

A fundamental DFT study of chalcopyrite surface evolution due to impurity divalent ions during leaching process

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ABSTRACT

Chalcopyrite leaching process is hindered predominantly due to the passivation layers formed on its surface. The impurity salts normally present in the leaching systems may influence chalcopyrite leaching process. In this work, density functional theory (DFT) was carried out to investigate the influence of Mg^{2+} and Ca^{2+} on chalcopyrite (0 0 1)-S surface using Materials Studio. The results indicated that the presence of $CaSO_4$ contributed to the breakage of S–S bonds on chalcopyrite (0 0 1)-S surface. Although Ca^{2+} was not found to bond with any of the S atoms derived from broken S_2^{2-} bond, a stable structure of $Ca-SO_4-Fe$ was formed. Similarly, the adsorption of $MgSO_4$ on chalcopyrite (0 0 1)-S surface contributed to the breakage of S_2^{2-} bond, forming a complex and stable structure of $S-Mg-SO_4-Fe$ as new passivation layers due to the bonding effects between Mg^{2+} and a S atom from the broken S_2^{2-} bond. The formation of these new structures covered on chalcopyrite (0 0 1)-S surface, further reducing chalcopyrite leaching rates. This study, therefore for the first time, reveals the influencing mechanisms of Mg^{2+} and Ca^{2+} sulfates on chalcopyrite leaching at an atomic level.

1. Introduction

Chalcopyrite ($CuFeS_2$), as one of the most abundant copper-bearing minerals in nature (Dutrizac, 1978), occupies approximately 70% of the Earth's copper reserve (Córdoba et al., 2008). Although pyrometallurgical methods are predominantly used to process high grade chalcopyrite concentrates effectively (Ruiz-Sánchez and Lapidus, 2017), it leads to extensive environmental problems especially air pollution including SO_2 emission (Mahajan et al., 2007). In addition, it is not economically suitable to treat chalcopyrite with progressively decreased grade. As an alternative to pyrometallurgical methods, hydrometallurgical strategies for chalcopyrite present various advantages such as lower costs and more environmentally friendly characteristics (Córdoba et al., 2008; Li et al., 2013).

It has been reported that copper produced worldwide via hydrometallurgy only accounts for 17% in 2016 (ICSG, 2016), mainly deriving from copper oxide and secondary sulfide minerals (Khoshkhou et al., 2014). To date, hydrometallurgical processing of chalcopyrite has not been widely adopted in industry implementation due predominantly to its extremely slow leach kinetics (Hiroyoshi et al., 2002; Nazari et al., 2012; Pan et al., 2012; Watling, 2013; Watling, 2014). The slow leaching process of chalcopyrite is generally ascribed to the formation of passivation layers on chalcopyrite surface, inhibiting efficient

contact between leaching lixiviant and chalcopyrite (Córdoba et al., 2009; Harmer et al., 2004; Klauber et al., 2001; Parker et al., 2003; Tshilombo, 2004). However, no unanimously accepted theories as to chalcopyrite passivation mechanisms (Córdoba et al., 2008; Li et al., 2010) were achieved due to various conditions applied for chalcopyrite leaching experiments (Nicol et al., 2010).

In addition, chalcopyrite normally co-exists with gangue minerals in natural environment, such as pyrite, gypsum, quartz, feldspar, talc, chlorite (Hiroyoshi et al., 2007; Leahy and Schwarz, 2009; Qian et al., 2014). These gangue minerals can be dissolved along with chalcopyrite dissolution, inevitably releasing various ions into the leach system. Although various chalcopyrite dissolution studies have been conducted (Debernardi and Carlesi, 2013; Li et al., 2013; Ruiz-Sánchez and Lapidus, 2017; Watling, 2013; Xian et al., 2012), the effects of soluble cationic impurities that generally available have not attracted much attention (Qian et al., 2014).

Some research indicated that these ions played differing roles in chalcopyrite leaching process. For example, Hiroyoshi et al. (2007) reported that the critical potential of solution was increased due to the induction of Ag^+ or Bi^{3+} during chalcopyrite leaching process. Dopson et al. (2009) reported that the dissolution of silicate minerals (olivine, biotite, augite and hornblende, etc.) affected heap bioleaching conditions, e.g. the solution pH was increased due to the dissolution of olivine

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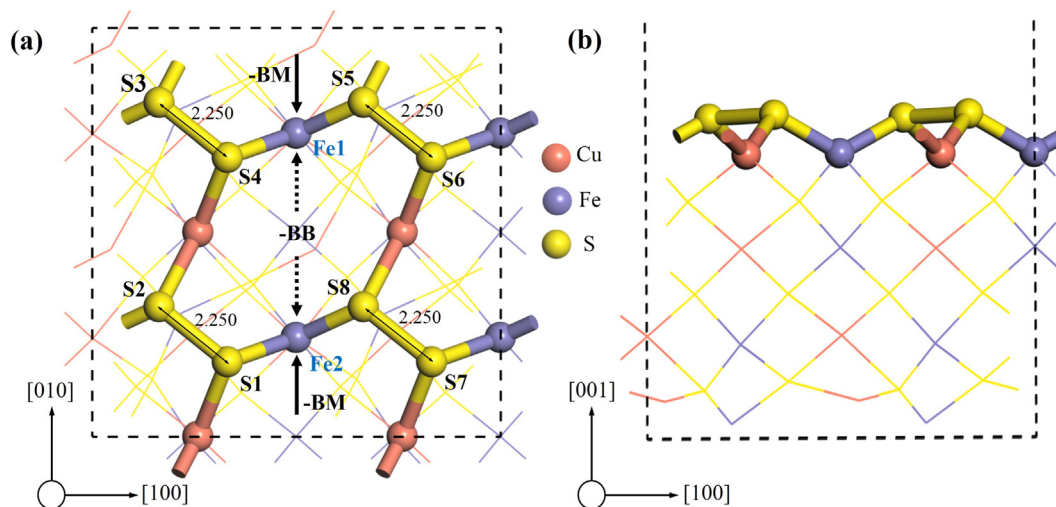


Fig. 1. Adsorption sites on chalcopyrite (001)-S surface. (a) top view, (b) side view.

and biotite while the dissolution of augite and hornblende resulted in the precipitation of jarosite on chalcopyrite surface. In addition, the presence of sulfate and some metal ions such as Na^+ , K^+ and Fe^{3+} could also produce jarosite during chalcopyrite leaching process (Córdoba et al., 2008). Therefore, metal ions (e.g. Na^+ , K^+ , Ca^{2+} , Mg^{2+}) can influence the formation of passivation layers (Córdoba et al., 2009; Dopson et al., 2009; Qian et al., 2014; Sokic et al., 2009), thereby resulting in different chalcopyrite leaching performance. This might also be one of the reasons that researchers cannot unify chalcopyrite leaching mechanisms due to the presence of various soluble impurities (e.g. Na^+ , K^+ , Ca^{2+} , Mg^{2+}) in differing leaching systems, although the effects of these impurities were not paid sufficient attention.

In order to better understand the modified chalcopyrite surface, density functional theory (DFT) simulation has been used to seek the underlying mechanisms (de Oliveira et al., 2012; de Oliveira and Duarte, 2010; Hung et al., 2002; Ke et al., 2016; Stirling et al., 2003; Von Oertzen et al., 2006). In addition to the reconstruction study of chalcopyrite surfaces (de Oliveira et al., 2012; de Oliveira and Duarte, 2010), de Lima et al. (2012) applied DFT to reveal the roles of sulfuric and hydrochloric acids on chalcopyrite surface. Wang et al. (2016) applied DFT, XPS and electrochemistry measurements to investigate the passivation mechanisms during chalcopyrite bioleaching process. However, not much fundamental attention has been paid to the effects of impurity ions on chalcopyrite surface during the leaching process.

Our previous leaching studies (Qian et al., 2017) indicated that the addition of 20 mM Fe, Al sulfate improved chalcopyrite leaching while the same amount of Mg or Ca sulfate reduced Cu extraction. However, no fundamental investigation was conducted to understand the negative roles of these two divalent impurities at an atomic scale. This work therefore will investigate the influence of divalent metal (i.e. Mg^{2+} and Ca^{2+}) sulfate on chalcopyrite leaching process at an atomic scale, based on our previous chalcopyrite leaching results (Qian et al., 2014; Qian et al., 2017) and methodology applied in the DFT modelling studies (Wei et al., 2016).

2. Methodology

The calculations in this study were performed using the same parameter settings as reported in our previous work (Wei et al., 2016), e.g. applying generalized gradient approximation (GGA) based on DFT in CASTEP module in Materials Studio. A kinetic energy cutoff of 351 eV and Monkhorst-Pack scheme with a $3 \times 3 \times 3$ k -point mesh for structure optimization and a $3 \times 3 \times 1$ k -point mesh for electronic structure calculation were applied, with the following valence configuration being adopted: Fe $3s^2 3p^6 3d^6 4s^2$, Cu $3d^{10} 4s^1$, S $3s^2 3p^4$, Mg

$2s^2 2p^6 3s^2$, Ca $3s^2 3p^6 4s^2$.

Similar to most of the published studies (de Lima et al., 2012; de Lima et al., 2011; de Oliveira et al., 2012; de Oliveira and Duarte, 2010; Li et al., 2014), the reconstructed chalcopyrite (001)-S surface (Wei et al., 2016) was selected for DFT simulation. The adsorption energy of ions adsorbed on chalcopyrite surface was calculated according to Eq. (1) (de Lima et al., 2012):

$$\Delta E_{\text{ads}} = E_{\text{surf}+\text{met}} - E_{\text{surf}} - E_{\text{met}} \quad (1)$$

where $E_{\text{surf}+\text{met}}$ is the total energy of the surface with the metal sulfate adsorbed, E_{surf} corresponds to the total energy of the reconstructed surface while E_{met} is the total energy of the metal sulfate. All these values were calculated in a box to calculate the surfaces at the Γ -point.

3. Results and discussion

3.1. Selection of adsorption sites

A $2 \times 2 \times 1$ reconstructed chalcopyrite (001)-S surface was used to simulate the adsorption process for both Mg^{2+} and Ca^{2+} . Our previous study (Wei et al., 2016) indicated that the adsorption sites for metal cations were more likely to be at S atom sites while the Fe atom was highly likely to be the most stable site for SO_4^{2-} adsorption in two possible coordination modes (de Lima et al., 2012), i.e. bidentate binuclear mode (-BB mode, dotted arrows) and bidentate mononuclear mode (-BM mode, solid arrow), as shown in Fig. 1.

Mg^{2+} or Ca^{2+} adsorption on different S sites (i.e. S1 ~ S8) was conducted on the reconstructed chalcopyrite (001)-S surface in the -BB mode where the SO_4^{2-} was found to be connected to both Fe1 and Fe2 sites. Once SO_4^{2-} was adsorbed at these two Fe sites, the adsorption of Mg^{2+} or Ca^{2+} at S atom sites 4 and 8 would be with low probability due to the short distance between the adsorbed metallic ion and SO_4^{2-} , e.g. Table 1 showed the greatest $d_{\text{Fe-O}}$ and ΔE values at both S4 and S8 sites. Apparently different ΔE values were observed between S3 and S4, S7 and S8. In contrast, no significant differences between S1 and S2, S5 and S6 were observed.

In -BM mode, S3, S4, S5 and S6 were not selected for the adsorption of metallic ions when Fe1 site was bonded with SO_4^{2-} due to short distance between the adsorbed metallic ion and SO_4^{2-} . In addition, slightly different ΔE values were observed between S1 and S2, S7 and S8 for the adsorption of Mg^{2+} , thus only S1 and S7 were selected for the adsorption of Ca^{2+} based on the symmetry.

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