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Study of H_2O adsorption on sulfides surfaces and thermokinetic analysis

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ABSTRACT

Adsorption of water on mineral surfaces was studied using density functional theory and microcalorimetry technique. The calculation results show that galena and molybdenite are hydrophobic, while pyrite and sphalerite is hydrophilic. Thermokinetic analysis shows that the heat of adsorption is in decreasing order of pyrite, sphalerite, galena and molybdenite, which is in good agreement with the calculation results. The adsorption kinetics parameters of hydrophobic galena and molybdenite surfaces are close, while those of hydrophilic pyrite and sphalerite surfaces are very different. The adsorption rate of water on the sphalerite surface is larger than that of water on the pyrite surface.

1. Introduction

Froth flotation is the most important technique for the recovery of valuable minerals from the ore [1]. Separation of minerals mixture may be accomplished by the selective attachment of hydrophobic solid particles (valuable mineral) to gas bubbles (typically air). The other hydrophilic solid particles (the undesired) remain in the liquid (typically water). Thus, water adsorption on sulfides surfaces determined by the hydrophobic or hydrophilic nature of the solids at the solid–liquid–gas interfacial region is very important in froth flotation, and collectors are often added to the flotation pulp in order to enhance the hydrophobicity of the desired minerals.

In the last study, the fundamentals of water interaction with solid surfaces were studied, which define two principal mechanisms of water adsorption as involving either associative or dissociative surface interaction [2]. However, the detailed analysis of water–sulphide interactions is rare. Works on natural minerals have been dominantly focused on sulphide mineral substrates, including pyrite [3,4], pyrrhotite [5,6], galena, chalcopyrite [7], and bomite [8]. These studies mainly showed the mechanisms of sulphide mineral oxidation. In fact, oxygen and water in the gas-phase environment of surface interaction play a critical role. Under ambient conditions exposed to air, most oxide surfaces react readily with water. Kevin studied the interaction of pyrite (1 0 0) surfaces with O_2 and H_2O by UPS (ultraviolet photoelectron spectroscopy). The results demonstrated that the combined gases with H_2O more aggressively oxidize the surface compared to equivalent exposures of pure O_2 [9]. As is well-known, the discharge acid mine drainage resulting from the oxidation of pyrite is very hazardous and often causes serious environmental problems [10,11]. The facile oxidation of sulfides, such as pyrite, by water and oxygen [9,12] remains a major problem that severely limits the potential applications in photoelectrochemical cells. In order to reduce unwanted oxidation of sulfides, it is necessary to ascertain the interaction mechanisms of sulfides surfaces with H_2O in the absence of oxygen.

In this paper, H_2O adsorption on sulfide surfaces was studied using density functional theory (DFT) method including pyrite, sphalerite, galena, and molybdenite. Adsorption heat and kinetic parameters were obtained through microcalorimetry technique. This study provides the microscopic explanations for the natural hydrophobicity and hydrophilicity of sulfide minerals.

2. Computational and experimental methods and models

2.1. Computational method

All calculations were carried out using CASTEP (Cambridge serial total energy package) program module developed by Payne

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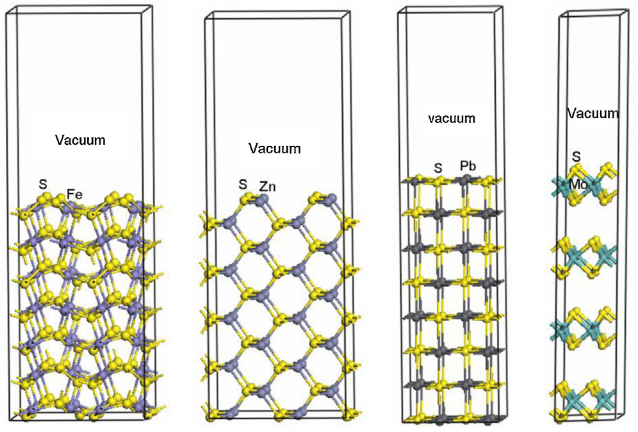

(a) FeS (b) ZnS (c) PbS (d) MoS_2

Fig. 1. Slab models of sulfides.

et al. [13], which is a first-principle pseudopotential method based on DFT. The DFT calculations have been performed using plane wave (PW) basis sets and ultrasoft pseudopotentials [14,15]. The exchange correlation functional used is the generalized gradient approximation (GGA), developed by Perdew and Wang (PW91) [14]. The interactions between valence electrons and ionic core were represented with ultrasoft pseudopotentials. Valence electrons configuration considered in this study included Fe $3d^64s^2$, S $3s^23p^4$ states. Based on the test results, a plane wave cutoff energy of 270 eV was used in all calculations. The convergence tolerances for geometry optimization calculations were set to the maximum displacement of 0.002 Å, the maximum force of 0.08 eV $Å^{-1}$, the maximum energy change of 2.0×10^{-5} eV $atom^{-1}$ and the maximum stress of 0.1 GPa, and the self-consistent field (SCF) convergence tolerance was set to 2.0×10^{-6} eV $atom^{-1}$.

2.2. Computational model

Common pyrite (FeS_2) possesses a cubic crystal structure and has a space group of $Pa3(T_h^6)$. The common cleavage plane is (1 0 0) face along Fe–S bond. Each Fe atom on the surface coordinates with adjacent five S atoms, while each S atom coordinates with adjacent two Fe atoms and one S atom (Fig. 1(a)). Sphalerite has cubic crystal structure with space group of $F-\bar{4}3m$ with (1 1 0) surface. Each Zn atom of the surface coordinates with three S atoms, while each S atom coordinates with two Zn atoms and one S atom (Fig. 1(b)). Galena (PbS) also belongs to cubic crystal structure with a space group of $Fm3m$. Common cleavage plane is (1 0 0) face along Pb–S bond. Each Pb atom of the surface coordinates with adjacent five S atoms, and each S atom coordinates with five Pb atoms (Fig. 1(c)). Molybdenite is a hexagonal crystal with a space group of P63/mmc, whose cleavage plane is (0 0 1). Slab model of molybdenite is shown in Fig. 1(d).

All surfaces were obtained from the bulk sulfides with the optimum unit cell volume and were modeled using a supercell approach ($2 \times 2 \times 1$), where the central cell, periodic in 3D, contains a slab with two surfaces and a vacuum gap above and below the surfaces separating adjacent mirror images of the slab. The surface energies of a range of surfaces with varying slab thicknesses were calculated to determine the slab size. Fig. 1(a)–(d) are the most stable slab models resulted from DFT calculations. During all geometry optimization calculations, the central atomic layer of the slab was kept fixed to prevent the slab from drifting vertically along the supercell.

2.3. Calculation of adsorption energy and heat

The adsorption energies of H_2O on sulfide surfaces were calculated as:

$$E_{ads} = E_{H_2O/surface} - E_{H_2O} - E_{surface} \tag{1}$$

where E_{ads} is the adsorption energy, E_{H_2O} is the energy of the H_2O molecules calculated in a cubic cell, $E_{surface}$ is the energy of the pyrite, sphalerite, galena, or molybdenite slab, $E_{H_2O/surface}$ is the energy of the pyrite, galena, sphalerite, or molybdenite slab with adsorbed H_2O.

2.4. Microcalorimetry experimental method

Adsorption heats of sulfide minerals were measured using RD496-III type microcalorimeter, which is a totally automatic instrument utilizing computer control, as shown in Fig. 2(a). Fig. 2(b) shows the cuvette and sleeve of adsorption reaction. The temperature of the calorimetric experiment was 298.15 K.

The first step in the microcalorimetry experiment was preparation of samples for examinations. The studied pyrite, galena, chalcocite, and molybdenite are natural minerals, whose purities are very large, with 99% pyrite, 99% galena, 96% sphalerite, and 96% molybdenite. Samples of 1.0 g with 20 mL of distilled water were put in a conical flask (50 mL). The mixture was vibrated using ultrasonic wave for 5 min and then rested for a while. The mixture components separated into two layers. After removing above clear liquid, 20 mL of distilled water was added to form the mineral samples.

In the second step, the adsorption heats were measured. 1 mL distilled water and 1 mL of the mineral samples were shaken and

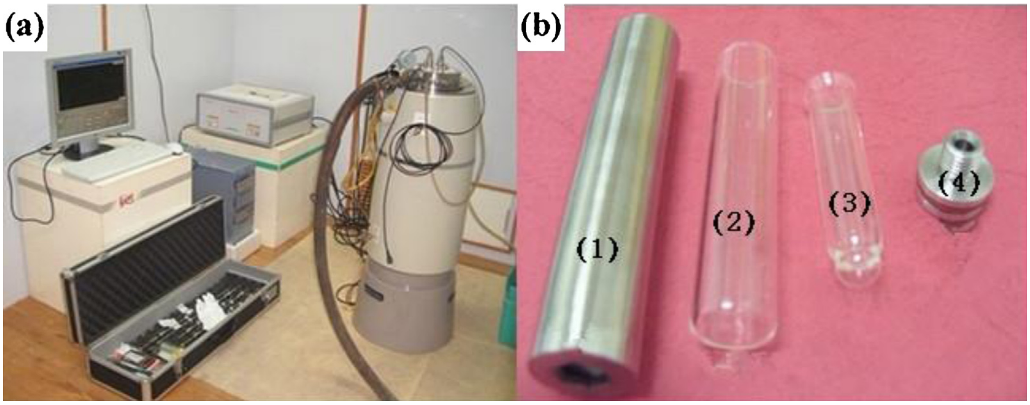

Fig. 2. Microcalorimetry experimental setup. (a) Microcalorimetry device; (b) parts used for study of enthalpy: (1) stainless steel casing, (2) large sample cell, (3) small sample cell, (4) stainless steel cover.