

Influence of hydrated Ca^{2+} and Mg^{2+} complexes on the sulfidization of smithsonite: Density functional based tight binding (DFTB+) study

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Abstract: Ca^{2+} and Mg^{2+} are the most dominating unavoidable ions in the smithsonite flotation. In this paper, the effect of Ca^{2+} (Mg^{2+}) on the surface of smithsonite sulfidization in a system where water molecules are present was investigated using density functional based tight binding (DFTB+) simulations for the first time. The results indicated that the adsorption of hydrated Ca^{2+} complexes is stronger than that of hydrated Mg^{2+} complexes on the hydrated smithsonite (101) surface. In addition, at low concentrations of sodium sulfide, there is no adsorption of HS^- on the surface pre-adsorbed with hydrated Ca^{2+} complexes, but only on the surface pre-adsorbed with hydrated Mg^{2+} complexes. At high concentrations of Na_2S , S^{2-} weakens the adsorption of hydrated Ca^{2+} complexes due to competitive adsorption, but the presence of S^{2-} could desorb hydrated Mg^{2+} complexes from the surface. The results compared the differences in effects of Ca^{2+} and Mg^{2+} on smithsonite sulfidization, which could provide an atomic scale basis for researching the surface sulfidization of oxide minerals.

Keywords: smithsonite, sulfidization, DFTB+, hydrated, adsorption

1. Introduction

Zinc is one of the most common nonferrous metals with good corrosion resistance and ductility, hence it is widely used in the production of zinc plating and alloys (Ejtemaei et al., 2011). Sulfide minerals are the main source of zinc, however, the resource of zinc sulfide minerals is gradually exhausted after a long period of mining (Irannajad et al., 2009; Feng et al., 2019). Thus, the beneficiation of zinc oxide minerals has become necessary to obtain sources of zinc. Smithsonite is one of the most typical components of zinc oxide minerals, which has important research significance (Ejtemaei et al., 2014). Compared with zinc sulfide minerals, the surface of smithsonite is more hydrophilic (Hales and Frost, 2008; Liu et al., 2019). Therefore, smithsonite is frequently pretreated by sulfidization to produce zinc sulfide on the surface, thereby enhancing the collector adsorption (Kalichini et al., 2017).

According to previous investigations, sulfidization-xanthate flotation and sulfidization-amine flotation are the commonly used method for beneficiation of zinc oxide minerals (Herrera-Urbina and Sotillo, 1998). The optimum pH for zinc oxide minerals flotation with amine as collector is approximately 12; under this condition, S^{2-} is the dominant species that interacts with zinc oxide minerals (Xie, 2020). As for sulfidization-xanthate flotation, the optimal pH is about 10, and HS^- mainly interacts with zinc oxide minerals (Feng et al., 2016a, 2016b). However, smithsonite is often associated with calcite (CaCO_3) and dolomite ($\text{CaMg}(\text{CO}_3)_2$), which are easily slimed (Hosseini and Forssberg, 2006; Deng et al., 2018). Moreover, the hard water in many areas also contains Ca^{2+} and Mg^{2+} (Liu et al., 2012), hence there could inevitably be a large number of Ca^{2+} and Mg^{2+} in the solution (Nunes et al., 2011; Luo et al., 2019).

The reaction mechanism of Ca^{2+} and Mg^{2+} with the smithsonite surface is the key issue to achieve efficient sulfidization, and many scholars have discovered that Ca^{2+} and Mg^{2+} have similar properties, but their effects on mineral flotation are distinct (Kiersznicki et al., 1981; Feng and Luo, 2013; Abkhoshk

et al., 2014; Chen et al., 2019). Fang et al. (2019) found that the recovery of diaspore hardly changed with the increase of Ca^{2+} concentration, while Mg^{2+} had a significant inhibitory effect. Li et al. (2013) demonstrated that Mg^{2+} had a greater inhibition on the smithsonite flotation. Different from the above views, Araújo and Lima (2017) discovered that Ca^{2+} causes the smithsonite to be strongly inhibited instead of Mg^{2+} in the smithsonite flotation. These researches have compared the effects of Ca^{2+} and Mg^{2+} on smithsonite recovery by flotation tests; however, these contradictory results for this phenomenon have not been clearly explained.

Density functional theory (DFT) has been widely used, which is an effective method to study the mechanism of mineral surface adsorption from a molecular perspective (Reich and Becker, 2006; Lejaeghere, 2014; Zhao et al., 2015; Luo et al., 2021a; Luo et al., 2021b). Liu et al. (2019) found that H_2O would strongly interact with S-species on the smithsonite surface. Luo et al. (2021) also confirmed that water molecules have a significant influence on the adsorption of smithsonite. Liu (2020) compared the effects of different carboxylic acid collectors on the smithsonite (101) surface with and without water molecules. Their results showed the existence of H_2O had a considerable influence on the adsorption of reagents on the smithsonite surface. In addition, previous studies indicated that metal ions are solvated in solution and form complexes with H_2O (Gowda and Benson, 1983; Teychené et al., 2019; Li et al., 2020). Based on this, Chen (2021) proposed the theory of flotation coordination chemistry and explained that the hydration of metal ions has a significant impact on adsorption. Furthermore, Luo and Chen (2022) compared the results of metal ion adsorption alone and adsorption after hydration, proving that metal ion hydration on mineral surfaces is more reliable. Nevertheless, the influence of hydrated metal ions on the smithsonite sulfidization is complicated, which makes it difficult for DFT to simulate. The density functional based tight binding (DFTB+) not only retains the accuracy of density functional theory (DFT) but also has the efficiency of tight binding method (TB) (Elstner et al., 1998; Selli et al., 2017), which could greatly reduce the cost of calculation while ensuring the accuracy of calculation (Seifert, 2007; Choi, 2013; Brandenburg and Grimme, 2014).

In this paper, DFTB+ method was used to investigate the adsorption of hydrated Ca^{2+} and Mg^{2+} complexes on smithsonite at the atomic scale. In particular, the difference in the effect of Ca^{2+} and Mg^{2+} on smithsonite sulfidization is compared, which provided a new light for studying the influence of metal ions on zinc oxide flotation.

2. Models and computational details

The optimization of smithsonite (101) surface and its surface adsorption was undertaken by performing density functional theory of tight binding (DFTB+) method (Frenzel, 2004). The 3ob set of Slater-Koster and dispersion correction were applied to simulation. The Monkhorst-Pack scheme was used for Brillouin zone sampling, and the k point gridding was selected as $2 \times 2 \times 1$ (Monkhorst and Pack, 1976). The convergence tolerances for calculation were set as (a) maximum energy of 8.37×10^{-2} kJ/mol, (b) maximum displacement of 1×10^{-3} Å, (c) maximum force of 4.18×10^{-1} kJ/mol \times Å $^{-1}$.

It is well acknowledged that smithsonite (101) surface has the lowest surface energy and is the most stable surface (Zhen et al., 2017), hence smithsonite (101) surface was selected for this study. In order to obtain smithsonite (101) surface, cleaving was carried out on the basis of optimized bulk. The calculated lattice parameters of bulk ZnCO_3 were $a = b = 4.83$ Å and $c = 15.31$ Å, which were close to the experimental value $a = b = 4.65$ Å and $c = 15.03$ Å. After the slab thickness was tested, the $(3 \times 3 \times 1)$ smithsonite (101) surface supercell with 7 atomic layers was constructed and separated by a 25 Å vacuum and the supercell of ZnCO_3 slab had a dimension of $17.45 \times 14.50 \times 38.21$ Å 3 , which was adequate for the surface sulfidization and reagent adsorption, as shown in Fig. 1. For the smithsonite (101) surface, the four outermost atomic layers of the substrate were allowed to relax, while the three bottom-most atomic layers were fixed to the bulk coordinates.

Before adsorption, the water molecules (H_2O), calcium ion (Ca^{2+}), magnesium ion (Mg^{2+}), and sodium sulfide (Na_2S) were pre-optimized in a $15 \times 15 \times 15$ Å 3 cubic cell. Adsorption energy of the adsorbate on smithsonite (101) surface could be calculated by the equation below:

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

where ΔE_{ads} is the adsorption energy, kJ/mol; $E_{surf+adsorbate}$ denotes the addition energy of smithsonite surface containing the adsorbate molecules after optimization, kJ/mol; E_{surf} represents the energy of the

smithsonite surface after optimization, kJ/mol; and $E_{adsorbate}$ is the energy of the adsorbate after optimization, kJ/mol.

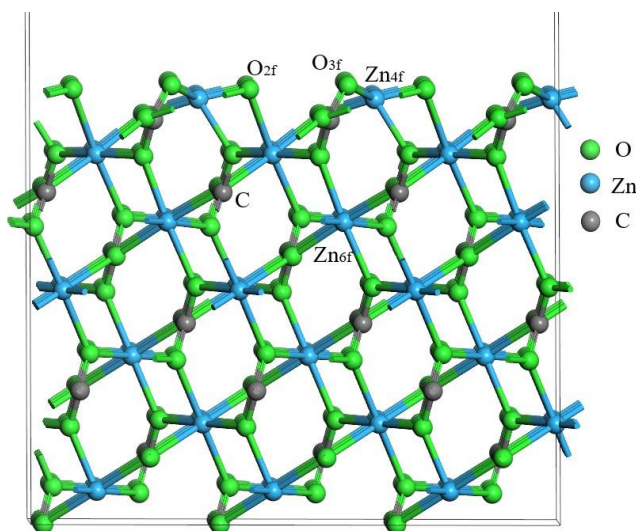


Fig. 1. The slab model of seven atomic layers smithsonite (101) surface after relaxation

3. Results and discussion

3.1. The adsorption of Ca^{2+} (Mg^{2+}) on the hydrated smithsonite (101) surface

In our previous study on the influence of multi-layer water molecules on the change of surface structure and electronic properties of smithsonite, it was found that when three layers of water molecules were adsorbed on the smithsonite (101) surface, the water molecules at the bottom dissociated into hydroxide ions and hydrogen ions, and hydroxide ions interacted with the smithsonite surface Zn sites, which can be regarded as forming a layer of zinc hydroxide, and accordingly result in the surface hydroxylation (Chen et al., 2014; Chen et al., 2018; Liu et al., 2020; Cui et al., 2021).

Nine OH^- were added to the smithsonite (101) surface to construct the hydrated smithsonite (101) surface. This optimized geometric configuration is depicted in Fig. 2. The interaction distance among OH^- -O with smithsonite surface Zn atoms on the smithsonite (101) surface is 2.028 Å, which is slightly smaller than the addition of atomic radii of Zn atom and O atom (2.140 Å), verifying that the optimized configuration is consistent with our previous research results (Chen et al., 2018).

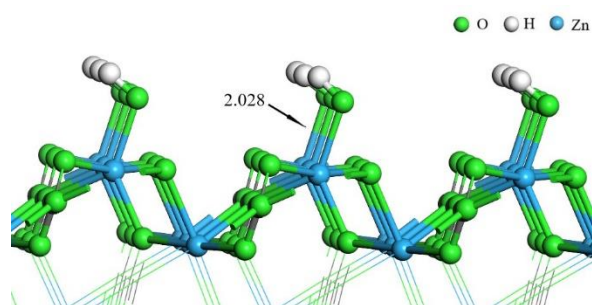


Fig. 2. Hydrated surface of smithsonite (101) (The Å is a unit of distance)

The effect of Ca^{2+} and Mg^{2+} on the hydrated smithsonite (101) surface is investigated. Fig. 3 (a) and (b) show the optimized geometric configurations. It is found that Ca^{2+} and Mg^{2+} adsorb on the hydrated smithsonite (101) surface via the interaction with OH^- -O atoms and smithsonite surface O atoms. For Ca^{2+} , the Ca-O interaction distances are 2.226 Å, 2.347 Å and 2.224 Å, respectively, which are close to the addition of atomic radii of Ca and O atoms (2.400 Å). The bonding distances of Mg-O for Mg^{2+} are 1.986 Å, 2.013 Å and 2.023 Å, which are much smaller than the addition of atomic radii of Mg and O atoms (2.260 Å). The calculated adsorption energies of Ca^{2+} and Mg^{2+} on the smithsonite surface are -340.32 kJ/mol and -246.77 kJ/mol. All these results indicate that Ca^{2+} and Mg^{2+} could strongly adsorb

on the hydrated smithsonite (101) surface, but the adsorption of Ca^{2+} is stronger than Mg^{2+} . However, it is well known that Mg^{2+} has little effect on the flotation of smithsonite, and only a small amount of Mg^{2+} can be adsorbed on the surface (Deng et al., 2018). The above simulation results are not consistent with the results of flotation practice. Meanwhile, considering that the metal ions in the solution are unstable, the adsorption of hydrated Ca^{2+} and Mg^{2+} complexes is further considered.

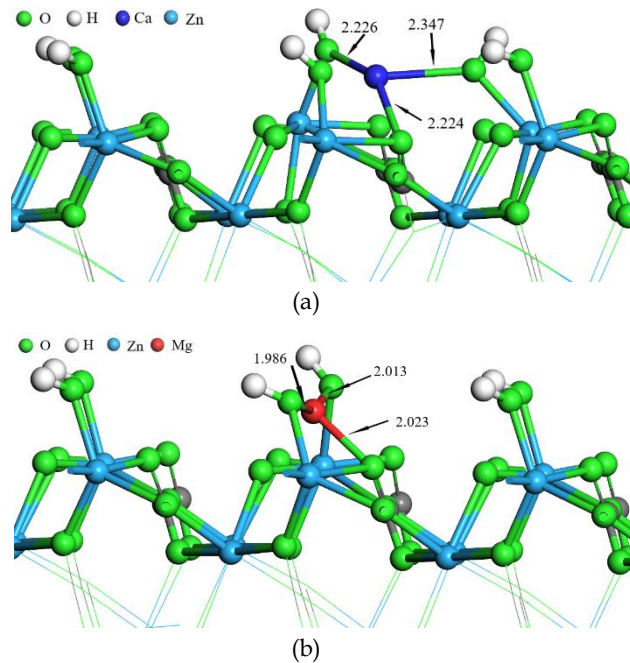


Fig. 3. The optimized geometric configurations of (a) Ca^{2+} and (b) Mg^{2+} adsorbed on the hydrated smithsonite (101) surface (The Å is a unit of distance)

3.2. The adsorption of hydrated Ca^{2+} (Mg^{2+}) complexes on the hydrated smithsonite (101) surface

According to the coordination chemistry of flotation, Ca^{2+} and Mg^{2+} could form stable magnesium-ion-hexahydrate and calcium-ion-hexahydrate in aqueous solutions, respectively, changing the properties and structure of ions. Therefore, the hydration coordination numbers of calcium and magnesium ions in aqueous solutions were investigated. The hydrated metal complexes, $[\text{Ca}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$, are shown in Fig. 4.

The Ca^{2+} could combine with six surrounding water molecules to form the $[\text{Ca}(\text{H}_2\text{O})_6]^{2+}$ ion with a regular octahedral structure, as depicted in Fig. 4(a). The Ca^{2+} interacts with O atoms in water molecules with an interacting distance around of 2.247 Å, which is smaller than the addition of the atomic radius of Ca and O atoms (2.400 Å), indicating that the Ca^{2+} cooperates with water molecules to form the stable hydrated Ca^{2+} complexes ($[\text{Ca}(\text{H}_2\text{O})_6]^{2+}$). The optimized $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ structure is depicted in Fig. 4(b). The Mg^{2+} reacts with O atoms of six water molecules with an interacting distance of around 2.093 Å, which is close to the addition of the radius of Mg and O atoms (2.260 Å), indicating that the hydrated Mg^{2+} complexes ($[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$) formed are stable.

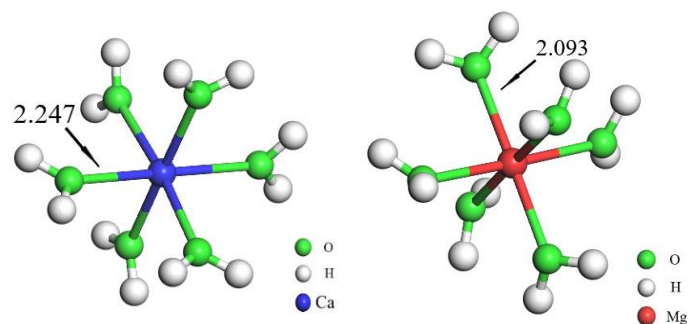


Fig. 4. Hydration structure model of Ca^{2+} (Mg^{2+}) complexes: (a) $[\text{Ca}(\text{H}_2\text{O})_6]^{2+}$, (b) $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$

To further investigate the effect of Ca^{2+} and Mg^{2+} on the smithsonite flotation, the adsorption of hydrated Ca^{2+} complexes and hydrated Mg^{2+} complexes on the hydrated smithsonite (101) surface is simulated. The geometric configurations of hydrated Ca^{2+} and Mg^{2+} complexes after adsorption are shown in Fig. 5(a) and (b). The adsorption energy after the adsorption of $[\text{Ca}(\text{H}_2\text{O})_6]^{2+}$ on smithsonite (101) surface is -182.067 kJ/mol. The results indicate that hydrated Ca^{2+} complexes could stably adsorb on the hydrated smithsonite (101) surface. It can be seen from Fig. 5(a), the distance between H_2O and the Ca^{2+} elongates to varying degrees and the average coordination distance of Ca-O is increased to 2.267 Å. In addition, the bonds of three water molecules and Ca^{2+} are broken, and the distances between the Ca^{2+} and O atoms vary from 2.247 Å to 2.720 Å, 2.754 Å and 2.843 Å, indicating that three water molecules are dissociated and the $[\text{Ca}(\text{H}_2\text{O})_6]^{2+}$ have become $[\text{Ca}(\text{H}_2\text{O})_3]^{2+}$. At the same time, the $[\text{Ca}(\text{H}_2\text{O})_3]^{2+}$ interacts with two hydroxyl groups on the hydrated smithsonite (101) surface to form Ca-O bonds with bond lengths of 2.295 Å and 2.282 Å, and also with an oxygen atom on the surface to constitute a Ca-O bond with the length of 2.420 Å, which are significantly smaller than the addition of atomic radius of Ca and O atom (2.400 Å). Therefore, it can be considered that the stable six-coordination structure of $[\text{Ca}(\text{OH})_2(\text{H}_2\text{O})_3]$ could be generated after the adsorption of hydrated Ca^{2+} complexes on the hydrated smithsonite (101) surface. It is confirmed by the SEM-EDS results that $\text{Ca}(\text{OH})_2$ is found on the smithsonite surface after flotation (Chen et al, 2019).

As could be seen from Fig. 5(b), after the adsorption of hydrated Mg^{2+} complexes, the adsorption energy after the adsorption of $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ on smithsonite (101) surface is -66.489 kJ/mol. This indicates that only a weak mutual effect occurs between hydrated Mg^{2+} ion and hydrated smithsonite (101) surface. Meanwhile, the distance between H_2O and the Mg^{2+} also elongates to varying degrees and the average coordination distance of Mg-O is increased to 2.081 Å. And the two water molecules break bonds with the magnesium ion and the interacting distances between O and Mg atom are as far as 2.720 Å and 2.843 Å, suggesting that only two water molecules are dissociated and the $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ have become $[\text{Mg}(\text{H}_2\text{O})_4]^{2+}$. Furthermore, the hydrated Mg^{2+} complexes interact with two hydroxyl groups on the hydrated smithsonite (101) surface to form two Mg-O bonds with the lengths of 2.187 Å and 2.196 Å, which are slightly smaller than the addition of atomic radius of Mg and O atom (2.260 Å). The results show that the stable six-coordination structure of $[\text{Mg}(\text{OH})_2(\text{H}_2\text{O})_4]$ could be formed when hydrated Mg^{2+} complexes are adsorbed on hydrated smithsonite (101) surface. The above results indicate that both hydrated Ca^{2+} complexes and hydrated Mg^{2+} complexes could adsorb on the smithsonite in the pulp, but the adsorption of hydrated Ca^{2+} complexes is much stronger than hydrated Mg^{2+} complexes.

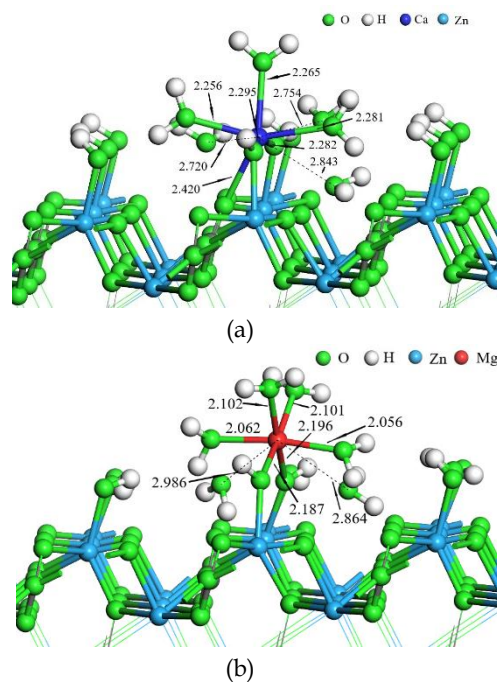


Fig. 5. The optimized geometric configurations of (a) hydrated Ca^{2+} complexes and (b) hydrated Mg^{2+} complexes adsorbed on the hydrated smithsonite (101) surface (The Å is a unit of distance)

The density of states (DOS) is a significant parameter to describe the state of electron motion, which can be used to analyze the reactivity of atomic orbitals (Diwaker, 2014; Fung et al,2022). In general, the localization decreases as the band widens, showing that the peak of the density of states becomes gentler. Fig. 6 presents the DOS of Ca in the hydrated Ca^{2+} complexes atom and O in the hydrated smithsonite (101) surface before and after adsorption. Before adsorption, the partial density of states (PDOS) of hydrated smithsonite (101) surface-O 2s orbital is located at deep energy levels (-20 ~ -15 eV), suggesting this orbital is hard to be involved in the interaction. Hydrated smithsonite (101) surface-O 2p orbital and Ca 3s orbital and Ca 3p occupy the orbital electrons of the upper valence band near the Fermi level (E_F), indicating these orbitals are more likely to participate in the interaction. After adsorption of hydrated Ca^{2+} complexes, it is found that the PDOS of hydrated smithsonite (101) surface-O and -Zn atoms are changed observably. The PDOS of Ca^{2+} has shifted to a deeper level with a larger span, from -3.80 ~ -1.40 eV to -5.40 ~ 0 eV, which indicates the PDOS of Ca^{2+} becomes more broadening and delocalization after adsorption. Near E_F , there is a strong overlap between Ca 3p state and O 2p state at -5.40 ~ -2.30 eV, which indicates Ca 3p orbitals prefer a mild PDOS and consequently are delocalized and overlapped with O 2p orbitals showing a strong bonding after adsorption. The O 2p state and Ca 3s state are hybridized at -5.40 ~ -2.10 eV. The result indicates a great Ca-O interaction between hydrated Ca^{2+} complexes and hydrated smithsonite (101) surface.

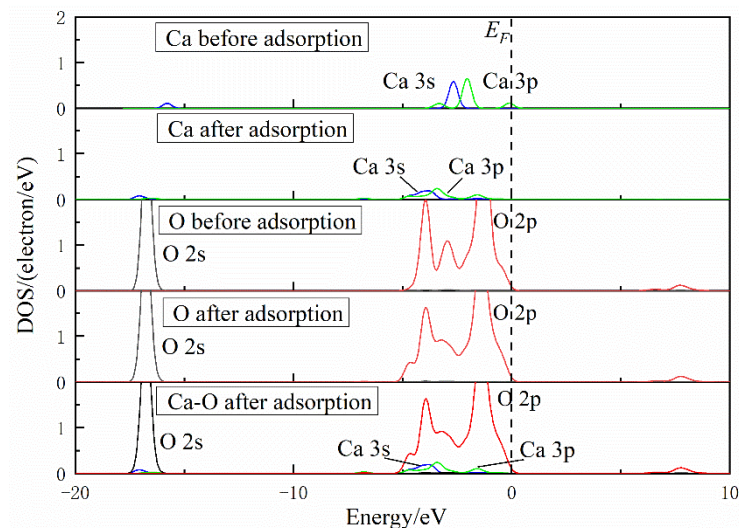


Fig. 6. DOS of hydrated calcium complexes Ca atom and hydrated smithsonite (101) surface O atom before and after interaction

The DOS of hydrated Mg^{2+} complexes Mg atom and hydrated smithsonite (101) surface O atom before and after the adsorption in the existence of water molecules is shown in Fig. 7. It can be found that Mg 2s orbital overlaps with O 2p orbital, indicating that hydrated Mg^{2+} complexes can be adsorbed on the surface. After adsorption, the PDOS of Mg-O peak that shifts toward a deep energy level implies a weak activity for the bonding reaction, and Mg 2s orbital overlaps with O 2p orbital to a small range, with a hybridization peak recorded at -5.00 eV ~ -2.50 eV, indicating a weak bonding reaction. Meanwhile, compared with the adsorption of the hydrated Ca^{2+} complexes on the hydrated smithsonite (101) surface (Fig. 6), the results suggest that the adsorption of hydrated Mg^{2+} complexes is weaker than hydrated Ca^{2+} complexes.

3.3. The influence of hydrated Ca^{2+} (Mg^{2+}) complexes with HS^- as the main component on sulfidization

Due to the inherent floatability of smithsonite being poor, a large amount of sodium sulfide is needed for sufficient sulfidization before adding amine reagents, thus transforming the surface of oxidized minerals into the surface of sulfide minerals and favoring the adsorption of amine reagents on the smithsonite surface (Bai et al., 2020; Luo et al, 2020). Fig. 8 presents the composition distribution of Na_2S aqueous solutions as a function of pH. It is found that HS^- is the main component in the Na_2S aqueous

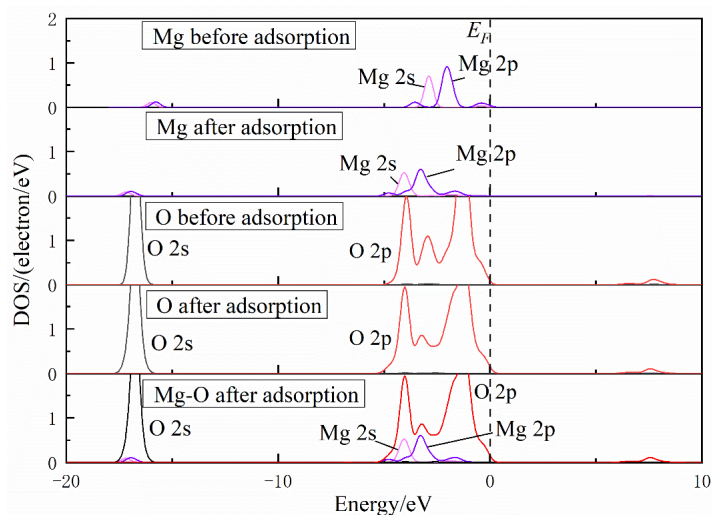


Fig. 7. DOS of hydrated magnesium complexes Mg atom and hydrated smithsonite (101) surface O atom before and after interaction

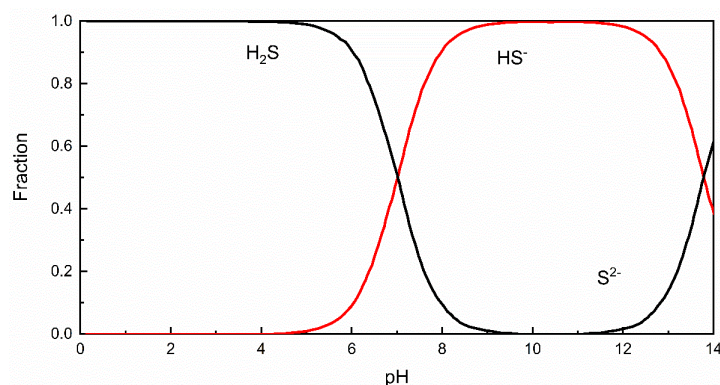


Fig. 8. Composition distribution of Na_2S in solution with pH changes

solution when the pH is in the range of 7-11, and S^{2-} in the solution increases rapidly when the pH > 11. In order to study the influence of Ca^{2+} (Mg^{2+}) on the sulfidization of smithsonite under different concentrations of Na_2S , the reaction of HS^- and S^{2-} on the hydrated smithsonite (101) surface pre-adsorbed with hydrated Ca^{2+} complexes and hydrated Mg^{2+} complexes are simulated.

At low concentrations of Na_2S , the pH of the solution is generally weak alkaline, and HS^- is the main component of Na_2S in solution. Therefore, six HS^- were added to the hydrated smithsonite (101) surface pre-adsorbed with hydrated Ca^{2+} complexes and hydrated Mg^{2+} complexes. The optimized adsorption geometric configurations are shown in Fig. 9(a) and (b), respectively.

As depicted in Fig. 9 (a), the pre-adsorbed hydrated Ca^{2+} complexes result in the inability of HS^- to interact with Zn atoms on the hydrated smithsonite (101) surface. At the same time, the existence of HS^- leads to the average interaction distance between hydrated Ca^{2+} complexes Ca and hydrated smithsonite (101) surface O elongating from 2.332 Å to 2.359 Å which is still smaller than the addition of atomic radius of Ca and O (2.400 Å), proving that HS^- ions weaken the interaction between the hydrated Ca^{2+} complexes and the surface, but cannot desorb hydrated Ca^{2+} complexes from the surface. Therefore HS^- cannot produce effective sulfidization on the smithsonite surface.

It can be seen from Fig. 9 (b) that after adsorption of HS^- , the bonding reaction distance between hydrated Mg^{2+} complexes Mg and surface O atoms is as far as 3.155 Å, which is much greater than the addition of atomic radius of Mg and O atom (2.260 Å), suggesting that the hydrated Mg^{2+} complexes are desorbed from the surface under the influence of HS^- . After desorption of hydrated Mg^{2+} complexes, the distance between HS^- -S atom and surface Zn atom is reduced to 2.399 Å, which is close to the addition of atomic radius of Zn and S (2.370 Å), indicating that HS^- can react with surface Zn atom, in which the surface is pre-adsorbed by the hydrated Mg^{2+} complexes.

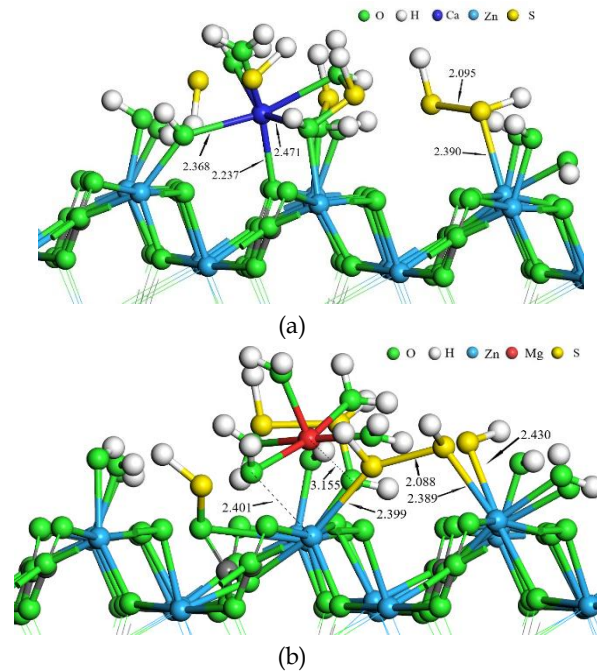


Fig. 9. The optimized geometric configuration of six HS⁻ adsorbed on the hydrated smithsonite (101) surface with (a) hydrated Ca²⁺ complexes and (b) hydrated Mg²⁺ complexes (The Å is a unit of distance)

3.4. The influence of hydrated Ca²⁺ (Mg²⁺) complexes with S²⁻ as the main component on sulfidization

As for further investigation of the influence of Ca²⁺ (Mg²⁺) on the smithsonite sulfidization under a high concentration of Na₂S condition (pH > 12), the presence of S²⁻ should be considered. The reaction of S²⁻ on the smithsonite surface pre-adsorbed with the hydrated Ca²⁺ complexes is conducted and the optimized geometric configuration is shown in Fig. 10. After the adsorption of S²⁻ on the surface, the bonding reaction distance of S²⁻ and surface Zn atoms is 2.391 Å, which is close to the addition of atomic radius of Zn and S (2.370 Å). And it is proved that S²⁻ can adsorb on the surface pre-adsorbed with the hydrated Ca²⁺ complexes, which is in accord with the excess Na₂S required for effective sulfidization in flotation practice

The optimized geometry of six S²⁻ reacting with the hydrated smithsonite (101) surface pre-adsorbed with the hydrated Mg²⁺ complexes is shown in Fig. 10. After the adsorption of S²⁻ on the surface, the average coordination distance between S²⁻ and surface Zn atoms is 2.409 Å which indicates that S²⁻ reacts with Zn, and part of Zn-S structure forms at the surface. In addition, due to the adsorption of S²⁻ on the surface, hydrated Mg²⁺ complexes are completely desorbed from the surface. Compared with hydrated Ca²⁺ complexes, the adsorption of S²⁻ on the hydrated smithsonite (101) surface is almost not affected by hydrated Mg²⁺ complexes, but competitive adsorption occurs between hydrated Ca²⁺ complexes and S²⁻, which is consistent with the smithsonite flotation practice that the existence of Ca²⁺ could affect the flotation recovery of smithsonite (Sun et al, 2019).

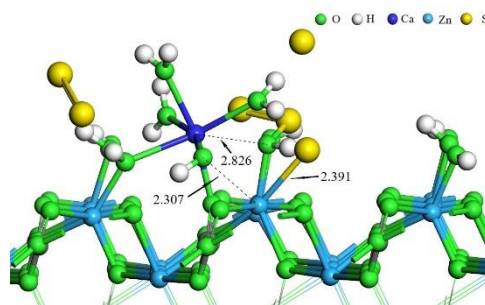


Fig. 10. The optimized geometry of six S²⁻ adsorbed on the hydrated smithsonite (101) surface with the hydrated Ca²⁺ complexes (The Å is a unit of distance)

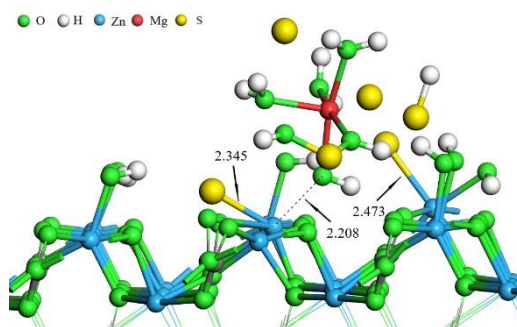


Fig. 11. The optimized geometry of six S^{2-} adsorbed on the hydrated smithsonite (101) surface with the hydrated Mg^{2+} complexes (The Å is a unit of distance)

4. Conclusions

To sum up, hydration should be considered regarding adsorption of Ca^{2+} and Mg^{2+} with the smithsonite surface. The adsorption of the hydrated Ca^{2+} complexes on hydrated smithsonite (101) surface indicates that the hydrated Ca^{2+} complexes dissociate three water molecules to form $[Ca(H_2O)_3]^{2+}$ and interact with the surface to form the hydrated calcium hydroxide ($[Ca(OH)_2(H_2O)_3]$), which confirms that Ca^{2+} can adsorb stably on the smithsonite surface and change its structure. Similar to the hydrated Ca^{2+} complexes, the hydrated Mg^{2+} complexes also desorb two water molecules to generate ($[Mg(H_2O)_4]^{2+}$) and adsorb with the surface to form the hydrated magnesium hydroxide ($[Mg(OH)_2(H_2O)_4]$). In addition, the adsorption strength of hydrated Mg^{2+} complexes is weaker than the hydrated Ca^{2+} complexes.

Under low concentrations of Na_2S , the sulfidization process of HS^- on the smithsonite surface is hard to be carried out due to the pre-adsorption of hydrated Ca^{2+} complexes on the surface. Oppositely, the pre-adsorption of hydrated Mg^{2+} complexes does not affect the sulfidization process of HS^- . Under high concentrations of Na_2S , the presence of S^{2-} partially desorb hydrated Ca^{2+} complexes pre-adsorbed on the surface, indicating that hydrated Ca^{2+} complexes produce some influence on the sulfidization process, but cannot completely depress this process. For Mg^{2+} , however, the presence of S^{2-} causes complete desorption of hydrated Mg^{2+} complexes from the surface. The results could provide a microscopic basis for the effect of Ca^{2+} and Mg^{2+} on the process of smithsonite sulfidization.

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