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ScienceDirect
Trans. Nonferrous Met. Soc. China 24(2014) 491−498

Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

Density functional theory study on natural hydrophobicity of sulfide surfaces

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Received 23 February 2013; accepted 28 July 2013

Abstract: Adsorption of water on sulfide surfaces and natural floatability of sulfide minerals were studied using density functional theory (DFT) method. All computational models were built in a vacuum environment to eliminate the effects of oxygen and other factors. H_2O molecule prefers to stay with pyrite and sphalerite surfaces rather than water, whereas for galena, chalcocite, stibnite, and molybdenite, H_2O molecule prefers to stay with water rather than the mineral surfaces. On the other hand, pyrite surface favors N_2 more than water, while sphalerite surface cannot adsorb N_2. These results show that galena, stibnite, chalcocite, and molybdenite are hydrophobic, while sphalerite is hydrophilic. Although pyrite has certain hydrophilicity, it tends to be aerophilic because the reaction of pyrite with H_2O is weaker than pyrite with N_2. Thus, pyrite, galena, chalcocite, stibnite and molybdenite all have natural floatability.

Key words: sulfide minerals; water adsorption; natural floatability; density functional theory

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1 Introduction

Flotation is a surface chemistry based process for the separation of fine solids, taking advantage of the difference in wettability of the solid particle surfaces. Hydrophobic surfaces solids are often naturally non-wettable by water. Such surfaces are also typically air attracting, known as aerophilic surface. They are strongly attracted to an air interface, readily displacing water on the solid surface. The floatability of minerals depends on the wettability degree of the surfaces with water. Over the last few decades, many studies have been performed on the natural floatability of certain sulfide minerals, but various researchers reached different conclusions [1−4]. For example, as early as 1940, RAVITZ [1] suggested that galena is naturally floatable; however, this premise has been object by other investigators [2−4]. Whether sulfides have natural floatability has been a controversial issue over the years.

FINKELSTEIN et al [4] and LEPETIC [5] observed natural floatability under certain conditions for chalcopyrite. HEYES and TRAHAR [6] showed that floatability in the absence of collectors occurs under oxidizing conditions and found that flotation could not be achieved under reducing conditions. GARDNER and WOODS [7] confirmed these observations with potentiostatic experiments. The presence of sulfur was suggested by these authors to be critical for chalcopyrite flotation in the presence of collectors. However, YOON [8] showed that chalcopyrite responds well to collectorless flotation process after sodium sulfide is added to the system. Sulfur was not detected on the chalcopyrite surface under these reducing conditions; thus, the natural floatability of sulfides depends on adsorption environment.

On the other hand, FUERSTENAU and SABACKY [9] studied the natural floatability of sulfide minerals (galena, chalcopyrite, chalcocite, pyrite and sphalerite) from various sources. The system used in this research was in an atmosphere containing less than 10^{-6} oxygen in mole fraction and water containing less than 5×10^{-6} oxygen without addition of any collector or frother. The results showed that chalcocite, chalcopyrite, galena, and

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Foundation item: Project (51164001) supported by the National Natural Science Foundation of China; Project (NCET-11-0925) supported by New Century Excellent Talents in University, China

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DOI: 10.1016/S1003-6326(14)63087-9

pyrite are naturally floatable under specific conditions (low oxygen content, pH 6.8, no collector, no frother), which disagrees with the results reported [2−4]. According to results of FUERSTENAU and SABACKY [9], oxygen is a critical factor affecting the natural floatability of sulfide minerals. In the presence of oxygen, oxidation of the surfaces of these sulfides to sulfur-oxy species occurs. Under these conditions, water molecules are hydrogen bonded to the surface and the sulfide minerals lose their natural floatability.

Influence of oxygen on the process cannot be completely eliminated in any flotation system, and absolutely clean surface of minerals is hardly obtained in certain conditions and environments, which may result in differences in natural floatability of sulfide minerals observed by several investigators.

In recent years, a great deal of research for H_2O adsorption on sulfide surfaces has been carried out. Our research group [10] studied the adsorption of water on sulfide surfaces (pyrite, sphalerite, galena and molybdenite) by microcalorimetry technique. The results showed that galena and molybdenite are hydrophobic, while pyrite and sphalerite are hydrophilic. The heat of adsorption is in decreasing order of pyrite, sphalerite, galena and molybdenite. 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. STIRLING [11] studied water interaction with the (100) surface of pyrite by means of ab initio molecular dynamics simulations. The results showed that a very strong preference for molecular adsorption on the surface iron sites. Hydrogen bonding plays an important role in the stabilization of the adsorbed water. Water forms a coordinative covalent bond with the surface iron. GUEVREMONT et al [12] investigated the interaction of water with atomically clean FeS_2 (100). The results showed that the binding sites on clean FeS_2 (100) can be broadly classified as being associated with stoichiometric FeS_2 (100) and a sulfur-deficient surface. These latter sites bind H_2O more strongly than the former. WRIGHT et al [13] studied the reaction of water on the surface of PbS (galena). The results from both semi-empirical and ab initio levels of theory suggested that on a perfect (001), water is a stable species and dissociation does not occur. However, at a small step-like feature the reaction $PbS+H_2O\rightarrow Pb(OH)^{+}+HS^{-}$ is exothermic with a sufficiently low barrier that a facile reaction occurs at ambient temperature. ROSSO et al [14] studied the interaction of gaseous O_2, H_2O and their mixtures with clean (100) surfaces of pyrite in ultra-high vacuum by scanning tunneling microscopy and spectroscopy (STM-STS), ultraviolet photoelectron spectroscopy (UPS) and ab initio calculations. The results indicated oxidative consumption of low binding-energy electrons occupying dangling bond surface states localized on surface Fe atoms, and the formation of Fe—O bonds. No such changes in the valence band spectra are observed for pyrite surfaces exposed to H_2O. The combined gases more aggressively oxidize the surface compared with equivalent exposures of pure O_2. Ab initio cluster calculations of adsorption energies and the interaction of O_2 and water species with the surface indicated that H_2O dissociatively sorbs when O_2 is present on the surface. The study on ROSSO suggests that O_2 can be influential on H_2O adsorption on sulfide surfaces.

In this work, H_2O adsorption on sulfide surfaces and the natural hydrophobicity of sulfide minerals were studied by density functional theory (DFT) method. The sulfide minerals studied included pyrite, sphalerite, galena, chalcocite, stibnite and molybdenite. All calculations were carried out in the vacuum environment to completely eliminate the effects of oxygen and other similar factors.

2 Computational and experimental methods and models

2.1 Computational method

Based on the DFT method, all calculations were performed by CASTEP (Cambridge serial total energy package) program module developed by PAYNE et al [15], 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 [16,17]. The exchange correlation functional used was the generalized gradient approximation (GGA), developed by PERDEW and WANG (PW91) [16]. 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 $3s^23p^4$, Cu $3d^{10}4s^1$, Pb $5d^{10}6s^26p^2$, Sb $5s^25p^3$, Zn $3d^{10}4s^2$ and Mo $4s^24p^64d^55s^1$ states. Based on the test results, plane wave cut-off energies of pyrite and galena are 270 eV and 280 eV, respectively, and others (sphalerite, chalcocite, stibnite, molybdenite) are all 300 eV. The thicknesses of vacuum layer for all six sulfides are 15 Å, which is the most stable. The convergence tolerances for geometry optimization calculations were set to be the maximum displacement of 0.002 Å, the maximum force of 0.08 eV/Å, the maximum energy change of 2.0×10^{-5} eV/atom and the maximum stress of 0.1 GPa, and the