Available online at www.sciencedirect.com
ScienceDirect
Trans. Nonferrous Met. Soc. China 27(2017) 1374−1384
Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

Relatedness between catalytic effect of activated carbon and passivation phenomenon during chalcopyrite bioleaching by mixed thermophilic Archaea culture at 65 °C

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Received 23 March 2016; accepted 21 February 2017

Abstract: The relatedness between catalytic effect of activated carbon and passivation phenomenon during chalcopyrite bioleaching by mixed thermophilic Archaea culture (*Acidianus brierleyi*, *Metallosphaera sedula*, *Acidianus manzaensis* and *Sulfolobus metallicus*) at 65 °C was studied. Leaching experiments showed that the addition of activated carbon could significantly promote the dissolution of chalcopyrite for both bioleaching and chemical leaching. The results of synchrotron-based X-ray diffraction, iron L-edge and sulfur K-edge X-ray absorption near edge structure spectroscopy indicated that activated carbon could change the transition path of electrons through galvanic interactions to form more readily dissolved secondary mineral chalcocite at a low redox potential (<400 mV) and then enhanced the copper dissolution. Jarosite accumulated immediately in the initial stage of bioleaching with activated carbon but copper dissolution was not hindered. However, much jarosite precipitated on the surface of chalcopyrite in the late stage of bioleaching, which might account for the decrease of copper dissolution rate. More elemental sulfur (S^0) was also detected with additional activated carbon but the mixed thermophilic Archaea culture had a great sulfur oxidation activity, thus S^0 was eliminated and seemed to have no significant influence on the dissolution of chalcopyrite.

Key words: chalcopyrite; bioleaching; activated carbon; passivation phenomenon; mixed thermophilic Archaea culture

1 Introduction

As the most abundant but refractory copper sulfide, chalcopyrite has still not been successfully bioleached on a commercial scale [1]. However, with the increasing consumption of global copper resources and the decreasing reserves of high grade copper ores, it is necessary to extend the application of bioleaching, which is eco-friendly for the treatment of low grade copper sulfide. Commercial application of chalcopyrite bioleaching has been restricted by its extremely slow dissolution kinetics and low copper recovery because of the formation of a passivation layer on the mineral surface [2].

Over the past decades, although comprehensive investigations employing surface analytical methods (such as X-ray photoelectron spectroscopy, X-ray absorption spectroscopy, and Raman spectroscopy) have been conducted to evaluate the passivation layer, researchers have not yet reached a consensus about the chemical compositions of the passivation layer, for example, ferric precipitates (jarosite) [3], elemental sulfur (S^0) [4] and polysulfide (S_n^{2-}) [5] were reported.

On the other hand, in order to enhance the leaching rate and overcome the inhibitory effect of the passivation

Foundation item: Project (51274257) supported by the National Natural Science Foundation of China; Project (U1232103) supported by the Joint Funds of National Natural Science Foundation of China and Large Scientific Facility Foundation of Chinese Academy of Sciences; Project (VR-12419) supported by the Beijing Synchrotron Radiation Facility Public User Program, China; Project (15ssrf00924) supported by the Shanghai Institute of Applied Physics Open Fund of Shanghai Synchrotron Radiation Facility, China
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DOI: 10.1016/S1003-6326(17)60158-4

layer, several strategies have been proved to be beneficial to increasing the copper recovery rate, for instance, bioleaching of chalcopyrite with thermophilic Archaea strains, adding modifier (surfactants, activated carbon and silver) and controlling the redox potential. WAN et al [6] exhibited for the first time that the formation of chalcopyrite/carbon aggregates enhanced the dissolution rate of chalcopyrite in the ferric sulfate leaching. After that, many researchers paid much attention to the positive effects of activated carbon on chalcopyrite bioleaching [7−11], which indicated that the catalytic effect was attributed to the galvanic interaction between chalcopyrite and activated carbon. Galvanic interaction is based on the contact between chalcopyrite and activated carbon with different rest potentials. The activated carbon with higher rest potential acts as cathode (Eq. (1)) and chalcopyrite with a lower rest potential serves as anode and is oxidized (Eq. (2)) [7].

$$O_2+4H^++4e \rightarrow 2H_2O \quad (1)$$

$$CuFeS_2 \rightarrow Cu^{2+}+Fe^{3+}+2S^0+5e \quad (2)$$

Chalcopyrite dissolution is a complex process including the chemical speciation transformation and evolution of three elements (S, Fe and Cu) on chalcopyrite surface [12−14]. When introducing activated carbon, the transition path of electrons could be changed and the composition and properties of chalcopyrite surface could be modified, finally affecting the sulfur oxidation activity of leaching microorganisms and the further dissolution of chalcopyrite [2]. It is still unclear how the passivation layer and the catalytic effect of additional activated carbon interact with each other to influence the dissolution of chalcopyrite.

The intermediate compounds formed during bioleaching are the keys to clarify the decomposition mechanism of chalcopyrite; however, usually their amounts are too small to be detected. Up to date, synchrotron radiation X-ray diffraction (SR-XRD) and X-ray absorption near edge structure (XANES) spectroscopy analysis have shown efficiency to study the composition on chalcopyrite surface with high spatial resolution and high sensitivity [15]. Therefore, by combining SR-XRD and XANES spectroscopy analysis, more details can be provided during chalcopyrite bioleaching with additional activated carbon.

In the present study, the relatedness between catalytic effect of activated carbon and passivation phenomenon during chalcopyrite bioleaching by mixed thermophilic Archaea culture (*Acidianus brierleyi, Metallosphaera sedula*, *Acidianus manzaensis* and *Sulfolobus metallicus*) and chemical leaching was investigated by combining iron L-edge and sulfur K-edge XANES spectroscopy as well as SR-XRD. It could be valuable for better understanding the dissolution mechanism of chalcopyrite during bioleaching by mixed thermophilic Archaea culture with additional activated carbon.

2 Experimental

2.1 Metal sulfide sample and activated carbon

The standard mineral samples including chalcopyrite ($CuFeS_2$), chalcocite (Cu_2S), covellite (CuS), bornite (Cu_5FeS_4), elemental sulfur (S^0) and jarosite ($KFe_3(SO_4)_2(OH)_6$) used in this study were provided by the School of Minerals Processing and Bioengineering, Central South University, China. The X-ray fluorescence analysis (Axios mAX, PANalytical, the Netherlands) showed that the original chalcopyrite contained 33.69% Cu, 29.62% Fe, 34.34% S, 1.91% O, 0.31% Si, 0.04% Al, 0.02% Ca, 0.01% Se and 0.02% P. XRD analysis (DX−2700, Haoyuan Instruments, Danyang, China) showed that the original chalcopyrite mineral is basically pure. Before the experiment, original chalcopyrite and activated carbon (spectrum grade) were first milled to powder and passed through a sieve of 37−74 μm.

2.2 Microorganisms and leaching experiments

It was reported that mixed culture of thermophilic Archaea could significantly promote the leaching rate of chalcopyrite due to a higher sulfur oxidation activity than that of the pure culture [16]. Consequently, a mixed culture of thermophilic Archaea containing *Acidianus brierleyi, Metallosphaera sedula, Acidianus manzaensis* and *Sulfolobus metallicus* was used as inoculum in the bioleaching experiment. The detailed description of these four thermophilic Archaea strains was as referred to Ref. [17]. The basal medium used for cell cultivation contained the following components: 3.0 g/L $(NH_4)_2SO_4$, 0.5 g/L $MgSO_4·7H_2O$, 0.5 g/L K_2HPO_4, 0.1 g/L KCl, 0.01 g/L $Ca(NO_3)_2$, and 0.2 g/L yeast extracts. The initial pH of the basal medium was adjusted to 1.5 with dilute sulfuric acid.

Bioleaching experiments were carried out in 250 mL of Erlenmeyer flasks containing 100 mL sterilized medium and 1 g chalcopyrite. According to previous research [11], the optimum concentration of activated carbon enhanced copper dissolution was 2 g/L during chalcopyrite bioleached by *Acidianus manzaensis* and the same concentration was applied in the present study. Activated carbon was mixed with chalcopyrite concentrate in a porcelain mortar and pestle for 5 min before they were added to the bioleaching system. The mixed thermophilic Archaea in the presence of 2 g/L or absence of activated carbon was incubated at 65 °C and 170 r/min in a high-temperature water-bath rotary shaker. The initial cell density was $1×10^7$ cell/mL. The two