Minerals Engineering 95 (2016) 74–78

Contents lists available at ScienceDirect

Minerals Engineering

journal homepage: www.elsevier.com/locate/mineng

Catalytic effect of polyethylene glycol on sulfur oxidation in chalcopyrite bioleaching by *Acidithiobacillus ferrooxidans*

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ARTICLE INFO

Article history:
Received 13 March 2016
Revised 18 June 2016
Accepted 19 June 2016
Available online 24 June 2016

Keywords:
Polyethylene glycol
Chalcopyrite
Acidithiobacillus ferrooxidans
Bioleaching
Elemental sulfur

ABSTRACT

Polyethylene glycol (PEG) was used as a catalyst to enhance chalcopyrite bioleaching with *Acidithiobacillus ferrooxidans* in shake flasks. The effects of PEG on the sulfur oxidation of *A. ferrooxidans* and on the process of chalcopyrite bioleaching were investigated. The morphology, main components and sulfur speciation of bioleached chalcopyrite surfaces were evaluated combining with XRD, SEM and XPS. It was demonstrated that addition of PEG could significantly improve the bioleaching of chalcopyrite. Furthermore, the results indicated that elemental sulfur and jarosite were the main components of the passivation layer during the bioleaching of chalcopyrite. PEG could promote the sulfur oxidation by *A. ferrooxidans* due to an increase in bacterial attachment, and therefore accelerate the biooxidation of elemental sulfur generated in leaching process. It was found that PEG eliminated inhibitory elemental sulfur from the chalcopyrite surface which could be the main reason for enhanced the leaching efficiency.

1. Introduction

Chalcopyrite ($CuFeS_2$) is the most abundant copper-containing mineral in the Earth's crust, accounting for approximately 70% of total copper reserves worldwide (Panda et al., 2015). The commercial application of mesophilic bioleaching to chalcopyrite is limited due to low copper recovery and slow dissolution kinetics. These phenomena have been attributed to its high lattice energy and the formation of a passivation layer such as elemental sulfur, jarosite, polysulphides and metal-deficient sulphides (Harmer et al., 2006; Kinnunen et al., 2006; Pradhan et al., 2008; Sasaki et al., 2009). It was reported that an increase in sulfur oxidation activity of bacteria could increase the dissolution rate of chalcopyrite through reducing the accumulation of sulfur by transforming it into sulfuric acid, suggesting the significance of enhancing the sulfur oxidation in chalcopyrite bioleaching (Zhang et al., 2008).

In addition, several studies have shown that the addition of surface-active compounds, especially non-ionic surfactants such as polysorbate (Tween) and polyoxyethylene alkylphenol ether (OP-10), could result in an enhanced bioleaching performance of minerals such as chromite overburden, cobalt ore, and sulphide gold ores (Deng et al., 2000; Behera and Sukla, 2012; Liu et al., 2015). In the case of chalcopyrite bioleaching, only Tweens such as Tween-20 (polyoxyethylene sorbitan monolaurate), Tween-60 (polyoxyethylene monostearate) and Tween-80 (polyoxyethylene monooleate) have been used (Duncan et al., 1964; Peng et al., 2012). For example, Peng et al. (2012) reported that the copper extraction yield of chalcopyrite increased by 16% with the addition of Tween-80. It is found that polyethylene glycol (PEG) is a potential surfactant for improving chalcopyrite leaching due to rich in oxyethylene groups, good wettability, non-toxicity and chemical stability (Duncan et al., 1964; Fruijtier-Pölloth, 2005; Marchal et al., 2008; Gullapalli and Mazzitelli, 2015). However, PEG was not used as a surfactant in chalcopyrite bioleaching in the previous studies.

This work aims to investigate chalcopyrite leaching by *A. ferrooxidans* in the absence and presence of PEG in order to evaluate the possibilities of PEG as a catalyst in chalcopyrite bioleaching. The effects of PEG on sulfur oxidation by *A. ferrooxidans* and on characteristics of bioleached chalcopyrite surfaces are studied to investigate the role of PEG in chalcopyrite bioleaching.

2. Materials and methods

2.1. Minerals and bacteria

Chalcopyrite was obtained from Yunnan province, China, for use in this study. The chalcopyrite lumps were crushed manually and hand selected. Next, the isolated high-purity samples were ground in an agate mortar until all particles passed through a 45-μm filter. The primary chemical composition was determined to be 32.84% Cu, 33.10% S and 29.62% Fe.

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http://dx.doi.org/10.1016/j.mineng.2016.06.021
0892-6875/

Acidithiobacillus ferrooxidans strain XZ11 (Accession number KJ573102 of 16S rDNA in GenBank) isolated from an acid mine drainage in Tibet, China, was used in this study. The 9 K and sulfur-containing media used in this work were composed of basal salts medium supplemented with 44.2 g/L $FeSO_4 \cdot 7H_2O$ and 1 g/L S^0 as energy substrates, respectively. Basal salts medium consisted of the following compounds (g/L): $(NH_4)_2SO_4$ 3.0; KCl 0.1; K_2HPO_4 0.5; $MgSO_4 \cdot 7H_2O$ 0.5; and $Ca(NO_3)_2$ 0.01. The initial pH value was adjusted to 2.0 with H_2SO_4. All reagents were of analytical grade, except PEG 2000, which was chemically pure.

2.2. Experimental procedures

A. ferrooxidans cells used for inoculums in bacterial attachment and bioleaching experiments were prepared as follows. Bacterial cells grown in 9 K medium were collected during the stationary phase. To remove precipitates, the culture was initially filtered with Whatman filter paper No. 42. The filtrate was then centrifuged at 10,000 rpm for 15 min. Finally, the cell pellet was washed and suspended in basal salts medium to obtain metabolite-free cells.

Bacterial attachment on sulfur was studied according to a published procedure (Otero et al., 1995). The experiment was conducted in 250-mL flasks, containing 100 mL basal salts medium, 1% (w/v) powdered sulfur and a predetermined amount of PEG 2000. The initial cell density was adjusted to 5×10^7 cells/mL. All flasks were shaken at 160 rpm and 30 °C for 30 min to allow for bacterial attachment. The obtained suspended liquid was then filtered to determine the cell number in the filtrates. The number of bacteria attached on the sulfur was calculated by the difference between initial cell number and residual cell number.

The effects of PEG on the sulfur oxidation by *A. ferrooxidans* were tested in 250-mL flasks on a rotary shaker at 160 rpm and 30 °C. Each flask contained 90 mL of sulfur-containing medium, a predetermined amount of PEG 2000, and 10 mL bacterial cells that had been harvested during the stationary phase in 9 K medium. The pH value of the sulfur-containing medium was determined at regular intervals.

Bioleaching experiments were conducted in 250-mL flasks, containing 100 mL basal salts medium, 1% (w/v) chalcopyrite sample and 90 mg/L PEG 2000. The flasks were maintained at 30 °C and shaken at 160 rpm. The initial cell density was adjusted to 1×10^7 cells/mL. Samples were collected at regular intervals to determine the concentrations of total iron, ferrous iron and copper ions. Evaporative water loss was compensated for with deionized water, and the sampling loss was compensated for with basal salts medium. After a 21-day leaching period, the residues were collected and washed with deionized water, and subjected to SEM, XRD and XPS tests after a drying treatment.

2.3. Analyses

The pH values were determined using a pH meter (Sartorius PB-10). The ferrous iron concentration was determined by titration with potassium dichromate using sodium diphenylamine sulphonate as the indicator. The concentrations of total iron and copper ions were measured by inductively coupled plasma optical emission spectroscopy (ICP-OES). The ferric iron concentration was calculated as the difference between total and ferrous iron. The cell density was monitored using blood cell counting chambers and a Motic BA210 microscope. The components of the leached residues were analyzed by X-ray diffractometer (XRD, PAN-alytical X'Pert Pro). The morphology of leached chalcopyrite surfaces was examined by scanning electron microscope (SEM, ZEISS Ultra Plus). The sulfur speciation of leached chalcopyrite surfaces was determined by X-ray photoelectron spectroscope (XPS, ESCALAB 250).

3. Results and discussion

3.1. Effect of PEG on sulfur oxidation by A. ferrooxidans

Since the attachment of *A. ferrooxidans* onto elemental sulfur is considered to be a necessary part of the bacterial oxidation process (Pakostova et al., 2013), the attachment of bacteria on sulfur was firstly examined. Fig. 1 shows the effect of PEG on the bacterial attachment to sulfur. The attachment percentage of *A. ferrooxidans* attachment on sulfur was relatively low in the absence of PEG. The addition of PEG significantly improved attachment performance, and the percentage increased with increasing PEG amount. This is because PEG molecules with ether and terminal hydroxyl groups can coordinate elemental sulfur (Wu et al., 2008; Niu et al., 2013), resulting in high hydrophilicity of elemental sulfur particles and increase in attachment ability of *A. ferrooxidans* with good hydrophilicity.

Along with elemental sulfur being oxidized to sulfuric acid by *A. ferrooxidans*, the pH value of sulfur-containing media decreases, as shown in Eq. (1). Therefore, the extent of the bacterial sulfur oxidation can be monitored indirectly by measuring the change in the pH of the solution. The variation in the pH of sulfur-containing media containing various PEG concentrations in the presence of *A. ferrooxidans* is shown in Fig. 2. These results indicated that the pH value of sulfur-containing media decreased more rapidly in the presence of PEG, regardless of concentration. The addition of

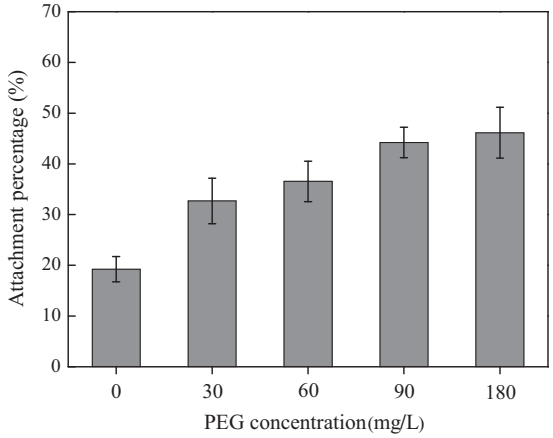

Fig. 1. Attachment percentage of *A. ferrooxidans* to sulfur at various PEG concentrations.

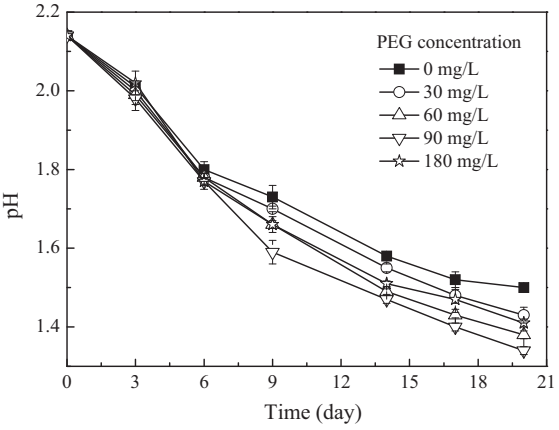

Fig. 2. Variations in the pH of sulfur-containing media in the presence of *A. ferrooxidans* at various PEG concentrations.