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First-principle study on the oxidative leaching mechanism of sphalerite in Ammoniacal solution

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ABSTRACT

The oxidative leaching mechanism of sphalerite in ammoniacal solution was investigated by the combination of experimental method and first-principle calculations based on density functional theory. The interaction machanism of NH_3, O_2, and $Na_2S_2O_8$ with the ZnS (110) surface was investigated by first-principle calculations. The NH_3 molecule preferred to interact with the ZnS (110) surface at T_{Zn} with an interaction energy of −366.17 kJ/mol. The active site changed to B_{Zn} site on the ZnS (110) surface with the addition of oxidant (O_2 or $Na_2S_2O_8$). The Zn−S bond on the ZnS (110) surface was dissociated, where S^{2-} was oxidized into S_2^{2-}. Zn extraction was enhanced by the addition of the oxidants. In water, $S_2O_8^{2-}$ is more active than the O_2 molecule to interact with the ZnS (110) surface with an interactional energy of −588.77 kJ/mol. The effects of the kinds and amount of the oxidant on the Zn extraction were determined under optimum leaching condition ($[NH_3]$: $[NH_4^+]$ = 5:3, liquid to solid ratio = 25, temperature = 383 K and leaching time = 4 h). Experiment results showed that Zn extraction was significantly enhanced from 4.32% to 70.30% within 4 h at O_2 partial pressure of 0.50 MPa or to 28.40% with the addition of persulfate.

1. Introduction

Zinc sulfide (ZnS) ore, which is widely distributed in China, is a major raw material for Zn extraction. However, low-grade Zn ores have gained increasing attention because of their exhaustive risk in the Zn industry. Low-grade Zn ores, also called mixed sulfide–oxidized Zn ores, usually contain Zn oxide ores (such as smithsonite, hydrozincite, hemimorphite, and willemite), ZnS ores (such as sphalerite), and gangues, such as quartz, calcite, dolomite, and other useless minerals. The traditional method for recovery of Zn from ZnS ore includes roasting, acid leaching, and electrowinning (Pandey et al., 1982). However, this method is unsuitable for low-grade-mixed sulfide–oxidized Zn ores. Acids are highly consumed during acid leaching due to abundant alkaline oxides; as such, the formation of SiO_2 (aq) led to conduct the purification process difficultly (Frenay, 1985; Feng et al., 2007). To overcome the negative effects of the traditional method, scholars have focused on alkaline leaching (Feng et al., 2007; Hua et al., 2011; Zhao et al., 2010). Ammonia (NH_3) leaching is commonly used to extract nonferrous metals due to the formation of stable metal ammine complexes, which are highly soluble in most cases. Other harmful impurities, such as Fe, Pb, Ca, and Mg, precipitate as hydroxides because of their poor complexation ability with NH_3. Moreover, NH_3 leaching–electrowinning can be used to recover electrolytic Zn from Zn ores (Abbott et al., 2011; Abkhoshk et al., 2014; Gu et al., 2018; Hubert et al., 2007). Thus, ammoniacal solution can be recycled between leaching and electrowinning to protect the environment. Therefore, NH_3 leaching–electrowinning is a promising technique for treating low-grade Zn oxide ores. Several studies have been conducted on NH_3 leaching for Zn oxide ores and Zn dust (Feng et al., 2007; Rao et al., 2017; Yang et al., 2017). However, Zinc sulfide such as sphalerite always coexists with low-grade oxidized Zn ores to produce mixed sulfide–oxidized Zn ores. Sphalerite is refractory with direct NH_3 leaching. The oxidative NH_3 leaching is an effective method for simultaneous treatment of sulfide and oxidized Zn ores (Liu et al., 2017; Ghosha et al., 2002; Wang et al., 2011). However, sulfide mineral leaching presents limitations considering that sulfide minerals are difficult to oxidize. To determine an effective oxidant for recovery of Zn, we investigated oxidative NH_3 leaching for ZnS and the interaction between leaching agents and sulfide mineral's surface.

A method used to forecast and understand the leaching process is modeling the reaction of leaching agent with the mineral surface by quantum chemistry calculation method. This method has been used to study the interfacial reactions of minerals in aqueous solutions. Xia et al. (2013) investigated the effects of sulfate (SO_4^{2-}) ions on the final

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morphology of boehmite (γ-AlOOH) by using the combination of hydrothermal synthesis and computational approach. The experimental results confirmed all the morphologies of boehmite suggested by the computational approach. Long et al. (2016) used the density functional theory (DFT) to study the ethyl xanthate molecule adsorption on unactivated and Cu-activated ZnS (110) surface in the presence of water molecules. The presence of water molecules reduced the reactivity between Zn atoms and xanthate. Steele et al. (2003) studied the possible modes of interaction of Pb^{2+} with the ZnS (110) surface by using a cluster model. The adsorption of hydrated PbO and $PbOH^{+}$ is energetically feasible. Chen and Chen (2010) studied the effect of vacancy defects and impurities on the adsorption of O_2 on sphalerite surfaces with the first-principle calculation. Therefore, quantum chemistry calculation is a promising approach to study the interfacial reactions in the leaching process.

In this paper, quantum chemistry calculation was employed to simulate the interaction of the ZnS (110) surface with leaching agent and oxidants (O_2 or $Na_2S_2O_8$) and forecast the effect of oxidants. The electronic properties of the band structure and partial density of states (PDOS) of the leaching models and the reaction sites were investigated. The leaching behavior of Zn from ZnS ore in NH_3- ammonium (NH_4^+) sulfate solution was investigated with two different oxidants, namely, oxygen (O_2), and sodium persulfate ($Na_2S_2O_8$), to verify their effect during ZnS ore leaching in ammoniacal solution.

2. Computational methods

2.1. Structure optimization

Sphalerite, as the most common ZnS mineral, was used to explore the oxidative behavior of ZnS mineral included in the low-grade sulfide-oxidized Zn ore by NH_3 leaching. The leaching process was simulated using sphalerite with the following parameters: space group of F-43 m (#216) (Burns et al., 1979) and unit cell parameters of $a = b = c = 5.414$ Å and $\alpha = \beta = \gamma = 90°$ (Mcmurdie et al., 1986). Calculations were performed using the density functional theory (DFT) (Hohenberg and Kohn, 1964; Levy, 1979; Dewar, 1983) implemented in the CASTEP (Cambridge Sequential Total Energy Package) (Clark et al., 2005; Segall et al., 2002) code for convergence test of sphalerite, with generalized gradient approximation (GGA) functional (Hammer et al., 1999; Perdew et al., 1992, 1996, 2008) of Perdew–Burke–Ernzerhof (PBE) (Perdew et al., 1996), energy cutoff of 370 eV, and k-point grid of 4 × 4 × 4. Ultrasoft pseudopotentials and a plane wave (PW) (Vanderbilt, 1990) basis set were adopted to describe the interaction between ionic and valence electrons. The convergence tolerances for geometric optimization calculations were set to the maximum tress of 0.1 GPa, displacement of 2.0×10^{-3} Å, energy change of 2.0×10^{-6} eV/atom, and force of 0.05 eV/Å.

Hamad et al. (2002) comprehensively investigated the exposed surfaces in ZnS crystals and found that the (110) surface was the most stable with a surface energy of 0.53 J/m^2. Therefore, ZnS (110) was cleaved to create sphalerite slab, which was optimized with all the atoms relaxed except the middle layer, with eight layers and a 12 Å vacuum space.

2.2. Leaching simulation

The computational model consisted of two parts, namely, the optimized ZnS (110) surface with a (3 × 3 × 3) slab of eight layers and leaching agents, namely, NH_3, O_2, and $Na_2S_2O_8$. These molecules were placed on the T_{Zn}, B_{Zn} and T_S sites on the ZnS (110) surface (Fig. 1). Periodic boundary conditions were employed to avoid any boundary effects. The interaction energy between the leaching agent molecules and the ZnS (110) slab was calculated according to Eq. (1):

$$\Delta E = E_{total} - E_{agent} - E_{ZnS(110)} \quad (1)$$

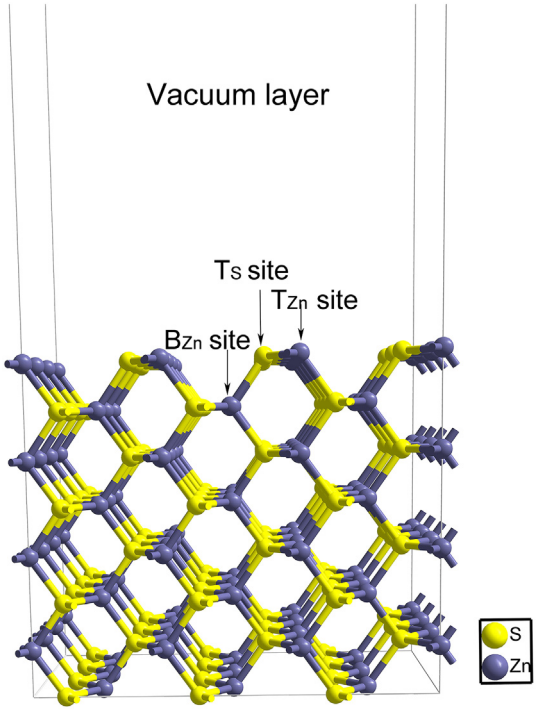

Fig. 1. Slab models of the (3 × 3 × 3) ZnS (110) surface structure with different reaction sites.

Where E_{total} is the total energy of the leaching agent molecule and ZnS surface; E_{agent} is the energy of the leaching agent; and $E_{ZnS\ (110)}$ is the energy of the ZnS (110) slab.

Calculations of the leaching behavior of sphalerite were performed using Dmol3 (Delley, 1990, 2000a, 2000b, 2010) module with GGA/PBE basis set, self-consistent field (SCF) tolerance of 1.0×10^{-5}, and k-point grid of 4 × 4 × 4. The spin-restricted and spin-unrestricted algorithms were used for closed- and open-shell systems, respectively. All-electron double-numerical basis set with diffusion functions (DND) was applied for all atoms. The convergence tolerances were set to the maximum energy change of 2.0×10^{-5} Ha, the maximum force of 4×10^{-3} Ha/Å, and the maximum displacement of 5×10^{-3} Å. The COSMO continuum solvation model was used to characterize the leaching process with recommended solvation parameters of water. All the calculations were performed at the High Performance Computing Center of Central South University.

3. Experimental details

3.1. Raw material

ZnS concentrate was obtained from Hengyang, Hunan, China and used to verify the oxidative behavior of sphalerite in NH_3 leaching. The concentrate was crushed and ground with an agate mortar and pestle into different sizes, ranging from 3.70×10^{-2} to 17.20×10^{-2} mm. A qualitative chemical composition of zinc sulfide concentrate was detected using an X-ray fluorescence spectrometer at 40 kV, 95 mA (XRF, Shimadzu-1800). The Zn phase analysis was carried out by chemical analysis. The mineralogical composition of zinc sulfide concentrate was determined by the X-ray diffraction (XRD, Rint-2000, Rigaku) using Cu Kα radiation. The results are listed in Table 1, Table 2, and Fig. 2, where sphalerite is the major phase along with minor quantities of PbS, FeS_2, and other minerals.