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Dissolution and passivation mechanisms of chalcopyrite during bioleaching: DFT calculation, XPS and electrochemistry analysis

Jun Wang, Xiaowen Gan, Hongbo Zhao *, Minghao Hu, Kaiyun Li, Wenqing Qin, Guanzhou Qiu

School of Minerals Processing & Bioengineering, Central South University, Changsha 410083, Hunan, PR China
Key Lab of Biohydrometallurgy of Ministry of Education, Changsha 410083, Hunan, PR China

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ABSTRACT

In this work, density functional theory (DFT) calculation, X-ray photoelectron spectroscopy (XPS) and electrochemistry analysis were carried out to investigate the dissolution process and passivation mechanisms of chalcopyrite in the presence of sulfur and iron oxidizing microorganisms. Both DFT calculation and XPS analysis indicated that the formula of chalcopyrite should be Cu + Fe^3 + $(S^{2-})_2$. Disulfide (S_2^{2-}) and polysulfide (S_n^{2-}) can be easily formed on the surface of chalcopyrite due to the surface reconstruction. The dissolution process of chalcopyrite in bioleaching was mainly dependent on redox potential. Chalcopyrite was predominantly directly oxidized to polysulfide when redox potential was lower than about 350 mV vs. Ag/AgCl and resulted in low dissolution rate. When redox potential was in the range of about 350–480 mV vs. Ag/AgCl, chalcopyrite was mainly transformed to intermediate species of Cu_2S rather than polysulfide, thus resulting in high dissolution rate. When redox potential was higher than about 480 mV vs. Ag/AgCl, chalcopyrite was principally directly oxidized to polysulfide which caused the passivation of chalcopyrite. Finally, a model of dissolution and passivation mechanisms of chalcopyrite in the presence of sulfur and iron oxidizing microorganisms was provided.

1. Introduction

Bioleaching of chalcopyrite ($CuFeS_2$) is an important research topic because it is still faced with the challenge of low dissolution kinetics (Li et al., 2013; Watling, 2006). To enhance chalcopyrite bioleaching, the dissolution and passivation mechanisms should be firstly interpreted. Many efforts have been made to investigate the dissolution and passivation mechanisms of chalcopyrite bioleaching. They mainly proposed that polysulfide (S_n^{2-}), elemental sulfur (S^0) and jarosite (SO_4^{2-}) were the plausible passivating species in chalcopyrite bioleaching. For example, Ghahremaninezhad et al. (2013) proposed that the formed metal-deficient polysulfide (S_n^{2-}) caused the passivation of chalcopyrite. Similarly, Parker et al. (1981) found that polysulfide was formed during oxidation of chalcopyrite semiconductor which hindered the transfer rate of electrons and ions. What is more, Hackl et al. (1995) utilized XPS to analyze the passivation layer mainly consisted of CuS_n polysulfide whose thickness is less than 1 μm and found that the dissolution process conformed with a mixed diffusion/chemical reaction model. Similar conclusion was also proposed by Yang et al. (2013), they investigated the dissolution process of chalcopyrite in bioleaching by XANES and found that polysulfide formed as the preferential dissolution of Fe and caused the passivation of chalcopyrite. Some researchers proposed that elemental sulfur should be the main passivating species, for instance, Klauber et al. (2001) used XPS to investigate the passivation mechanisms of chalcopyrite and proposed that elemental sulfur (S^0) rather than polysulfide should be the main passivating species. Similar mechanisms were also proposed by some other researchers (Bevilaqua et al., 2004; Dutrizac, 1989; Khoshkhoo et al., 2014; Munoz et al., 1979). As for passivating species of jarosite, Sandström et al. (2005) studied the dissolution process of chalcopyrite during bioleaching in the presence of extremely thermophilic microorganism and proposed that elemental sulfur can be oxidized to sulfate (SO_4^{2-}) even at low redox potential, and the formed sulfate mainly consisting of jarosite caused the final passivation of chalcopyrite. Similar viewpoint was also provided by Zhu et al. (2011), they used Raman spectrum and XANES to prove that jarosite was the main component of passivation layer during chalcopyrite bioleaching. However, Crundwell (2015) and Crundwell et al. (2015) proposed that the rate of chalcopyrite dissolution was not limited by passivation film or layers, but was intrinsically slow due to the semiconducting properties of chalcopyrite. He identified chalcopyrite anodic dissolution as depletion region

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* Corresponding author at: Key Lab of Biohydrometallurgy of Ministry of Education, Changsha 410083, PR China.
E-mail address: alexandercsu@126.com (H. Zhao).

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(0.3–0.6 V vs. SCE) and inversion region (more than 0.7 V vs. SCE) for ideal n-type semiconductor. In the depletion region, the current was limited by the depletion of electrons in the space-charge layer, and no reactions took place at the surface to supply electrons in this region. Hiskey (1993) proposed that chalcopyrite was predominantly an n-type semiconductor and holes were the minority charge carrier, so the anodic dissolution initially involved the consumption of a hole and Fermi level pining should account for the charge-transfer behavior for various redox couples. In addition, thin metal-deficient surface layer produced in passive region with thickness of about 3 nm also hindered the further dissolution of chalcopyrite. Hence, the proposed passivation mechanisms are different and the specific mechanism is still in debate even though many efforts have been made before. Moderately thermophilic microorganisms (*Acidithiobacillus caldus*, *Sulfobacillus thermosulfidooxidans* and *Leptospirillum ferriphilum*, etc.) are considered promising in the industrial application due to their advantages when compared to mesophilic microorganisms and extremely thermophilic microorganisms (Olson et al., 2003; Rohwerder et al., 2003; Watling, 2006). Surface reconstruction refers to a process by which atoms at the crystal surface assume a different structure than that of the bulk. When a surface is introduced to the system by terminating the crystal along a given plane, the altered forces would change the equilibrium positions of the remaining atoms and cause the atoms near the surface assuming positions with different spacing and/or symmetry from the bulk atoms, resulting in creating a different surface structure. Density functional theory (DFT) can be used for calculating and simulating the structure of chalcopyrite and surface reconstruction of chalcopyrite. X-ray photoelectron spectroscopy (XPS) is a sensitive surface analysis method to analyze thin films. Electrochemistry analysis is essential for interpreting the dissolution mechanisms because the bioleaching process of chalcopyrite is consisted of complex oxidation-reduction reaction.

Therefore, DFT calculation, XPS and electrochemistry analysis were carried out to investigate the dissolution process and passivation mechanisms of chalcopyrite in the presence of moderately thermophilic microorganisms. A model of dissolution and passivation mechanisms of chalcopyrite bioleaching was provided.

2. Materials and methods

2.1. Structure input of chalcopyrite

The structure for bulk chalcopyrite structure geometry optimization was obtained from online crystal database and verified by other references (Burdick and Ellis, 1917; de Lima et al., 2012; de Oliveira et al., 2012; de Oliveira and Duarte, 2010; Elliot, 2010; Hall and Stewart, 1973; Li et al., 2013; Wen et al., 2013). Chalcopyrite is a ternary metal sulfide which contains copper, iron and sulfur, with a molecular formula of $CuFeS_2$. Chalcopyrite is a covalent compound which means that the bonds between metal atoms and sulfur atoms are not like ionic bonds and the oxidation states of copper and iron should not be stoichiometric. And the structure of chalcopyrite is isostructural with sphalerite (ZnS), while the c-parameter of unit cell of chalcopyrite is approximately twice the length of the unit cell of sphalerite. The chalcopyrite unit cell contains 4 Cu atoms, 4 Fe atoms and 8 S atoms. In each half unit cell of chalcopyrite along the c-parameter, the four Zn atoms in the corresponding sphalerite unit cell are replaced by 2 Cu atoms and 2 Fe atoms in the tetrahedral interstices produced by S atoms. Each S atom is coordinated by a tetrahedron of four metal atoms (two Fe and two Cu) while in contrast each metal atom is coordinated by a tetrahedron of S atoms, but the positions of S atoms are slightly skew due to influences of the metal atoms.

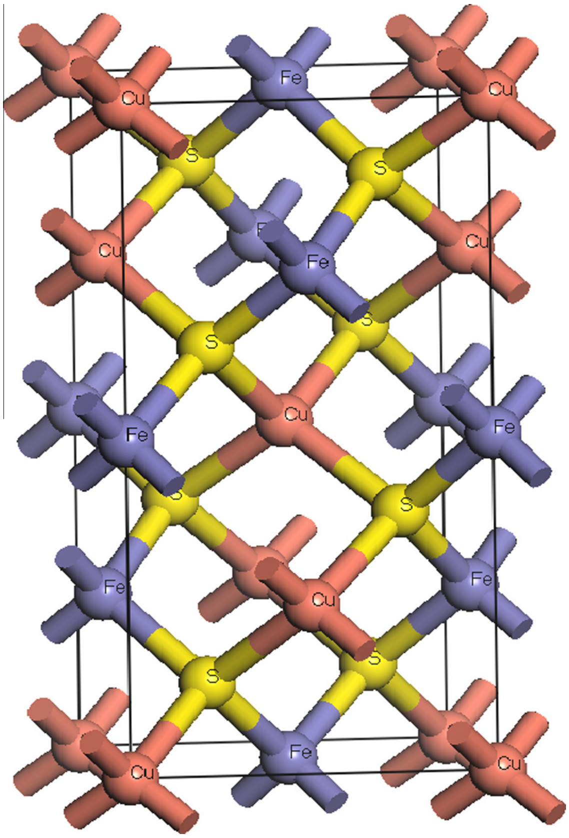

Fig. 1. Initial structure of chalcopyrite.

The cell of chalcopyrite crystal is shown in Fig. 1. Chalcopyrite is in the tetragonal system and its space group is I-42d, and the cell parameters of perfect chalcopyrite cell in the database are listed below: a = b = 5.289 Å, c = 10.4230 Å (Hall and Stewart, 1973; Li et al., 2013). Chalcopyrite is an antiferromagnetic substance at room temperature, so different spin directions of Fe atoms at

Table 1
Comparison of simulation and references.

Properties	In this simulation (Å)	Values of references (Å)
Crystal constants	a = b = 5.30532 c = 10.3985	a = b = 5.28900 c = 10.4230
Distances between atoms	Fe—S = 2.258 Cu—S = 2.307	Fe—S = 2.257 Cu—S = 2.302

Table 2
Bond population analysis.

Bond	Population	Length (Å)
S—Fe	0.50	2.25773
S—Cu	0.35	2.30690

Table 3
Mulliken population analysis.

Species	s	p	d	Total	Charge (e)
S	1.82	4.50	0.00	6.32	−0.32
Fe	0.49	0.64	6.40	7.54	0.46
Cu	0.53	0.51	9.79	10.83	0.17