Effect of Cu^{2+} Activation on Interfacial Water Structure at the Sphalerite Surface as Studied by Molecular Dynamics Simulation

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Abstract: In the first part of this paper, an experimental contact angle study of fresh and Cu^{2+} activated sphalerite-ZnS surfaces as well as the covellite-CuS (001) surface is reported describing the increased hydrophobic character of the surface during Cu^{2+} activation. In addition to these experimental results, fresh sphalerite-ZnS (110), copper-zinc sulfide- CuZnS_2 (110), villamaninite- CuS_2 (100), and covellite-CuS (001) surfaces were examined using Molecular Dynamics Simulation (MDS). Our MDS results on the behavior of interfacial water at the fresh sphalerite-ZnS (110), copper-zinc sulfide- CuZnS_2 (110), villamaninite- CuS_2 (100), and covellite-CuS (001) surfaces include simulated contact angles, water number density distribution, water dipole orientation, water residence time, and hydrogen-bonding considerations. The copper content at the Cu^{2+} activated sphalerite surface seems to account for the increased hydrophobicity as revealed by both experimental and MD simulated contact angle measurements. The relatively greater hydrophobic character developed at the Cu^{2+} activated sphalerite surface and at the copper sulfide surfaces has been described by MDS, based on the structure of interfacial water and its dynamic properties.

Keywords: MDS, DFT, contact angle, interfacial water structure

1. Introduction

It is well known that most sulfide minerals are naturally hydrophobic under anaerobic conditions, but sphalerite has a relatively weak hydrophobic surface state compared to other sulfide minerals, such as pyrite, chalcopyrite and galena. In the virtual absence of oxygen (i.e., in water containing less than 5 ppb oxygen), pyrite, chalcopyrite and galena can be completely floated, while sphalerite shows a relatively weak floatability under such conditions, indicating only a modest level of hydrophobicity (Fuerstenau and Sabacky, 1981). The relatively weak floatability of sphalerite in the absence of collectors has been confirmed by other researchers (Fornasiero and Ralston, 2006). Several sphalerite investigations involving contact angle measurements reported a 46° contact angle for a synthetic sphalerite particle bed (38 to 75 μ m) and a captive bubble contact angle of 44° for a pure sphalerite crystal surface, also indicative of the modest hydrophobicity of sphalerite (Jin et al., 2014; Subrahmanyam et al., 1996). This modest natural hydrophobicity of sphalerite may account, in part, for the fact that sphalerite is not satisfactorily floated with short chain sulfhydryl collectors. Sphalerite's floatability can be improved by using long chain sulfhydryl collectors at high concentration, but a more satisfactory method is using certain metal ions, which are able to displace Zn at sphalerite surfaces, as activators. By adding metal ions, such as Cu^{2+} , Pb^{2+} , Ag^+ , Au^+ , Cd^{2+} , and Fe^{2+} , sphalerite can be activated in the flotation with short chain collectors (Finkelstein, 1997, 1999).

Copper ions are of particular interest. It has been well established that copper activation of sphalerite follows an ion exchange mechanism which is generally represented by equation 1 (Buckley et al., 1989; Finkelstein, 1997; Popov and Vučinić, 1990; Sutherland and Wark, 1955).

In this reaction, the Zn atoms in the sphalerite crystal are substituted by the Cu atoms from solution. The reaction products during copper activation at the sphalerite surface have been studied by X-ray Photoelectron Spectroscopy (XPS), which provides a valuable means of determining the surface composition of minerals under flotation related conditions. The Cu^{2+} activated sphalerite surface has been identified, and possible end products are CuS (covellite) and Cu_2S (chalcocite), according to a previous XPS study (Buckley et al., 1989). Other researchers have reached a similar conclusion based on an electrochemical study of sphalerite activation by Cu^{2+} (Chen and Yoon, 2000).

It has been well established that sulfide flotation depends on the proportion of hydrophobic and hydrophilic sites at the sulfide mineral surface. Though the fresh sphalerite is not floated completely in the absence of collector, the Cu^{2+} activated sphalerite has a strong floatability under the same conditions (Fornasiero and Ralston, 2006; Fuerstenau and Sabacky, 1981). These results indicate that the hydrophobic character of the sphalerite surface increases significantly after Cu^{2+} activation. Surface wettability of the Cu^{2+} activated sphalerite surface is of significant importance in explaining the complete floatability of sphalerite in collectorless flotation. In our study, experimental contact angles at fresh sphalerite and at Cu^{2+} activated sphalerite crystal surfaces are reported to examine the nature of the Cu^{2+} activation reaction. Chalcocite, the other possible product from the Cu^{2+} activation of sphalerite, is scheduled for our future research because of its complex crystal structure and range of copper content.

Macroscopic results, such as experimental contact angle and flotation recovery, are related to microscopic behavior (molecular or atomic level). Consequently, the structure of interfacial

water molecules at mineral surfaces is of significant importance in the understanding of the hydrophobicity of such surfaces. Different spectroscopic methods have been applied to study interfacial water structure at mineral surfaces. For example, the interfacial water structure at soluble salt surfaces has been studied with Fourier Transform Infrared spectroscopy (FTIR) (Cao et al., 2011; Cheng et al., 2013; Yalamanchili et al., 1991). Also, Vibrational Sum-Frequency Generation spectroscopy (SFG) has been used to explore the structure of water molecules at oxide mineral surfaces (Ostroverkhov et al., 2005; Shen, 1994; Shen and Ostroverkhov, 2006; Yeganeh et al., 1999) and fluorite surfaces (Eftekhari-Bafrooei and Borguet, 2009; Zhang et al., 2013). However, the spectroscopic signal has been difficult to analyze, and the experimental results require further analysis at the molecular level.

Because of the remarkable increase in computational capabilities in recent years, MDS can now be used to provide important molecular-level information about the structure and dynamic properties of interfacial water at mineral surfaces. Much research based on MDS has been reported on water structure and the dynamic and thermodynamic characteristics of water at mineral surfaces (Du and Miller, 2007a; Gallo et al., 2002; Kalinichev and Kirkpatrick, 2002; Lee and Rossky, 1994; Rustad, 2001; Rustad et al., 2003; Spohr et al., 1999; Wang et al., 2004). Recently, quantum chemical calculations providing electron-level information about atomic interactions, such as Density Functional Theory (DFT), have also been used in the study of sulfide minerals, such as molybdenite (Todorova et al., 2004) and pyrite (Blanchard et al., 2007; Hung et al., 2003; Zhao et al., 2014). However, due to the magnitude of the DFT calculation, it is difficult to study the interfacial water structure using DFT when compared to MDS. Using simplified pair potential models, MDS has a much greater capacity for the study of a system with a large number of atoms (tens of thousands of atoms), so MDS is more suitable for the

examination of the interfacial water at mineral surfaces. Because of this remarkable ability to simulate large systems, the contact angles of nanodrops at solid surfaces can even be measured by MDS (Shi and Dhir, 2009; Werder et al., 2003). Simulated contact angles provide important information regarding the hydrophobic state of mineral surfaces.

In addition to the results from contact angle measurements, the following simulated surface states were examined using MDS: the fresh sphalerite-ZnS (110) surface; copper-zinc sulfide-CuZnS₂ (110) surface; villamaninite-CuS₂ (100) surface; and covellite-CuS (001) surface. The copper-zinc sulfide-CuZnS₂ is considered to be an intermediate product in Cu²⁺ activation of the sphalerite surface, as expected, based on the metathetic exchange reaction. The selected surfaces for MDS analysis are all preferred cleavages for their corresponding crystals. In this study, only the covellite cleavage between two sulfur atoms was reported, but the other cleavage of trigonally or tetrahedrally coordinated copper layers is also important and will be considered in our future research (Rosso and Hochella, 1999).

It is apparent that the reliability of MDS depends critically on the accuracy and efficiency of the interatomic potential models (i.e., force fields). In recent decades, much effort has been made to establish force fields for selected minerals (Cygan, 2001), and many useful force fields have been developed, such as CLAYFF (Cygan et al., 2004) and the soluble salts force fields (Dang, 1994, 1995; Dang and Kollman, 1995; Dang and Smith, 1995; Du and Miller, 2007b; Du et al., 2007). As for sphalerite, several MDS investigations of the sphalerite structure have been reported using functional forms of the Buckingham potential, but no information about the interaction between a sphalerite surface and water molecules were provided (Buckingham, 1938; Hamad et al., 2002; Wright and Gale, 2004). Another MDS study using the potential parameters

from the universal force field (UFF) (Rappé et al., 1992) and partial charges determined by Mulliken population analysis (Mulliken, 1955) for interfacial water at the sphalerite (110) and chalcopyrite (012) surfaces gave a reasonable prediction of the surface hydrophobicity (Jin et al., 2014). Thus, the same UFF force field parameters for the Zn, Cu and S atoms are utilized in our MDS study. The interfacial water structure and dynamic properties at the fresh sphalerite-ZnS (110), copper-zinc sulfide-CuZnS₂ (110), villamaninite-CuS₂ (100), and covellite-CuS (001) surfaces are discussed including simulated contact angles, water number density profiles, water residence time, water dipole orientation, and hydrogen bonding.

2. Methods

2.1. Experimental Procedures

Yellow transparent sphalerite crystals from Chirera City, Sonora, Mexico, with a purity of 99% by weight, examined by EDAX analysis, were used to prepare samples for our experimental contact angle measurements. No iron or copper was found in these specimens. Each of the sphalerite crystals had a flat surface with a surface area of about 20mm × 20mm. Roughness on the natural flat surfaces was eliminated by polishing with an 8-inch aluminum diamond lap using 150 grit diamond powder for 2 minutes, and fine polishing with a 600 grit metal bonded diamond lap for another 2 minutes. Polishing procedures involved coarse polishing with a 6 micron diamond suspension on the polishing cloth, and fine polishing with a 1 micron diamond suspension on a "Boehler Trident" polishing cloth. After quick washing with water and drying with Kimwipes, the sphalerite crystals were put into a nitrogen-filled ziplock plastic bag, in order to minimize surface oxidation. Then all sphalerite crystals were used for contact angle measurements as fresh sphalerite or Cu²⁺ activated sphalerite crystal surfaces.

Contact angles were measured with a Rame-Hart goniometer using the captive bubble method. A bubble was released from the needle tip after formation with a syringe. The bubble was then captured and attached at the sphalerite surface. Since the contact angle was measured for cases when attachment occurred, contact angles reported in this study are intermediate contact angles, which are between advancing and receding contact angles. Before each measurement of the fresh sphalerite surface, the sphalerite crystal was cleaned with acetone and ethanol to remove possible organic contaminations on the surface and then rinsed with DI water. Then, at least ten bubbles were generated and contact angles measured. The reported contact angle values are the average of these measurements. The maximum experimental variation in contact angle values was found to be $\pm 1^\circ$. For each of the contact angle measurements at the Cu^{2+} activated sphalerite crystal surfaces, the sphalerite crystal was cleaned using the same procedures as described above and soaked in a 1.0×10^{-5} mol/L CuSO_4 solution at pH = 5.3. After 5 minutes, at least five bubbles were generated and contact angles were measured. Three sphalerite crystal samples were used to reproduce the results of contact angle measurements at the Cu^{2+} activated sphalerite crystal surfaces.

It is well known that covellite has a perfect cleavage on the (001) surface (Dana and Salysbury, 1944). A (001) covellite crystal surface which had a $1.5\text{cm} \times 1.5\text{cm}$ area was polished parallel to the (001) cleavage plane using the same polishing procedures used for sphalerite polishing. The contact angles were measured by the captive bubble method.

2.2. Density Functional Theory (DFT) Calculations

The Quickstep package of the CP2K program can perform accurate and efficient DFT calculations on large, complex systems including liquids, crystals, proteins and interfaces

(Mundy et al., 2000; VandeVondele et al., 2005). Quickstep is based on the Gaussian and plane waves method (GPW) and its augmented extension (GAPW). In our study, Quickstep was used to optimize a copper-zinc sulfide-CuZnS₂ crystal structure.

Although the copper-zinc sulfide-CuZnS₂ thin film can be synthesized chemically, its crystal lattice parameter is still not available (Chukwuemeka Uhuegbu et al., 2008; Innocenti et al., 2013). Because sphalerite and chalcopyrite have the same crystal structure, a chalcopyrite crystal structure with the Fe atoms substituted by Zn was used as the initial crystal structure of copper-zinc sulfide-CuZnS₂. The chalcopyrite crystal lattice parameters are from a previous X-ray Diffraction (XRD) study of chalcopyrite (Knight et al., 2011). This initial copper-zinc sulfide-CuZnS₂ crystal structure is set as the input for the DFT quantum chemical calculation to get crystal geometry optimized by energy minimization. The DZVP-MOLOPT-SR-GTH shorter range basis set (VandeVondele and Hutter, 2007) and PBE correlation functional (Perdew et al., 1996) were used in our DFT quantum chemical calculation. The crystal structure of this copper-zinc sulfide-CuZnS₂ crystal after DFT quantum chemical geometry optimization was used for subsequent MDS to determine simulated contact angles and accomplish interfacial water analysis.

2.3. Molecular Dynamics Simulation

Amber, an MDS program, was used for the simulation and analysis of interfacial water at the fresh sphalerite-ZnS (110), copper-zinc sulfide-CuZnS₂ (110), villamaninite-CuS₂ (100), and covellite-CuS (001) surfaces. The total energy in MDS was determined by evaluating the appropriate energy terms for every atom-atom interaction in the system. In the Amber program, this total energy is expected to include the Coulombic (electrostatic) interactions, the short-range interactions (van der Waals energy term), and the bonded interactions. The bonded terms include

the bond stretch and angle bend energy terms that are represented in the water models as harmonic terms. The Coulombic energy is represented by equation 2 in which the energy of the interaction is inversely proportional to the distance of separation r_{ij} . The terms q_i and q_j are partial charges for atoms i and j. The term e is the charge of an electron, and ϵ_0 is the dielectric permittivity of vacuum (8.85419×10^{-12} F/m).

$$E_{Coulombic} = \frac{e^2}{4\pi\epsilon_0} \sum_{i \neq j} \frac{q_i q_j}{r_{ij}} \quad (2)$$

The van der Waals energy term, represented by the conventional Lennard-Jones (12-6) function (Jones, 1924), includes the short-range repulsion associated with the increase in energy as two atoms approach each other and the attractive dispersion energy. The term ϵ_{ij} is the depth of the potential well, and $r_{m,ij}$ is the distance at which the potential reaches its minimum.

$$E_{VDW} = \sum_{i \neq j} \epsilon_{ij} \left[\left(\frac{r_{m,ij}}{r_{ij}} \right)^{12} - \left(\frac{r_{m,ij}}{r_{ij}} \right)^6 \right] \quad (3)$$

The interaction parameters between unlike atoms are calculated according to the arithmetic mean rule for the distance parameter, r_m , and the geometric mean rule for the energy parameter, ϵ :

$$r_{m,ij} = \frac{1}{2(r_{m,i} + r_{m,j})} \quad (4)$$

$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j} \quad (5)$$

In recent decades, various kinds of molecular water models have been developed. The rigid SPC/E water model has the closest average configurational energy to the experimental value (-41.5 KJ mol⁻¹) (Kusalik and Svishchev, 1994; Mahoney and Jorgensen, 2000). Thus, we selected

the SPC/E water model for exploring the interfacial water at the fresh sphalerite-ZnS (110), copper-zinc sulfide-CuZnS₂ (110), villamaninite-CuS₂ (100), and covellite-CuS (001) surfaces.

The Lennard-Jones parameters r_m , ϵ and atomic partial charge q for all the atoms in the simulation are listed in Table 1. Lennard-Jones parameters for the Zn, Cu and S atoms in the sphalerite-ZnS, copper-zinc sulfide-CuZnS₂, villamaninite-CuS₂, and covellite-CuS crystals are from the UFF. Atomic partial charges for the Zn, Cu and S atoms in these crystal are Mulliken charges determined from the periodic DFT quantum chemical calculations of well-defined sphalerite-ZnS, copper-zinc sulfide-CuZnS₂, villamaninite-CuS₂, and covellite-CuS unit cells using the Perdew-Wang 1991 (PW91) functional theory and the generalized gradient approximation (Perdew et al., 1996; Perdew et al., 1991). The quantum program DMol3 was used to assign the Mulliken charges (Delley, 2000). Sphalerite-ZnS, villamaninite-CuS₂, and covellite-CuS are the sulfide minerals found in nature. Our MD simulation used the crystal lattice parameters for these sulfide minerals from the corresponding X-ray Diffraction studies (Evans and Konnert, 1976; King and Prewitt, 1979; Skinner, 1961). The copper-zinc sulfide-CuZnS₂ crystal structure is from our DFT quantum chemical calculations.

To measure the simulated contact angle of water drops at the fresh sphalerite-ZnS (110), copper-zinc sulfide-CuZnS₂ (110), villamaninite-CuS₂ (100), and covellite-CuS (001) surfaces by MDS, a water drop containing 1270 water molecules was put on the surface at the bottom of a simulation periodic box. According to a previous MDS study (Jin et al., 2014), in the size range from 850 to 1700 water molecules, drop size doesn't have much effect on the simulated contact angle measured by MDS. In order to remove the periodic images of the droplets in measuring the simulated contact angle, the surface needs to have sufficient area. In our study, the horizontal

extent of the fresh sphalerite-ZnS (110), copper-zinc sulfide-CuZnS₂ (110), villamaninite-CuS₂ (100), and covellite-CuS (001) surfaces used for simulated contact angle measurement are around $150\text{\AA} \times 150\text{\AA}$. Also, the vertical extent of the periodic simulation boxes was set at $100\text{\AA}$ to avoid the influence of periodic conditions on the water drops. One water molecule in this periodic volume of about $3.0 \times 10^6\text{\AA}^3$ would provide a saturated atmosphere, so the water drop is stable under these conditions. Because of the large number of atoms (over 20,000) in this simulation, we used a total simulation time of 1 ns (1×10^6 steps each of 1 fs), including a 500 ps equilibration period and another 500 ps analysis period. The contact angles were measured on an average for the second 500 ps. It is well known that the solubilities of sulfide minerals are very low. In order to improve the calculation efficiency, crystal atoms were fixed in their respective initial positions during the simulation. Each simulation was for a constant number, constant volume and constant temperature assembly (the NVT ensemble) with the temperature fixed at 298K.

To study the structure of interfacial water and its dynamic properties at the fresh sphalerite-ZnS (110), copper-zinc sulfide-CuZnS₂ (110), villamaninite-CuS₂ (100), and covellite-CuS (001) surfaces, we made a simulation periodic box containing a vacuum space in the top, a water phase in the middle (about $50\text{\AA}$ thick), and a sulfide crystal (around $45\text{\AA} \times 45\text{\AA} \times 12\text{\AA}$) at the bottom. The purpose for having a vacuum space was to make sure the water phase experienced the same pressure for all simulations. After a simulation time of 2 ns for equilibration, we performed another 2 ns simulation for interfacial water analysis.

3. Results and Discussion

3.1. Simulated and Experimental Contact Angles

To determine contact angles from simulation, we post-processed the water number densities using a grid size of 0.5 Å in two center planes: the x-z plane and y-z plane. A two-dimensional droplet with a contour line corresponding to the average of the liquid and vapor densities defines the boundary of the water droplet (Peng et al., 2012; Shi and Dhir, 2009). The results for the fresh sphalerite-ZnS (110), copper-zinc sulfide-CuZnS₂ (110), villamaninite-CuS₂ (100), and covellite-CuS (001) surfaces for the x-z plane are expressed as a best fit contour line in Figure 1. The contact angle was measured by drawing a tangent from a point at the foot of the contour line at a height of 8 Å from the selected sulfide mineral surfaces to avoid the influence from density fluctuations at the water-mineral surface (Werder et al., 2003). For each contact angle measurement, the contact angles were measured in the x-z and y-z planes and then averaged (Shi and Dhir, 2009).

Table 2 lists the simulated contact angles and experimental values for the fresh sphalerite-ZnS (110), Cu²⁺ activated sphalerite, copper-zinc sulfide-CuZnS₂ (110), villamaninite-CuS₂ (100), and covellite-CuS (001) surfaces. For both our experimental and simulated contact angles, the values for the fresh sphalerite ZnS crystal surface were very close to values reported the literature (Jin et al., 2014). The relatively small contact angle for the sphalerite-ZnS (110) surface indicated its modest hydrophobic character, which also has been revealed by the incomplete flotation of sphalerite in the absence of collectors (Fornasiero and Ralston, 2006; Fuerstenau and Sabacky, 1981).

The experimental contact angle for Cu^{2+} activated sphalerite surface showed a 15° increase from the fresh sphalerite surface. Under similar Cu^{2+} activation conditions (i.e. $\text{pH} = 5.3$, $1 \times 10^{-5} \text{ M Cu}^{2+}$), previous investigation showed that the collectorless flotation recovery of sphalerite increased from 45% to around 80% (Fornasiero and Ralston, 2006). This increase in hydrophobicity after Cu^{2+} activation as revealed by experimental contact angles is consistent with the improved sphalerite floatability.

Compared to the fresh sphalerite-ZnS (110) surface, the villamaninite- CuS_2 (100) and covellite-CuS (001) surfaces had much larger simulated and experimental contact angles, which reveals their natural hydrophobic character. For the villamannite- CuS_2 (100) surface, due to the lack of a specimen, the experimental contact angle has not yet been measured. For the covellite-CuS (001) surface, the simulated and experimental contact angles both indicated its hydrophobic character, but the simulated contact angle was relatively larger. Though the covellite-CuS (001) surface was polished parallel to the cleavage plane, the cleavage plane itself was not smooth and flat enough, as shown in the photograph taken from microscopic examination (see Figure 2). As a result, there would be other unknown covellite surfaces exposed on the specimen surface during polishing, which might compromise the hydrophobic character of the covellite-CuS (001) surface. The oxidation/weathering of the covellite mineral sample might also be the reason for the difference between the experimental and simulated contact angles (Chander, 1991). Note that the covellite-CuS (001) surface is relatively more hydrophobic than the villamaninite- CuS_2 (100) surface, based on their simulated contact angles.

As listed in Table 2, the simulated contact angle of the copper-zinc sulfide- CuZnS_2 (110) surface was close to the experimental contact angle measured for the Cu^{2+} activated sphalerite surface,

and its value was between the contact angles of the fresh sphalerite-ZnS (110) surface and the copper sulfide surfaces (i.e. villamaninite-CuS₂ (001) and covellite-CuS (001) surfaces). This possible copper-zinc sulfide product formed during the Cu²⁺ activation of the sphalerite surface was more hydrophobic than the fresh sphalerite surface. Our simulated and experimental contact angle measurements suggest that the more hydrophobic state of the possible copper-zinc sulfide and/or copper sulfide product at the surface of the Cu²⁺ activated sphalerite accounts for the complete floatability of Cu²⁺ activated sphalerite as revealed by the previous collectorless flotation studies (Fornasiero and Ralston, 2006; Fuerstenau and Sabacky, 1981).

In MD simulation, inter-atomic interaction between two atoms within the cut off distance (11 Å for our study) will be considered. However, the first stoichiometric crystal layer, i.e. the outermost crystal layer around 1.5 Å from the crystal surface, has the most significant effect on the behavior of the interfacial water molecules at the crystal surface. By comparing the composition of the first stoichiometric crystal layer of these sulfide surfaces, it was found that the sulfide with greater copper content had a relatively more hydrophobic surface character. More details about the effect of the copper content on the interfacial water and the corresponding hydrophobic surface state will be discussed for the fresh sphalerite-ZnS (110), copper-zinc sulfide-CuZnS₂ (110), villamaninite-CuS₂ (100), and covellite-CuS (001) surfaces in the following section.

3.2. Interfacial water structures and dynamic properties

MDS snapshots in the x-z plane (left column) and in the y-z plane (right column) for interfacial water at the fresh sphalerite-ZnS (110), copper-zinc sulfide-CuZnS₂ (110), villamaninite-CuS₂ (100), and covellite-CuS (001) surfaces are presented in Figure 3. The gap found between the

water phase and the crystal surface, reflecting the "water-excluded volume" (Abraham, 1978; Yu et al., 1999) or "water exclusion zone," indicates the interaction between the water molecules and the surface. For the fresh sphalerite-ZnS (110), copper-zinc sulfide-CuZnS₂ (110), villamaninite-CuS₂ (100), and covellite-CuS (001) surfaces, according to the snapshots, the gaps showed the following sequence: sphalerite-ZnS (110) surface < copper-zinc sulfide-CuZnS₂ (110) surface < villamaninite-CuS₂ (100) surface < covellite-CuS (001) surface. The larger gap indicated relatively weak interaction between interfacial water and the surface, which is believed to account for the macroscopic hydrophobic character of the surface. Thus, the hydrophobicity for these crystal surfaces should follow the same sequence, which is consistent with the simulated contact angle results. The gaps between the interfacial water molecules and the crystal surfaces in the snapshots confirmed the assumption that the greater the copper content for the copper-zinc sulfide the more hydrophobic the surface state. More details of the interfacial water structure and the water-exclusion zone for selected sulfide crystal surfaces will be discussed later.

3.2.1. Number density distribution of interfacial water molecules

In the analysis of the number density distribution of interfacial water molecules, the simulation periodic box was divided into 0.5Å bins parallel to the fresh sphalerite-ZnS (110), copper-zinc sulfide-CuZnS₂ (110), villamaninite-CuS₂ (100), and covellite-CuS (001) surfaces. The number of water molecules in each bin was counted. In this study, the position of a water molecule was defined as the position of the center of mass for the water molecule. The numbers of water molecules in all the bins were plotted versus the bin's distance from the surface, making the number density profile. The relative number density is the fraction of the absolute number density over an average number density for the bulk water.

The number density profiles for the fresh sphalerite-ZnS (110), copper-zinc sulfide-CuZnS₂ (110), villamaninite-CuS₂ (100), and covellite-CuS (001) surfaces are shown in Figure 4. The first peak of the relative water number density distribution for which the value is greater than 1 was considered as the "primary water density peak" for this surface, which meant that the water in this region was more condensed than in the bulk. As expected, due to the hydrophobicity of the copper-zinc sulfide-CuZnS₂ (110), villamaninite-CuS₂ (100) and covellite-CuS (001) surfaces, water molecules were excluded from these surfaces. The primary water density peaks for these surfaces were located at least 3 Å away from the surface, and this distance was greater than the distance between hydrogen-bonded water/water interactions, which is approximately 2.8 Å (Dang and Pettitt, 1990; Lee and Rasaiah, 1996; Lynden-Bell and Rasaiah, 1997; Rasaiah and Zhu, 1990; Smith and Dang, 1994). These results demonstrated the weak interaction between the water molecules and the sulfide mineral surfaces. Also, the comparably sharper primary water density peak for the covellite-CuS (001) surface indicated a weaker water-surface interaction and a more hydrophobic character when compared to the villamaninite-CuS₂ (100) surface. Note that for the copper-zinc sulfide-CuZnS₂ (110) surface, the relative water number density had a shoulder around 0.9 at 2 Å away from the surface, which indicated a greater interaction between interfacial water and the copper-zinc sulfide-CuZnS₂ (110) surface than at the villamaninite-CuS₂ (100) and covellite-CuS (001) surfaces. This analysis was consistent with our simulated contact angle results which showed that the villamaninite-CuS₂ (100) and covellite-CuS (001) surfaces were more hydrophobic than the copper-zinc sulfide-CuZnS₂ (110) surface. For the fresh sphalerite-ZnS (110) surface, water molecules interacted more strongly with the Zn and S atoms at the sphalerite-ZnS (110) surface. The distance between the surface and the primary water density peak for the fresh sphalerite-ZnS (110) surface was around 2.2 Å, which was much

smaller than the distance found for other hydrophobic surfaces and consistent with results from a previous MDS study (Jin et al., 2014).

The distinct differences in the water-excluded volume for the fresh sphalerite-ZnS (110), copper-zinc sulfide-CuZnS₂ (110), villamaninite-CuS₂ (100), and covellite-CuS (001) surfaces, which are indicated by the primary water density peak, confirmed the different interfacial water characteristics for the surfaces with different degrees of hydrophobicity. It also confirmed the trend of hydrophobicity of these surfaces revealed from the simulated contact angles and the MDS snapshots. Other MDS analyses in our study, especially the water residence time and water dipole orientation sections, gave further evidence of the relationship between hydrophobicity and interfacial water characteristics.

3.2.2. Water residence time

Besides the structural analysis of interfacial water, the dynamic properties of interfacial water molecules, such as water residence time, can also be studied using MDS. The water residence time, τ , is described as the time a water molecule spends in each water layer at the surface and is calculated using the residence-time correlation function defined by Eq. (6). The term $\langle R(t) \rangle$ is derived from time correlation functions (Berendsen et al., 1987; Chowdhuri and Chandra, 2001; Koneshan et al., 1998) and is defined by Eq. (7).

$$\tau = \int_0^{\infty} \langle R(t) \rangle dt \quad (6)$$

$$R(t) = \frac{1}{N_h} \sum_{i=1}^{N_h} [\theta_i(0) \theta_i(t)] \quad (7)$$

Note that the term $\theta_i(t)$ is the Heaviside unit step function, which has the value 1 if a water molecule, i , is in the hydration shell of the reference water molecule at time t , and is zero otherwise. Water molecules in the hydration shell for more than 2 ps are considered to constitute the hydration shell. The term N_h is the apparent dynamic hydration number.

The water residence time distributions along the surface normal of the fresh sphalerite-ZnS (110), copper-zinc sulfide-CuZnS₂ (110), villamaninite-CuS₂ (100), and covellite-CuS (001) surfaces are shown in Figure 5. The magnitude and position of the first peak of the water residence time for the surfaces in this study and some other surfaces from several previous MDS studies are listed in Table 3 (Du and Miller, 2007a; Du and Miller, 2007b; Jin et al., 2014; Yin, 2012). The magnitudes of water residence times at the fresh sphalerite-ZnS (110), copper-zinc sulfide-CuZnS₂ (110), villamaninite-CuS₂ (100), and covellite-CuS (001) surfaces were very close to other hydrophobic selected sulfide mineral surfaces reported in previous research, such as for the pyrite (100) surface (Jin et al., 2014). More importantly, these values were much smaller than water residence times at hydrophilic surfaces, such as for halite (100), sylvite (100), muscovite, kaolinite alumina and silica surfaces (Du and Miller, 2007a; Du and Miller, 2007b; Yin, 2012). These results indicated the relatively weak interaction between interfacial water and the sulfide mineral surfaces, which is consistent with the natural hydrophobic character of sulfide mineral surfaces under anaerobic conditions.

For the fresh sphalerite-ZnS (110), copper-zinc sulfide-CuZnS₂ (110), villamaninite-CuS₂ (100), and covellite-CuS (001) surfaces, the trend found in the simulated contact angles and water number density profiles was found again in the water residence time analysis. According to Figure 5 and Table 3, the distances of the first peak for water residence time from the fresh

sphalerite-ZnS (110), copper-zinc sulfide-CuZnS₂ (110), villamaninite-CuS₂ (100), and covellite-CuS (001) surfaces had the following sequence: sphalerite-ZnS (110) surface < copper-zinc sulfide-CuZnS₂ (110) surface < villamaninite-CuS₂ (100) surface < covellite-CuS (001) surface. The closer distance of the first water residence time peak from the surface indicated stronger interaction between the interfacial water molecules and the surface as well as a relatively more hydrophilic surface state. Thus, the water residence time analysis for the fresh sphalerite-ZnS (110), copper-zinc sulfide-CuZnS₂ (110), villamaninite-CuS₂ (100), and covellite-CuS (001) surfaces gave the same trend for the hydrophobicity of these surfaces as described in earlier sections. In the next section, the water dipole orientation analysis revealed more details about the interaction between interfacial water molecules and the surfaces of interest.

3.2.3. Water dipole orientation analysis

A schematic illustration describing the orientation of the water dipole moment and the hydrogen position relative to the surface normal is shown in Figure 6. Angle α is the angle between the water dipole moment (oriented from negative to positive) and the surface normal. Angle β is the acute angle between the surface normal and a line connecting the two hydrogen atoms.

The water dipole and hydrogen position relative density distributions for the fresh sphalerite-ZnS (110), copper-zinc sulfide-CuZnS₂ (110), villamaninite-CuS₂ (100), and covellite-CuS (001) surfaces are shown in Figure 7. For the fresh sphalerite-ZnS (110) surface, approximately 2 Å from the surface, a large peak with the angle α at 90° and angle β around 50° indicated that the majority of water molecules in the first water layer had their dipole perpendicular to the surface normal (i.e. water dipole parallel to the surface) and two hydrogen atoms oriented about 50° to the surface normal (i.e., one of the two hydrogen atoms in the water molecule was inclined

toward the surface). The results revealed relatively stronger interaction between the interfacial water molecules and the sphalerite-ZnS (110) surface, which is consistent with a previous study (Jin et al., 2014). This peak did not show up in the case of the copper-zinc sulfide-CuZnS₂ (110), villamaninite-CuS₂ (100), and covellite-CuS (001) surfaces. For the copper-zinc sulfide-CuZnS₂ (100) surface, instead of a peak, a shoulder with the same α and β angles can be observed at the same position (approximately 2 Å from the surface), indicating a relatively weak interaction between the water molecules in the first layer and the copper-zinc sulfide-CuZnS₂ (110) surface when compared to the sphalerite-ZnS (110) surface. The orientation of the hydrogen atom of interfacial water toward the sphalerite-ZnS (110) and copper-zinc sulfide-CuZnS₂ (110) surfaces is because of the electrostatic interaction between the positively charged hydrogen atoms and the negatively charged S atoms at the surface. This organization can be observed from the MDS snapshots of interfacial water molecules at the sphalerite-ZnS (110) and copper-zinc sulfide-CuZnS₂ (110) surfaces in Figure 3 (a) and (c). The reason that this interaction is weaker at the copper-zinc sulfide-CuZnS₂ (110) surface is the comparably smaller atomic partial charge for the S atoms in the copper-zinc sulfide-CuZnS₂ structure than in the sphalerite-ZnS structure, as listed in Table 1. Though the crystal structures for the copper-zinc sulfide-CuZnS₂ and sphalerite-ZnS crystals are similar, atomic partial charges for both the Zn and S atoms in the copper-zinc sulfide-CuZnS₂ crystal are smaller than they are in the sphalerite ZnS crystal. When copper substitutes at the zinc sulfide surface, the Zn and S atomic partial charges are reduced, making the surface less "polar". It is well established that a polar surface exhibits a hydrophilic surface state because of stronger interaction between water and the surface whereas the non-polar surface has a hydrophobic character due to the relatively weak water/surface interactions (Miller,

2000). Thus, when activated, it is the copper substitution which makes the sphalerite-ZnS surface less polar, resulting in less interaction with water, i.e. hydrophobicity.

For the villamaninite-CuS₂ (100) and covellite-CuS (001) surfaces, there was neither a peak nor a shoulder shown at 2 Å from the surface. Instead, for both of these surfaces, there was a large peak at around 3 Å from the surface, which had an α angle of 90° (i.e. water dipole parallel to the surface) and a β angle of 90° (i.e. two hydrogen atoms parallel to the surface). This confirmed our water density distribution results that the primary water density peaks for the villamaninite-CuS₂ (100) and covellite-CuS (001) surfaces were around 3 Å from the surface. Also, these results indicated that the water molecules in the first water layer were mostly parallel to the surface, which confirmed the much weaker interaction between the interfacial water and the villamaninite-CuS₂ (100) and covellite-CuS (001) surfaces as compared to the sphalerite-ZnS (110) and copper-zinc sulfide-CuZnS₂ (110) surfaces. Note that the peak at the covellite-CuS (001) surface was higher and sharper than the peak at the villamaninite-CuS₂ (100) surface. The water molecules in the first water layer were more oriented parallel to the covellite-CuS (001) surface than for the villamaninite-CuS₂ (100) surface, indicating the relatively weaker interaction between interfacial water and the covellite-CuS (001) surface than for the villamaninite-CuS₂ (001) surface. This was consistent with the trend of hydrophobicity of the fresh sphalerite-ZnS (110), copper-zinc sulfide-CuZnS₂ (110), villamaninite-CuS₂ (100), and covellite-CuS (001) surfaces as discussed in the previous sections on simulated contact angle, water number density and water residence time. As listed in Table 1, the atomic partial charges and the surface polarity decreased according to the sequence in which the copper content increased: sphalerite-ZnS (110) surface; copper-zinc sulfide-CuZnS₂ (110) surface; villamaninite-CuS₂ (100) surface; covellite-CuS (001) surface. As a result, the electrostatic interactions between interfacial water and the

surface decrease but the surface hydrophobicity increases following the same sequence. In addition to the decrease of surface polarity caused by the copper substitution, according to UFF parameters, Cu atoms have more VdW repulsive interaction with the interfacial water molecules than the Zn atoms (Rappé et al., 1992). This might also have an effect on the relatively greater hydrophobic character for the Cu^{2+} activated sphalerite surface.

3.2.4. Hydrogen bonding

MDS results also provided information about the hydrogen bonding between water molecules at the fresh sphalerite-ZnS (110), copper-zinc sulfide- CuZnS_2 (110), villamaninite- CuS_2 (100), and covellite- CuS (001) surfaces. For the SPC/E water model, two water molecules are defined as hydrogen bonded if the distance between the two oxygen atoms is less than 3.5 Å and the $\text{O}\cdots\text{O}-\text{H}$ angle is simultaneously less than 30° (Luzar and Chandler, 1996).

Distribution of the average number of hydrogen bonds per water molecule along the surface normal for the fresh sphalerite-ZnS (110), copper-zinc sulfide- CuZnS_2 (110), villamaninite- CuS_2 (100), and covellite- CuS (001) surfaces are presented in Figure 8. For the fresh sphalerite-ZnS (110), copper-zinc sulfide- CuZnS_2 (110), villamaninite- CuS_2 (100), and covellite- CuS (001) surfaces, from the surface to the bulk water, the total number of hydrogen bonds per water molecule increased until it reached a plateau value close to 3.35 about 4 Å from the surface, very close to the value of 3.5 reported in the literature (Nieto-Draghi et al., 2003). Although the number of hydrogen bonds per water molecule for the fresh sphalerite-ZnS (110), copper-zinc sulfide- CuZnS_2 (110), villamaninite- CuS_2 (100), and covellite- CuS (001) surfaces fluctuated somewhat before they reached the plateau, none of the surfaces exceeded the plateau value for hydrogen bonding of 3.35 for bulk water. According to previous MDS research for the quartz

surface, the distribution of the number of hydrogen bonds per water molecule at the hydrophilic quartz surface had a large and distinct peak of about 4, less than 1 Å from the surface (Wang et al., 2012), indicating that most of the interfacial water molecules were tetrahedrally bonded at the hydrophilic quartz surface. However, because of the exclusion of water molecules at the fresh sphalerite-ZnS (110), copper-zinc sulfide-CuZnS₂ (110), villamaninite-CuS₂ (100), and covellite-CuS (001) surfaces, there were very few hydrogen bonds in the interfacial region over a distance of 1 Å from the surface. The distinct differences between the distribution of the number of hydrogen bonds per water molecule for the hydrophilic quartz surface and the fresh sphalerite-ZnS (110), copper-zinc sulfide-CuZnS₂ (110), villamaninite-CuS₂ (100), and covellite-CuS (001) surfaces reveals the natural hydrophobic character for the fresh sphalerite-ZnS (110), copper-zinc sulfide-CuZnS₂ (110), villamaninite-CuS₂ (100), and covellite-CuS (001) surfaces.

4. Conclusions

Results of experimental contact angle measurements for fresh and Cu²⁺ activated sphalerite surfaces as well as for the covellite-CuS (001) surface indicated that the modest hydrophobicity of the sphalerite surface would be altered toward the strong hydrophobicity of the covellite-CuS (001) surface during the Cu²⁺ activation process. These results are consistent with previous collectorless flotation studies (Fornasiero and Ralston, 2006; Fuerstenau and Sabacky, 1981).

Based on the metathetic exchange reaction for Cu²⁺ activation of sphalerite, a copper-zinc sulfide-CuZnS₂ crystal was established from the chalcopyrite crystal structure. Force fields including the UFF Lennard-Jones parameters and Mulliken charges were used in our MD simulations to predict the interfacial water characteristics at the fresh sphalerite-ZnS (110), copper-zinc sulfide-CuZnS₂ (110), villamaninite-CuS₂ (100), and covellite-CuS (001) surfaces.

The simulated contact angle measurements were consistent with the experimental measurements and confirmed the increase in hydrophobicity of the sphalerite surface during the Cu^{2+} activation process. According to the simulated contact angles, the hydrophobicity increased according to the following sequence: sphalerite-ZnS (110) surface; copper-zinc sulfide- CuZnS_2 (110) surface; villamaninite- CuS_2 (100) surface; covellite- CuS (001) surface, i.e. the copper content increased.

This trend was confirmed by our MDS results regarding the interfacial water structure and dynamic properties, including water density distribution, water residence time, water dipole orientation, and hydrogen bonding analysis. It has been revealed that the interactions between interfacial water and the surface decrease according to the same sequence, mainly because of the decrease of surface polarity caused by the increased copper content and the relatively stronger VdW repulsive force of the copper atoms than of the Zn atoms. Thus, the possible copper sulfide product at the sphalerite surface as a result of Cu^{2+} activation was the origin of stronger hydrophobicity.

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Table 1 Force Field Parameters for Selected Sulfide Minerals

Sulfide Mineral	Atom	r_m (Å)	ϵ (Kcal/mol)	Atomic Partial Charges (q)
Sphalerite ZnS	Zn	2.763	0.124	0.459
	S	4.035	0.274	-0.459
CuZnS ₂	Cu	3.495	0.005	0.230
	Zn	2.763	0.124	0.390
	S	4.035	0.274	-0.310
Villamaninite CuS ₂	Cu	3.495	0.005	0.172
	S	4.035	0.274	-0.086
Covellite CuS	Cu	3.495	0.005	0.110
	S	4.035	0.274	-0.110

Table 2 Simulated Contact Angles and Experimental Values for Zinc and Copper Sulfide Surfaces

Mineral Surface	Simulated Contact Angles, degree	Experimental Contact Angles, degree
Fresh Sphalerite (110) Surface	48	42
Cu ²⁺ Activated Sphalerite Surface	-	57
CuZnS ₂ (110) Surface	54	-
Villamaninite (100) Surface	71	-
Covellite (001) Surface	85	65

Table 3 Comparison of Interfacial Water Residence Times

Surface State	Mineral Surface	First Peak for Water Residence Time	
		Distance from Surface (Å)	Magnitude (ps)
Hydrophilic	Kaolinite Alumina Face	2.0	29.3
	Muscovite (001) Surface	1.0	25.0
	Halite (100) Surface	-	30.0
	Sylvite (100) Surface	-	20.0
Hydrophobic	Sphalerite ZnS (110) Surface	2.2	7.8
	CuZnS ₂ (110) Surface	3.2	6.4
	Villamaninite CuS ₂ (100) Surface	3.4	6.9
	Covellite CuS (001) Surface	3.5	6.7
	Pyrite (100) Surface	3.5	7.5

Figure Captions:

Figure 1. Droplet contour at selected mineral surfaces: (a) fresh sphalerite ZnS (110) surface; (b) CuZnS₂ (110) surface; (c) villamaninite CuS₂ (100) surface; (d) covellite CuS (001) surface.

Figure 2. Optical microscopy photograph for the cleavage plane of the covellite CuS crystal with reflected light.

Figure 3. MDS snapshots of mineral/water interfaces: (a), (b), fresh sphalerite ZnS (110) surface; (c), (d), CuZnS₂ (110) surface; (e), (f), villamaninite CuS₂ (100) surface; (g), (h), covellite CuS (001) surface. The atoms' color codes are as follow: yellow, S; green, Zn; blue, Cu; red, O; white, H.

Figure 4. Relative water number density profiles at selected mineral surfaces: (a) fresh sphalerite ZnS (110) surface; (b) CuZnS₂ (110) surface; (c) villamaninite CuS₂ (100) surface; (d) covellite CuS (001) surface.

Figure 5. Water residence time profiles for selected mineral surfaces: (a) fresh sphalerite ZnS (110) surface; (b) CuZnS₂ (110) surface; (c) villamaninite CuS₂ (100) surface; (d) covellite CuS (001) surface.

Figure 6. Schematic illustration describing the orientation of a water dipole moment (α) and hydrogen position relative to the surface normal (β).

Figure 7. Water dipole moment (angle α) and hydrogen position (angle β) relative density distribution along the surface normal at selected mineral surfaces: (a) fresh sphalerite ZnS (110) surface; (b) CuZnS₂ (110) surface; (c) villamaninite CuS₂ (100) surface; (d) covellite CuS (001) surface.

Figure 8. Distribution of hydrogen-bonding number per water molecule along the surface normal for selected mineral surfaces: (a) fresh sphalerite ZnS (110) surface; (b) CuZnS_2 (110) surface; (c) villamaninite CuS_2 (100) surface; (d) covellite CuS (001) surface.

Graphic Abstract

Interfacial water at the fresh sphalerite-ZnS (110), copper-zinc sulfide-CuZnS₂ (110), villamaninite-CuS₂ (100) and covellite-CuS (001) surfaces.

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Figure 7.

Figure 8.