation of arsenopyrite were comparatively studied.
- Surface properties were investigated by synchrotron radiation based techniques.
- Passivation occurred during acid leaching and bioleaching of arsenopyrite.
- Elemental sulfur cannot lead to depressed dissolution of arsenopyrite.
- This study helps assess the environmental risk of arsenic.

GRAPHICAL ABSTRACT



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ABSTRACT

The surface properties of arsenopyrite during chemical and biological oxidation were investigated by synchrotron X-ray diffraction (S-XRD), X-ray absorption near-edge structure (XANES) and scanning electron microscope (SEM), accompanying with leaching behaviors elucidation. The moderate thermophile *S. thermosulfidooxdians* was used as the bioleaching microorganism. Leaching experiments showed that only 16.26% and 44.37% of total arsenic extractions were obtained for sterile acid and culture medium controls, whereas 79.20% of total arsenic was recovered at the end of bioleaching. SEM indicated that new products were layered on the surface of arsenopyrite after chemical and biological oxidation. As displayed in S-XRD patterns, scorodite and elemental sulfur were formed after acid leaching, while only elemental sulfur was detected in the residue leached by acid culture medium. During bioleaching, elemental sulfur was produced from day 4 and jarosite was produced from day 9. The results of iron and arsenic L-edge XANES were in good consistence with S-XRD. The accumulation of scorodite and jarosite on arsenopyrite surface should be the main reason for the hindered dissolution of arsenopyrite during acid leaching and bioleaching. These studies are pretty meaningful for better understanding the oxidation mechanism of arsenopyrite and evaluating arsenic risk to the environment.

1. Introduction

With the unceasing depletion of the oxidized gold ore deposits, more and more attention has been focused on the gold-containing ores (Sanchez and Hiskey, 1988). Arsenopyrite, as one of the most important gold-bearing minerals, often carries a significant portion of "invisible" gold that can be liberated via chemical and biological oxidation in acidic conditions (Beattie and Poling, 1987; Cruz et al., 1997; Maddox et al., 1998). However, the oxidation of arsenopyrite in mine wastes would release considerate sulfates, protons and toxic arsenic ions, and then contribute to the generation of acid mine drainage (AMD), which

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is one of the challenging environmental problems in the world (Pagnanelli et al., 2008; Lefebvre et al., 2012). As to optimize the pretreatment process of refractory gold ores and to control AMD, an in-depth study on the dissolution mechanisms during the chemical and biological oxidation of arsenopyrite is required.

In most cases, the dissolution of arsenopyrite is inhibited due to the formation of passivation layers on the surface. Therefore, in order to make the passivation mechanism clear, it is necessary to study the surface chemistry during the chemical and biological oxidation of arsenopyrite. A range of techniques such as X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Raman microspectroscopy and scan electron microscopy (SEM), have been widely used in the detection of the surface products. It is found that elemental sulfur, arsenolite, jarosite, iron hydroxides, amorphous ferric arsenate/scorodite and ferric phosphate are possible intermediate and secondary products in the oxidation process of arsenopyrite (Corkhill et al., 2008; Henao and Godoy, 2010; Fantauzzi et al., 2011; Márquez et al., 2012; Fomchenko and Muravyov, 2014; Zhu et al., 2014). But the chemical composition of the passivation layers is still matter of debate. Lin and Zheng (1996) investigated the electrochemical oxidation of arsenopyrite and found that the oxidation of arsenopyrite was retarded by the elemental sulfur coating, which was confirmed by Cruz et al. (1997). Cruz et al. also proposed that ferric arsenate was another major component of passivation layers on arsenopyrite surface, as reported by Fernandez et al. (1995). In addition, Buckley and Walker (1988) and Nesbitt et al. (1995) pointed out that the formation of metal-deficient, S-rich surface layers accounted for the hindered dissolution of arsenopyrite.

Synchrotron radiation provides a very intense and tunable source of continuous radiation from the far-IR to the hard X-ray (Acres et al., 2010; Young, 2014), and it has been successfully used in studies on mineral surface chemistry due to the high spatial resolution and high surface sensitivity. For example, to uncover the dissolution mechanism of chalcopyrite, the intermediate and secondary phases formed during chalcopyrite leaching have been widely characterized by S-XRD (Synchrotron X-ray diffraction), XANES (X-ray near-edge absorption structure), and S-XPS (Synchrotron X-ray photoelectron spectroscopy) (He et al., 2009; Acres et al., 2010; Xia et al., 2010; Majuste et al., 2013; Yang et al., 2013; Yang et al., 2015a). These studies are of significant guidance for investigating the chemical and biological oxidation of arsenopyrite.

In this paper, the surface chemical information of arsenopyrite leached in sterile acid, sterile acid culture medium with and without the moderate thermophile *S. thermosulfidooxidans* were studied by SEM, S-XRD and XANES. Based on these studies, we hope to provide some new information for arsenopyrite dissolution during the chemical and biological oxidation.

2. Materials and methods

2.1. Mineral samples

The arsenopyrite samples used in the study were obtained from Huangganglang Mining Area in eastern Inner Mongolia, China. The samples were prepared by crushing, hand-sorting to remove the gangue minerals, grinding and dry-sieving to 0.037–0.074 mm (200–400 mesh, Tyler series). Then the samples were placed in a 125 mL jar purged with nitrogen and stored in the refrigerator at 4 °C for experiments. Fig. 1 presents the S-XRD pattern and SEM photograph of the arsenopyrite samples. The chemical composition analysis showed that the samples contained Fe 33.93%, As 43.58%, S 22.74% (94.92% FeAsS).

The jarosite samples for XANES were synthesized by reference (Dutrizac and Kaiman, 1976). The scorodite samples were provided by the School of Metallurgy and Environment, Central South University, China.

2.2. Microorganisms

The *S. thermosulfidooxidans* strains used in the study were provided by the Key Laboratory of Biometallurgy, Ministry of Education, Central South University, China. *S. thermosulfidooxidans* was cultivated aerobically at 48 °C in the 9 K medium composed of $(NH_4)_2SO_4$ 3 g/L, K_2HPO_4 0.5 g/L, $MgSO_4 \cdot 7H_2O$ 0.5 g/L, $Ca(NO_3)_2$ 0.01 g/L, KCl 0.1 g/L and $FeSO_4 \cdot 7H_2O$ 44.7 g/L (Silverman and Lundgren, 1959). 0.02% (wt/vol) yeast extracts were also added in the medium. The initial pH was adjusted to 1.6 with 20% sulfuric acid. The rotating speed of the rotary shaker was set as 165 r/min.

2.3. Leaching tests

The leaching tests were performed in 250 mL Erlenmeyer flasks containing 100 mL sterilized acid or iron-free 9 K medium. The sterilized acid was prepared from 100 mL sterilized distilled water and then adjusted to pH = 1.6 with 20% sulfuric acid. The sterilized iron-free 9 K medium was the same as the culture medium mentioned above, except for no $FeSO_4 \cdot 7H_2O$, and the initial pH was adjusted to 1.6 with 20% sulfuric acid. 1 g arsenopyrite was added in each flask. The initial cell concentration was 2×10^7 cells/mL for inoculated systems. The rotating speed and temperature of the rotary shaker were set as 165 r/min, 48

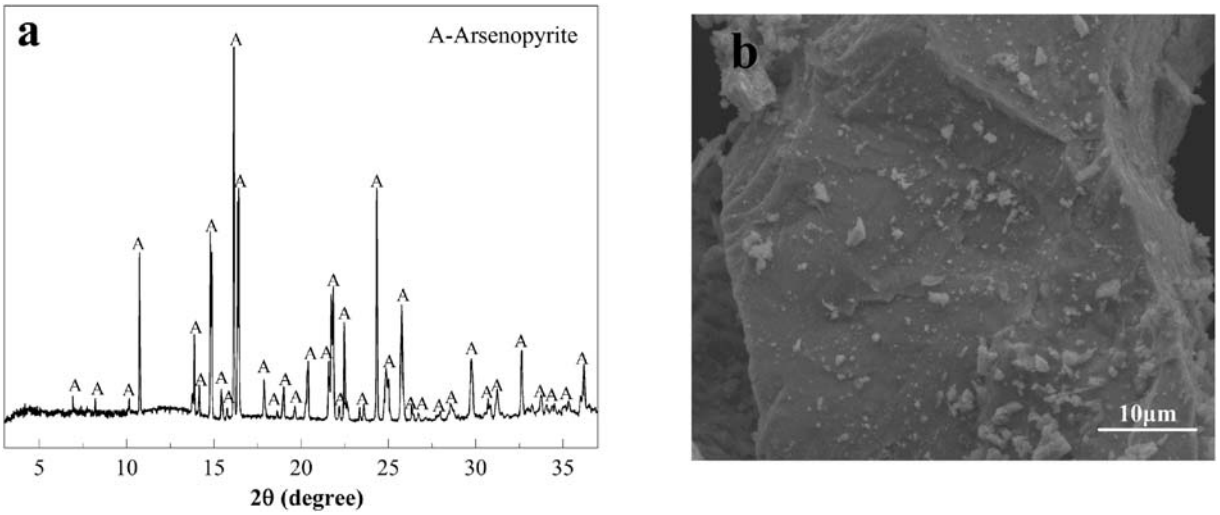

Fig. 1. The S-XRD pattern (a) and SEM image (b) of the arsenopyrite samples.