

Article

Fundamental Studies of SHMP in Reducing Negative Effects of Divalent Ions on Molybdenite Flotation

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Abstract: Seawater has been considered as an alternative to freshwater for flotation. However, many ions in seawater were reported to depress molybdenite (MoS_2), with the depressing mechanisms being insufficiently understood. In this study, the influence of divalent ions (e.g., Ca^{2+} and Mg^{2+}) and dispersant on MoS_2 flotation was systematically investigated. It was found that the detrimental effects of Ca^{2+} and Mg^{2+} on the natural flotability of MoS_2 were mainly due to the attachment of formed CaMoO_4 precipitates and $\text{Mg}(\text{OH})_2$ colloids onto MoS_2 surface. However, the addition of sodium hexametaphosphate (SHMP) reduced the negative effects. Various measurements, including contact angle, zeta potential, fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and atomic force microscope (AFM), were conducted to understand the influencing mechanisms of divalent ions and the beneficial effects of SHMP on MoS_2 flotation. In addition, the Extended Derjugin–Landau–Verwey–Overbeek (EDLVO) theory was applied to investigate the total interaction energy between MoS_2 particles and formed colloids, revealing that the reduced attraction force between MoS_2 and $\text{Mg}(\text{OH})_2$ colloids in the presence of SHMP primarily resulted in the increased MoS_2 recovery. In addition, SHMP combined with Mg^{2+} and Ca^{2+} to form dissolvable complexes, thereby reducing insoluble Mg^{2+} and Ca^{2+} compounds or precipitation. Thus, this study demonstrated for the first time two influencing mechanisms of SHMP in improving MoS_2 recovery in the presence of Ca^{2+} and Mg^{2+} .

Keywords: flotation; SHMP; molybdenite; divalent ions; seawater

1. Introduction

Molybdenite (MoS_2) is the most important molybdenum (Mo) containing mineral source with a sandwich-like S–Mo–S hexagonal layer structure. The adjacent S–S sheets are bonded to each other by van der Waals forces while the individual Mo–S is covalently bonded [1–3]. MoS_2 presents two types of surfaces, namely hydrophobic faces and hydrophilic edges, which are formed by the rupture of weak S–S molecular bonds and strong covalent Mo–S bonds at different crystal faces, respectively, resulting in an anisotropic surface property [3–5]. For instance, López-Valdivieso et al. [6] found a heterogeneous face consisting of many micro-edges on MoS_2 particle surface via atomic force microscopy (AFM). In addition, the face/edge aspect influences MoS_2 flotation significantly [3,7], e.g., high face/edge aspect ratio indicates a high recovery while low face/edge aspect ratio normally results in a low recovery. In addition, the MoS_2 particle is normally deformed during grinding, resulting in a high exposure of edges and micro-edges on the MoS_2 surface [5].

MoS_2 is usually recovered with copper minerals from Cu–Mo ores [8,9], followed by selective flotation of MoS_2 from Cu–Mo concentrate [10]. However, a massive amount of freshwater is consumed

in flotation every year while the continuous growth of population and industrial development decrease the overall water quality, resulting in the scarcity of high quality freshwater [11] and a series of economic and environmental problems [12].

Therefore, some flotation plants use saline water including seawater, showing a promising way to relieve freshwater shortages [11], especially for sulfide mineral flotation [13,14]. For instance, Las Luces in Chile utilizes seawater and tailing dam water to grind and float Cu-Mo sulfides [15] while the Mt Keith plant in Australia utilizes bore water to process nickel minerals [16].

However, seawater usually contains many inorganic ions (e.g., K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Cl^- , and SO_4^{2-}) which can change the frothing properties (e.g., froth stability and bubble coalescence) of the pulp as well as the surface properties (e.g., hydrophobicity and electrostatic force) of the minerals particles, further influencing mineral flotability [11,13,17,18]. Laskowski et al. [18] found a reduced mineral recovery in aqueous solutions containing primary ions (e.g., Na^+ , Cl^- , Mg^{2+} , Ca^{2+} , and SO_4^{2-}) in seawater. Some monovalent salts (e.g., NaCl and KCl) were found to compress electrical double layers, reducing the energy barrier for particle-bubble attachment, further enhancing mineral flotability. For instance, Lucay et al. [10] reported that NaCl decreased the electrostatic repulsion between bubbles and the molybdenite particles, enhancing its flotation kinetics and recovery. In addition, increased hydrophobicity of some minerals treated in a saline environment was found by Troncoso [19]. Moreover, Liu et al. [12] and Ramos et al. [20] reported that salt ions at high concentrations inhibited bubble coalescence and stabilized the froth layer, further increasing mineral recovery. Furthermore, increased electrolyte concentration reduced the bubble size and increased the bubble rise velocity, providing adequate frothing ability, similar to the role of frother [12]. Therefore, the flotation process in some concentrators has been carried out without frothers when using seawater. For instance, Raglan concentrator in Northern Quebec, Canada, utilizes saline water with a salt concentration ranging from 20,000 to 35,000 ppm in the absence of frother [21]. However, the presence of some divalent cations such as Ca^{2+} and Mg^{2+} was reported to have a negative effect on mineral flotation due to the adsorption of metal hydroxyl-complexes and colloidal precipitates onto mineral surfaces, reducing hydrophobicity [22–25].

Many investigators indicated that seawater played a negative role on MoS_2 flotation under alkaline conditions [20,26–29], mainly due to the formation of divalent metallic complexes and colloidal precipitates on mineral surfaces, reducing hydrophobicity and the adsorption of collectors. Therefore, it is necessary to investigate the effect of divalent cations in seawater on MoS_2 flotation. However, limited work has been attempted to investigate the effective methods to relieve MoS_2 depression using seawater. For instance, Suyantara et al. [28] and Hirajima et al. [22] reported that the addition of emulsified kerosene in the flotation process hindered the adsorption of hydrophilic $Mg(OH)_2$ precipitates on the MoS_2 surface. Jeldres et al. [30] showed an improved MoS_2 recovery when using $CaO-Na_2CO_3$ to remove divalent cations before flotation. Although these studies investigated the ways to increase mineral recovery, the mechanisms were not clear.

SHMP commonly plays a strong dispersing role in the flotation process [31–34]. For instance, Li et al. [34] reported that the adsorption of SHMP on serpentine prevented the aggregation between serpentine and ascharite. Xu et al. [32] found that SHMP adhered on a particle surface had a dispersing effect which increased the electrostatic repulsion between valuable minerals and gangues. Some published studies showed an ability of SHMP to dissolve metallic ions from mineral surface into solution by complexation [35–38]. However, the influencing mechanisms of SHMP on MoS_2 flotation when using seawater as the flotation media were not sufficiently investigated.

In this work, the roles of SHMP in improving MoS_2 recovery in the presence of divalent ions (i.e., Ca^{2+} and Mg^{2+}) were investigated. The influencing mechanisms were systematically studied by various measurements such as contact angle, zeta potential, XPS and AFM. Furthermore, the extended Derjaguin–Landau–Verwey–Overbeek (EDLVO) theory model was applied to examine the interaction force between MoS_2 and colloids formed during the flotation process.

2. Materials and Methods

2.1. Minerals and Reagents

MoS₂ was obtained from Guilin, Guangxi province, China. The original sample chunk was crushed, ground in a three head grinding machine (RK/XPM, Wuhan Rock Grinding Equipment Manufacturing Co., Ltd., Wuhan, China) and wet sieved using filter sieve. The obtained powders were thoroughly washed using ethanol to remove fines and the surface filmy oxide layer was removed via sonication. After drying at 30 °C in a DZ-2BC II-type vacuum oven (Tianjin Tester instrument Co., Ltd., Tianjin, China) for 24 h, the obtained particles were sealed in plastic tubes and transferred into a freezer prior to use. The X-ray diffraction (XRD) analysis shown in Figure 1 indicated that the majority of this sample was well-crystallized MoS₂.

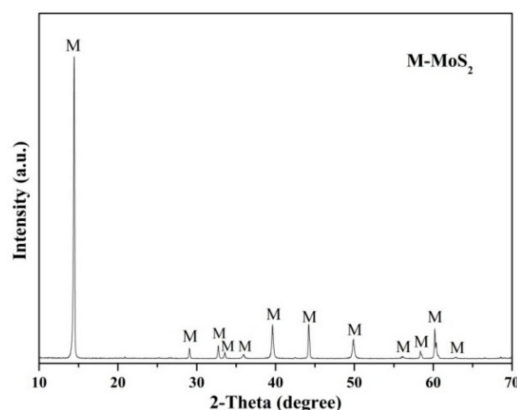


Figure 1. X-ray Diffraction pattern (XRD) of MoS₂.

The elemental composition of the MoS₂ sample is given in Table 1, indicating a high Mo concentration with a small portion of impurities, consistent with the XRD results.

Table 1. Chemical composition of MoS₂ sample.

Element	Mo	S	Si	Bi	Cl	Ca	Al	Fe	Ba	K	Pb
Concentration (%)	53.10	43.25	1.07	0.72	0.53	0.35	0.26	0.25	0.22	0.18	0.07

In addition, Figure 2 shows the cumulative size distribution of the MoS₂ sample used for flotation experiment, indicating that more than 90% of the particles were within 38–75 µm as the d_{10} , d_{50} and d_{90} (which refer to the particle size of MoS₂ sample when its cumulative size distribution reaches 10%, 50%, 90%, respectively) were 48, 66 and 74 µm, respectively.

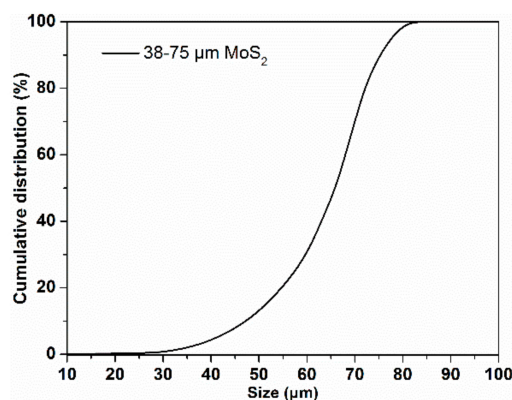


Figure 2. Cumulative size distribution of MoS₂.

Reagents including SHMP, anhydrous calcium chloride (CaCl_2) and magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) from China Sinaopharm Chemical Reagent Co., Ltd. were analytical grade and used as supplied. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) supplied by China Sinaopharm Chemical Reagent Co., Ltd. (Shanghai, China) were used as pH regulators. All experimental solutions were prepared using Millipore[®] ultrapure water (Billerica, MA, USA) with a resistivity of $18.2 \text{ M}\Omega \cdot \text{cm}$.

2.2. Flotation

MoS_2 flotation tests were performed in a mechanical agitation XFG II-type flotation machine made by Wuhan Exploration Machinery Factory (Wuhan, China). First, 0.25 g MoS_2 (38–75 μm) and 25 mL conditioned solution were added into the 40 mL flotation cell, followed by maintaining pulp pH at a desired value during the first 6 min with an agitation speed of 1200 rpm. The geometry of the flotation cell is shown in Figure 3. Thereafter, froth collection was consecutively carried out every 10 s with an air flow rate of 0.1 L/min. Both froth concentrates and tailing were filtered and air dried at 70 °C prior to weighing. The concentrations of Ca^{2+} (0.01 M) and Mg^{2+} (0.05 M) selected in this study were the same as those contained in seawater [23], thereby providing evidence to understand the primary ions playing the most significant inhibition role. The recovery shown in the Figures 4–6 was the average value of three repeated experiments, with the error bar being as one standard deviation.

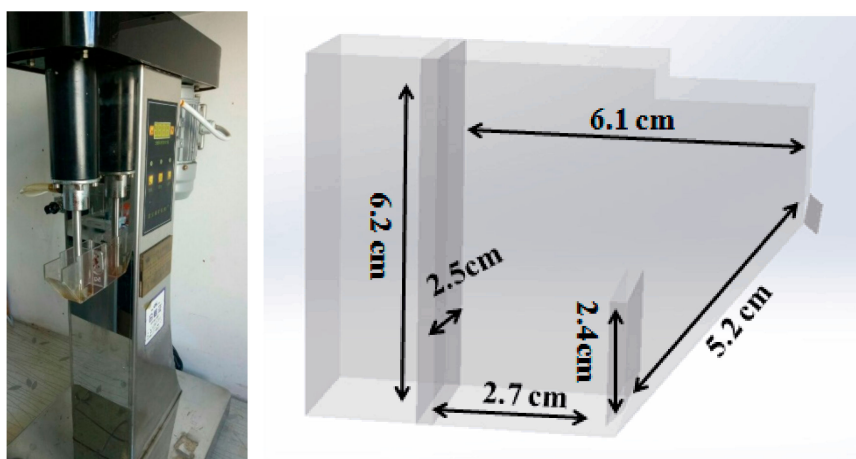


Figure 3. Geometry of flotation cell.

2.3. Contact Angle Measurements

A JC2000C type measuring device (Shanghai Zhongchen Digital Technology Company, Shanghai, China) was used to measure the contact angle of MoS_2 treated under different conditions. The freshly cleaved surface was obtained by peeling off the top layers of the MoS_2 sample using adhesive tape and then conditioning in the testing solution for 10 min. After rinsing three times using ultrapure water and air drying, a 0.25 μL drop of ultrapure water was placed onto the sample surface through a microliter syringe. Thereafter, the contact angle was obtained by analyzing the drop profile. The average value of three different measurements was presented herein as the final contact angle.

2.4. Zeta Potential Measurements

Zeta potentials of MoS_2 were determined in different aqueous solutions using a Nano-ZS90 zeta potential analyzer (Malvern Co., Ltd., Malvern, UK). The MoS_2 with a particle size of $\sim 38 \mu\text{m}$ was further ball ground to less than 5 μm for zeta potential measurements. Then, 0.05 g of finely ground sample was poured into 50 mL test solution and conditioned by magnetic stirring for 10 min so that the suspension was homogenized. The pulp pH was adjusted to a desired value using NaOH or HCl . Subsequently, the agitated suspension was transferred into a sample cell and then tested.

Each experiment was repeated at least thrice with a typical variation of ± 5 mV and the average was reported as the result presented herein. The zeta potential measurement of $\text{Mg}(\text{OH})_2$ precipitate formed in the 0.05 M MgCl_2 solution was determined by a similar same way as that for MoS_2 particles, i.e., the 0.05 M MgCl_2 solution was firstly adjusted for 10 min to pH 10 to allow for precipitation. The solution with precipitation was then stirred to homogeneity and transferred into a sample cell for zeta potential tests.

2.5. XPS Measurements

First, 0.25 g of 38–75 μm MoS_2 samples was placed into 25 mL solution containing 0.01 M CaCl_2 or 0.05 M MgCl_2 with or without 50 mg/L SHMP, followed by pH adjustment and magnetic stirring for 30 min. After that, the sample was filtered and freeze-dried for XPS analysis using Thermo Fisher ESCALAB 250Xi spectrometer (Waltham, MA, USA) with an Al $K\alpha$ monochromatic X-ray source. All wide survey spectra were collected from 1350 to 0 eV with a pass energy of 100 eV and a step size of 1.0 eV while the high resolution XPS spectra for each element were collected with a pass energy of 30 eV and a step size of 0.1 eV. Both survey and high resolution spectra had a dwell time of 0.1 s and 5 sweeps. The XPS Peak 4.1 software was used for data analysis. The charge compensation for all spectra was calibrated based on the C 1s binding energy at 284.8 eV.

2.6. AFM Measurements

A MultiMode 8 atomic force microscope (AFM, Bruker, Santa Barbara, CA, USA) with tapping mode in air was applied to investigate the morphology (256 $\times$ 256 pixel resolution) of MoS_2 surfaces, thereby providing the layer thickness and roughness. ScanAsyst-Air Si_3N_4 probe with a radius of 2 nm was used. For each test, freshly cleaved MoS_2 surface was obtained by peeling off the top layers of the molybdenite sample using a sticky tape, followed by dropping 10 mL conditioned solution (e.g., 0.05 M MgCl_2 solution at pH 10 with or without 50 mg/L SHMP addition) on the freshly cleaved surface for 10 min. After that, the MoS_2 surface was washed 3 times with ultrapure water, and then air-dried prior to imaging.

2.7. Theory Calculation

Usually, the total interaction energies (V_T) between particles in aqueous solution are quantitatively predicted by the extended Derjaguin–Landau–Verwey–Overbeek (EDLVO) theory, in which the energies of the Van der Waals interaction V_W , the electrostatic interaction V_E , and steric hindrance effects V_{SR} are taken into consideration, as described in Equation (1) [31,38–40].

$$V_T = V_W + V_E + V_{SR} \quad (1)$$

V_W and A can be calculated according to Equations (2) and (3).

$$V_W = -\frac{A}{6H} \left(\frac{R_1 R_2}{R_1 + R_2} \right) \quad (2)$$

$$A = \left(\sqrt{A_{11}} - \sqrt{A_{33}} \right) \left(\sqrt{A_{22}} - \sqrt{A_{33}} \right) \quad (3)$$

The Hamaker constant of MoS_2 (A_{11}) in vacuum is 9.38×10^{-20} J [41]. As Hamaker constant of $\text{Mg}(\text{OH})_2$ in vacuum cannot be found in the literature, it is replaced by that of MgO , $A_{22} = 10.6 \times 10^{-20}$ J [42]. The Hamaker constant of water A_{33} is 3.7×10^{-20} J [42,43]. H (nm) refers to the distance between particles.

The electrostatic interaction energy V_E between MoS_2 particles and $\text{Mg}(\text{OH})_2$ colloids can be expressed by Equation (4) [42].

$$V_E = \frac{\pi\epsilon_0\epsilon_r R_1 R_2}{R_1 + R_2} (\psi_1^2 + \psi_2^2) \cdot \left\{ \frac{2\psi_1\psi_2}{\psi_1^2 + \psi_2^2} \cdot \ln \left[\frac{1 + \exp(-\kappa H)}{1 - \exp(-\kappa H)} \right] + \ln[1 - \exp(-2\kappa H)] \right\} \quad (4)$$

where ϵ_0 and ϵ_r are the vacuum dielectric constant and the relative dielectric constant of the continuous phase and the value of $\epsilon_0\epsilon_r$ is $6.95 \times 10^{-10} \text{ C}^2/(\text{J}\cdot\text{m})$ [31]. ψ_1 and ψ_2 refer to the surface potentials of MoS_2 particles and $\text{Mg}(\text{OH})_2$ colloids, respectively, usually represented by zeta potentials [39]. κ^{-1} is the thickness of electric double-layer, $\kappa = 0.180 \text{ nm}^{-1}$ [44].

The adsorption of SHMP on the mineral surface can increase the steric repulsion among particles [27,38]. The steric hindrance interaction energy V_{SR} is calculated according to Equation (5) [30,37].

$$V_{SR} = \frac{4\pi R^2 \left(\delta - \frac{H}{2} \right)}{Z(R + \delta)} kT \ln \left(\frac{2\delta}{H} \right) \quad (5)$$

where R represents the radius of particles. δ stands for the thickness of adsorbed layer after SHMP adsorption, with a given value of 5.45 nm [31]. Z is the covering area of the macromolecules (i.e., SHMP molecule) on the particle surface, $1.9 \times 10^{-16} \text{ m}^2$ [31]. k refers to the Boltzmann constant, $k = 1.381 \times 10^{-23} \text{ J/K}$ [38].

3. Results

3.1. Flotation Results

Figure 4 shows MoS_2 recovery at 5 min as a function of pH from 4 to 12 in the absence of flotation reagents. All experiments named Without $\text{Ca}^{2+}/\text{Mg}^{2+}$ represent the experiments treated in ultrapure water but with pH being adjusted using NaOH or HCl. MoS_2 recovery was over 80% at pH 4–10 without Ca^{2+} and Mg^{2+} , which was dramatically decreased to 72% at pH 12. However, in the presence of 0.01 M CaCl_2 and 0.05 M MgCl_2 , MoS_2 recovery decreased with increased pH value, achieving a minimum value of 45% and 1% at pH 12, respectively. This indicates that both divalent ions have a negative effect on MoS_2 flotation. It should be noted that the depressing effect due to MgCl_2 was more apparent than that of CaCl_2 . Although Nagaraj and Farinato [45] reported that Ca^{2+} had a negligible effect on Mo floatability, many other studies indicated that both Mg^{2+} and Ca^{2+} played negative roles on sulfide mineral flotation, [22,23,26,29,46], consistent with this study. The differences were probably due to the different mineral samples and flotation conditions used.

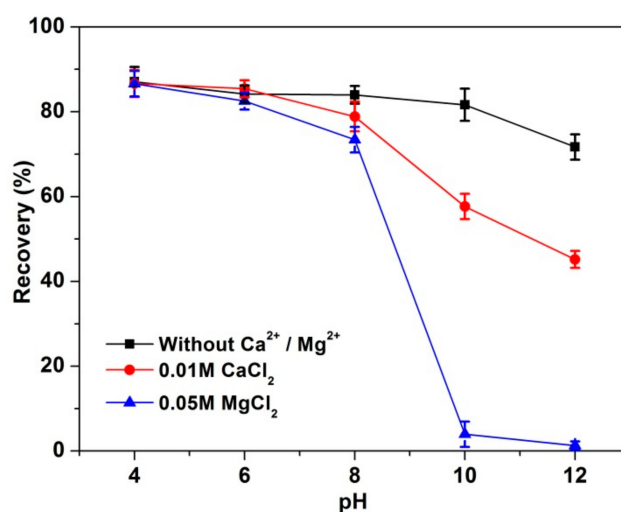


Figure 4. MoS_2 recovery at various pH values.

In the flotation of Cu-Mo sulfide minerals, pH adjustment to 9.5–12 is usually used to depress pyrite flotation [30]. The selected pH of 10 for MoS_2 flotation was consistent with many other studies [22,47–49].

Figure 5 shows the MoS_2 flotation in 0.05 M MgCl_2 solution as a function of SHMP dosage. With the increase of SHMP dosage from 0 to 40 mg/L, MoS_2 recovery was increased significantly. A further but slight increase was found when SHMP dosage was increased from 40 to 50 mg/L, indicating that the optimal SHMP dosage was 50 mg/L.

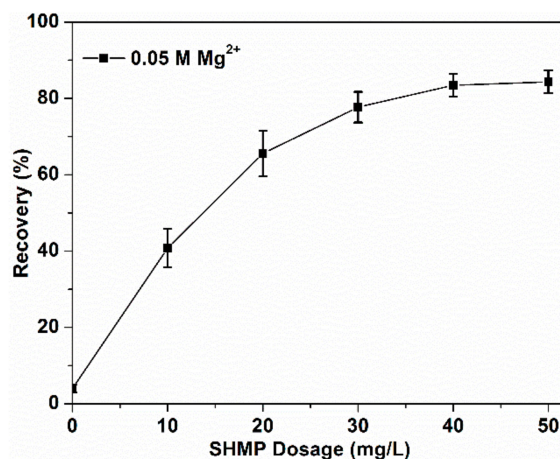


Figure 5. MoS_2 recovery as a function of SHMP dosage at pH 10.

Figure 6 shows the effects of SHMP (50 mg/L) on MoS_2 flotation at pH 10. Insignificant difference was observed for MoS_2 recovery without Ca^{2+} and Mg^{2+} , regardless of SHMP addition, suggesting that SHMP had a negligible impact on MoS_2 recovery in the absence of flotation reagents and salts. In addition, MoS_2 recovery was increased dramatically within the first 3 min, achieving a recovery of more than 70%. Afterwards, MoS_2 recovery was increased slowly and eventually achieved approximately 91% at 10 min. This indicates fast flotation kinetics and a high recovery of MoS_2 .

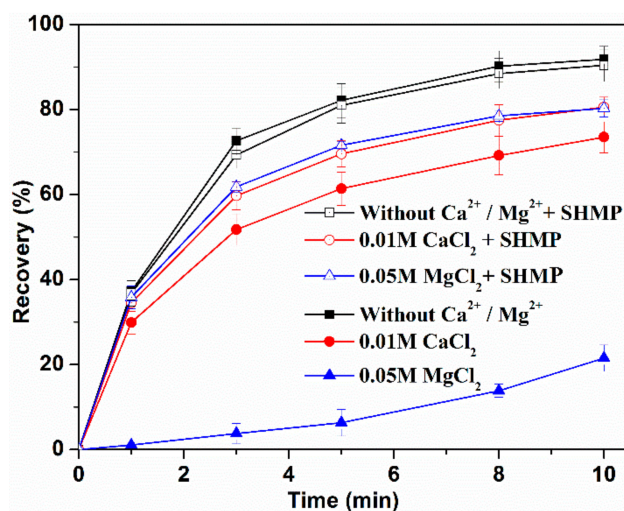


Figure 6. MoS_2 recovery at pH 10.

When 50 mg/L SHMP was added, MoS_2 recovery in CaCl_2 solution was increased from 73% to 79% while a more significant increase from 25% to 79% was observed when MoS_2 was exposed to MgCl_2 solutions. This means that the increase of MoS_2 recovery in MgCl_2 solution due to SHMP was 54% while that in CaCl_2 solution was only 6% within 10 min, indicating that SHMP played a more beneficial role on MoS_2 flotation in the presence of MgCl_2 as compared to CaCl_2 .

3.2. Contact Angle Analyses

Figure 7 shows that the contact angle of the MoS₂ surface (fresh surface treated in solution for 10 min) was gradually decreased to various extents with increased pH under the conditions examined. Specifically, the contact angle of MoS₂ surface was decreased from 88° to 82° from pH 4 to 12 without divalent ions, exhibiting the inherent hydrophobicity of MoS₂ and the insignificant role of pH. Tabares et al. [1] also reported that higher pH resulted in a slightly lower hydrophobicity of the MoS₂ surface. More significant declines from 88° to 75° and 48° were found in the presence of 0.01 M CaCl₂ and 0.05 M MgCl₂, respectively when pH was increased from 4 to 12, indicating that both Ca²⁺ and Mg²⁺ ions reduced MoS₂ hydrophobicity, consistent with flotation results, e.g., MgCl₂ increased MoS₂ wettability more significantly than that of CaCl₂.

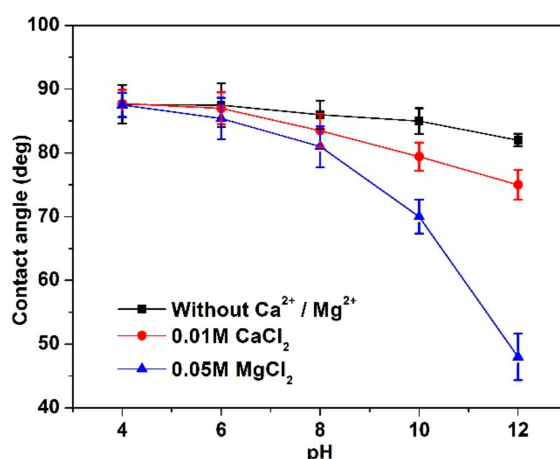


Figure 7. Contact angle of MoS₂ surface at different pH.

Figure 8 shows that the contact angle of the MoS₂ surface treated without Ca²⁺ and Mg²⁺ was not obviously changed after the addition of SHMP. A slight increase in contact angle was observed in 0.01 M CaCl₂ solutions when 50 mg/L SHMP was added into the solution, indicating that the addition of SHMP reduced the negative effects of Ca²⁺ on MoS₂ surface. A more apparent increase in contact angle was found for MoS₂ treated in 0.05 M MgCl₂ solution when SHMP was present.

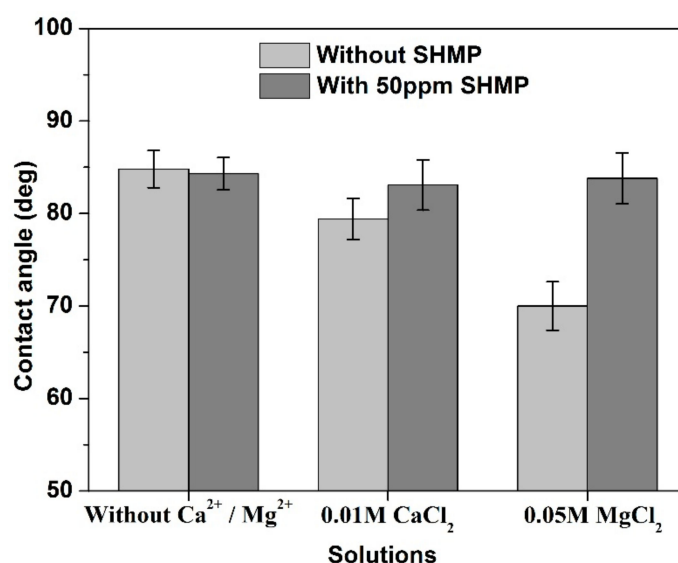


Figure 8. Contact angle of MoS₂ treated in various solutions at pH 10.

3.3. Zeta Potential Analyses

Figure 9 shows the zeta potentials of MoS₂ in the absence of SHMP. Without Ca²⁺ and Mg²⁺, zeta potential was always negative over the pH range tested, consistent with that found in other study [26]. The zeta potential was more negative with increased pH value. An increased zeta potential was observed in MgCl₂ solution within pH 2–7, which was reversed when pH was greater than 9, e.g., a zeta potential of 18.2 mV was observed when solution pH was 10.

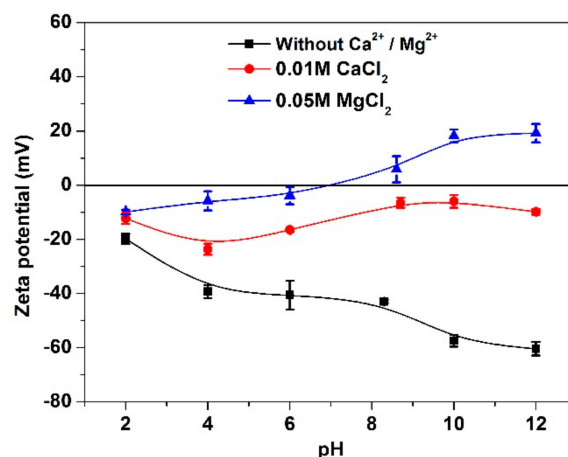


Figure 9. Zeta potential of MoS₂ at different pH values.

Table 2 indicates that the zeta potentials of MoS₂ treated without Ca²⁺/Mg²⁺ or in CaCl₂ solution were more negative in the presence of 50 mg/L SHMP. Li et al. [23] found a similar change of zeta potential on chalcopyrite surface once adding SHMP into the solution. However, the zeta potential was reversed again from a positive value to a negative value in 0.05 M MgCl₂ solution, which might be due to the reduced formation or adsorption of Mg precipitation on MoS₂ surface.

Table 2. Zeta potential of MoS₂ treated in various solutions at pH 10.

Conditions	Without Ca ²⁺ /Mg ²⁺	0.01 M CaCl ₂	0.05 M MgCl ₂
MoS ₂	−57.5	−6.0	18.2
MoS ₂ + SHMP	−71.9	−16.9	−5.1

4. Discussion

4.1. XPS Analyses

4.1.1. Survey Spectra

A previous study [23] showed that the calcium hydroxide precipitate (Ca(OH)_{2(s)}) and magnesium hydroxide precipitate (Mg(OH)_{2(s)}) was formed at pH greater than 12.4 and 9.3 in 0.01 M CaCl₂ and 0.05 M MgCl₂ solution, respectively. When pulp was controlled at pH 10, three Mg complexes, namely MgOH⁺, Mg(OH)_{2(aq)} and (Mg(OH)_{2(s)}), were present in 0.05 M MgCl₂ solution while two Ca complexes, namely CaOH⁺ and Ca(OH)_{2(aq)}, were present in 0.01 M CaCl₂ solution. These complexes may be adsorbed on the negatively charged mineral surface. Therefore, XPS was conducted to obtain the chemical information of surface species formed on MoS₂ surface [23,50,51]. The broad survey spectra of untreated and treated MoS₂ and the main elemental quantifications are presented in Figure 10 and Table 3, respectively. As shown in Figure 10, no obvious Ca 2p peak was formed on all MoS₂ surfaces. Table 3 shows that only approximately 1% Ca was found on the surface when MoS₂ was treated in 0.01 M CaCl₂ solution, indicating same adsorption of Ca

species on MoS₂ surface. However, Ca was removed after 50 mg/L SHMP was added, suggesting that SHMP prevented the formation of Ca species on the MoS₂ surface.

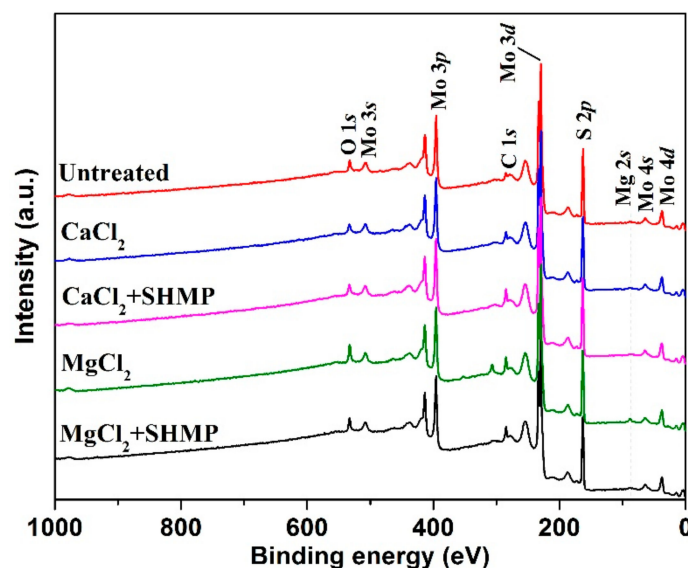


Figure 10. XPS survey spectra of MoS₂ treated in different solution at pH 10.

Table 3. Elemental quantification (at %) of MoS₂ surface.

Element	BE (eV)	Conditions				
		Untreated	CaCl ₂	CaCl ₂ + SHMP	MgCl ₂	MgCl ₂ + SHMP
S 2p	162.4	57	57	58	53	56
O 1s	533.2	7	6	6	11	7
Mo 3d	230.0	35	35	35	32	35
Ca 2p	351.0	0	1	0	0	0
Mg 2s	89.5	1	1	1	4	2

Note: BE represents Binding Energy while Untreated refers to untreated MoS₂.

In addition, Figure 10 shows that untreated MoS₂ presented a relatively weak peak for Mg 2s at 89.5 eV, while a relatively stronger Mg 2s peak was observed on MoS₂ surface treated in MgCl₂ solution, indicating the adsorption of Mg precipitate on MoS₂. However, SHMP prevented Mg precipitation on the MoS₂ surface seen by significantly decreased Mg 2s peak intensity, consistent with contact angle and zeta potential measurements. Furthermore, Mg 1s and O 1s were decreased from 4 at. % to 2 at. % and from 11 at. % to 7 at. %, respectively, when 50 mg/L SHMP was added in 0.05 M MgCl₂ solution. The simultaneous and stoichiometric declines in Mg and O highly supported that SHMP reduced the formation and adsorption of Mg(OH)₂ on the MoS₂ surface, thereby improving recovery.

4.1.2. Mo 3d, S 2p and O 1s XPS Spectra

To further estimate the change of surface species, high resolution Mo 3d, S 2p and O 1s XPS spectra were collected, as presented in Figure 11. Each Mo spectra consisted of two Gaussian–Lorentzian bands separated by 3.2 eV with the intensity of Mo 3d_{5/2} being doubled that of Mo 3d_{3/2} [51,52]. As shown in Figure 11a, three peaks located at 229.8 eV, 232.7 eV and 227.0 eV corresponded to MoO₃, MoS₂ and S 2s components [2,51,52], respectively. The Mo 3d spectra indicate that both untreated MoS₂ and MoS₂ treated in various solutions experienced slight oxidation.

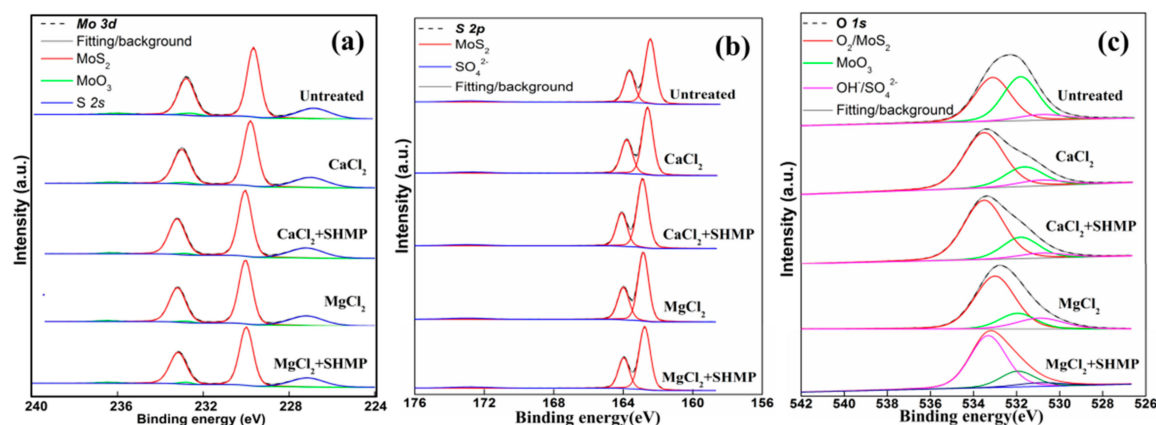


Figure 11. XPS spectra of: (a) Mo 3d; (b) S 2p; and (c) O 1s.

Each S component of the S 2p spectrum was composed of two peaks separated by 1.2 eV with the intensity of the lower binding energy peak (S 2p_{3/2}) being double that of the peak (S 2p_{1/2}) at a higher binding energy, based on two Gaussian–Lorentzian bands [53]. Figure 11b shows that the S 2p spectra was divided into two components at 162.6 eV and 172.7 eV, representing MoS₂ and SO₄^{2−}, respectively, with the latter being likely derived from the oxidation of MoS₂. Figure 11c indicates the O 1s binding energies of 533.3 eV, 531.1 eV and 530.9 eV for attached oxygen on the MoS₂ surface (O₂/MoS₂), Mo trioxide (MoO₃) and hydroxide/sulfate (OH[−]/SO₄^{2−}), respectively. It should be noted that the binding energies of hydroxide and sulfate overlapped at 530.9 ± 0.15 eV [54].

Table 4 presents the binding energy and atomic percentage of the elements investigated. The percentage of Mo due to MoO₃ was decreased from 3.6% Mo (untreated) to 3.0% Mo and 2.2% Mo in 0.01 M CaCl₂ solution and 0.05 M MgCl₂ solution, respectively, probably due to the dissolution of MoO₃ into solution. In addition, the MoO₃ content in CaCl₂ solution was greater than that in MgCl₂ solution, highly due to the formation of CaMoO₄ precipitate on the surface, which increased the MoS₂ oxide content. The MoO₃ was further reduced to 2.2% Mo when SHMP was added into the CaCl₂ solution, indicating that the addition of SHMP prevented the formation of CaMoO₄ on the surface.

Table 4. Species content (% element) on MoS₂ surfaces.

Species	BE (eV)	FWHM (eV)	Conditions				
			Untreated	CaCl ₂	CaCl ₂ + SHMP	MgCl ₂	MgCl ₂ + SHMP
Mo 3d	MoS ₂	229.8	78.9	79.2	79.5	79.9	79.5
	MoO ₃	232.7	3.6	3.0	2.2	2.2	2.5
	S 2s	227.0	17.5	17.8	18.3	17.9	18.0
S 2p	MoS ₂	162.6	95.4	96.7	96.9	96.1	96.3
	SO ₄ ^{2−}	172.7	4.6	3.3	3.1	3.9	3.7
O 1s	O ₂ /MoS ₂	533.3	46.9	68.2	80.8	66.1	72.5
	MoO ₃	531.9	45.2	23.4	13.1	17.9	20.9
	OH [−] /SO ₄ ^{2−}	530.9	7.9	8.4	6.1	16.0	6.6

Note: All BE with a typical variation of ± 0.15 eV and all FWHM refers to full width half maximum.

The atomic proportion of S due to MoS₂ and SO₄^{2−} of untreated MoS₂ was 95.4% S and 4.6% S, respectively, indicating a weak oxidation of MoS₂, consistent with Mo 3d XPS measurements. The SO₄^{2−} was further reduced to 3.3% S and 3.9% S in CaCl₂ and MgCl₂ solution, respectively, possibly due to the dissolution of SO₄^{2−} from surface into solution. In addition, a further decrease was observed when 50 mg/L SHMP was added, indicating that the addition of SHMP was beneficial to SO₄^{2−} dissolution, in accordance with a previous study [23].

In addition, the MoO₃ concentration was decreased from 45.2% O to 23.4% O and 17.9% O when MoS₂ was treated in CaCl₂ and MgCl₂ solution, respectively. The atomic proportion of OH[−]/SO₄^{2−} species was increased from 7.9% O to 8.4% O and 16.0% O when MoS₂ was treated in CaCl₂ and MgCl₂

solution, respectively. As S 2p XPS analysis indicated that SO_4^{2-} was decreased for the MoS_2 surface treated in both salt solutions, the increase of $\text{OH}^-/\text{SO}_4^{2-}$ further confirmed the adsorption of more hydroxide species on the MoS_2 surface, especially treated in MgCl_2 solution. However, a decrease was observed when 50 mg/L SHMP was added, e.g., from 8.4% O to 6.1% O and from 16% O to 6.6% O, respectively, further suggesting that the addition of SHMP decreased the adsorption of Ca and Mg complexes onto the MoS_2 surface due primarily to its dispersion and complexing effects.

4.2. TMAFM Imaging

Figure 12 shows the tapping mode AFM images of the MoS_2 surface exposed to different conditions. A clean surface with some scratches was observed on the untreated MoS_2 surface. The scratches were probably due to the peeling treatments, consistent with other published studies [6,22,55]. The height and root mean square (RMS) roughness for the untreated surface were 0.42 nm and 0.07 nm, respectively, illustrating that the untreated MoS_2 surface was relatively flat and smooth [56].

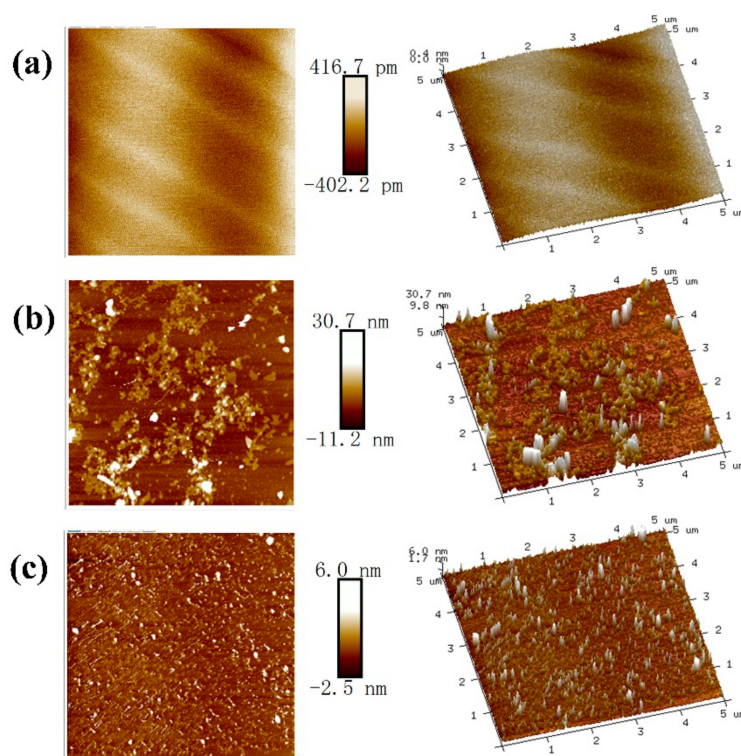
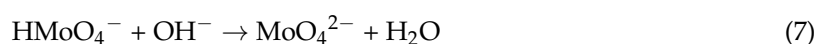
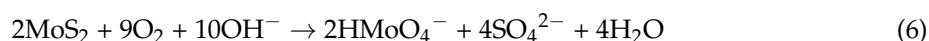


Figure 12. Typical 2D and 3D AFM images ($5\ \mu\text{m} \times 5\ \mu\text{m}$) of: (a) untreated MoS_2 ; and MoS_2 treated in: (b) 0.05 M MgCl_2 ; and (c) 0.05 M MgCl_2 with 50 mg/L SHMP at pH of 10.

However, Figure 12b shows many colloidal particles with various sizes and irregular shapes on the MoS_2 surface treated in 0.05 M MgCl_2 solution, which can be explained by the adsorption of $\text{Mg}(\text{OH})_2$ colloid aggregation. Suyantara et al. [24] also reported that MoS_2 surface treated in MgCl_2 solution at high alkaline condition presented a number of white spots and mountainous features. Compared to the untreated surface, the treated surface gave a significant greater height (30.7 nm) and RMS roughness (5.47 nm). These changes revealed that the adsorption of $\text{Mg}(\text{OH})_{2(s)}$ on the MoS_2 surface increased the surface roughness and decreased the surface homogeneity. In contrast, when MoS_2 was treated in 0.05 M MgCl_2 solution with 50 mg/L SHMP, the size of bright spots became smaller while its height (6.0 nm) and RMS roughness (1.36 nm) apparently decreased, suggesting that the presence of SHMP reduced the adsorption $\text{Mg}(\text{OH})_2$ precipitates on the MoS_2 surface, thereby increasing the contact angle and improving MoS_2 flotation.

4.3. Mechanisms

The variation in MoS₂ recovery might be attributed to different mechanisms. The crystal structure of MoS₂ consists of hydrophobic faces and hydrophilic edges with the face consisting of micro-faces and micro-edges [3]. Generally, MoS₂ edges and micro-edges are easily oxidized to form molybdate ions (MoO₄^{2−}) or hydromolybdate ions (HMoO₄[−]) (Equations (6) and (7)):



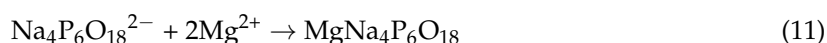
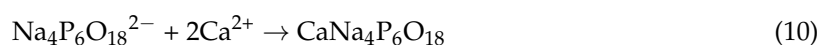
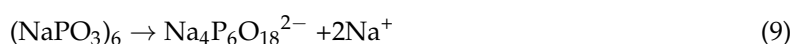
HMoO₄[−] is the main oxidation product when pH is lower than 6 while the main oxidation product is MoO₄^{2−} under neutral and alkaline conditions [3,55]. With increased solution pH, more negative MoO₄^{2−} can be formed on the edge and micro-edge of the face, causing a more negatively charged MoS₂ surface [55], as shown in Figure 9. Moreover, the increased electric charge due to the formation of MoO₄^{2−} ions on the micro-edges of the face, decreases MoS₂ hydrophobicity due to oxidation [1]. Tabares et al. [1] also reported that the oxidation occurring on the micro-edges adjacent to the face of MoS₂ enhanced the surface hydration layer, thereby decreasing surface hydrophobicity and MoS₂ recovery. Therefore, the slightly reduced recovery and contact angle in solution without Ca²⁺ and Mg²⁺ was highly likely due to the oxidation of the MoS₂ surface.

When MoS₂ was treated in either CaCl₂ or MgCl₂ solution, the metal ions were easily adsorbed on the MoS₂ edge, reducing the hydrophobicity of MoS₂ particles [5,57]. Specifically, the adsorbed Ca²⁺ onto the edges spontaneously reacts with MoO₄^{2−} to form CaMoO₄ precipitation based on Equation (8) [58,59]. In addition, as described in a previous study [23], two Ca species including CaOH⁺ and Ca(OH)₂(aq) were increased in 0.01 M CaCl₂ solution when solution pH was increased from 4 to 12. Therefore, in addition to the adsorption of CaMoO₄, the adsorption of positive CaOH⁺ on the edges of negative MoS₂ particles by electrostatic interaction contributes to the increased zeta potential [1]. Therefore, the CaMoO₄ precipitate depositing on both the edges and micro-edges of the faces reduced MoS₂ hydrophobicity and further deteriorated MoS₂ flotation [1].



In 0.05 M MgCl₂ solution, the MgOH⁺ and Mg(OH)₂(aq) concentrations were increased when pH was increased from 4 to 9.3. With the formed MgOH⁺ being mainly adsorbed on micro-edges, MoS₂ recovery (Figure 6) was decreased due to the decreased hydrophobicity (Figure 7) [26]. When pH was greater than 9.3, the positively charged Mg(OH)₂ precipitate was formed [23] and deposited on both the micro-edges on the faces and edges of MoS₂ particles [26] due to electrostatic interaction [46], thereby resulting in a lower recovery.

Some published studies showed that SHMP had a good complexing ability for hydrolyzed metallic ions [35–38]. For instance, Ding et al. [35] and Feng et al. [37] reported that Ca²⁺ from the minerals surface was selectively dissolved into solution due to the complexation of SHMP. In other words, SHMP can react with Ca²⁺ or Mg²⁺ to form soluble complexes (Equations (9)–(11)), thereby reducing the formation of Ca and Mg precipitates (e.g., CaMoO_{4(s)} and Mg(OH)_{2(s)}) [36,38] and relieving their negative effects on MoS₂ flotation.



In addition, SHMP can disperse slime that might attach on valuable mineral surfaces, through changing the surface potential of the particle and increasing the electrostatic repulsive energy between

particles [31–33]. Therefore, the presence of SHMP may prevent $\text{Mg}(\text{OH})_2$ colloids attaching onto the MoS_2 surface via its dispersing role. Therefore, the interaction energy between MoS_2 particles and $\text{Mg}(\text{OH})_2$ colloids were investigated based on EDLVO theory model.

In the absence of SHMP, the zeta potentials of MoS_2 and $\text{Mg}(\text{OH})_2$ colloids were -57.5 mV and 11.6 mV, respectively, which were further decreased to -71.9 mV and -23.2 mV after 50 mg/L SHMP addition. Particle size analysis showed that the average diameter (d_{50}) of MoS_2 particles was approximately 66 μm and that of $\text{Mg}(\text{OH})_2$ colloids was 7.6 μm . Consequently, the radius of MoS_2 particle (R_1) and $\text{Mg}(\text{OH})_2$ particle R_2 were 33 μm and 3.8 μm , respectively.

Figure 13 shows the interaction energy between MoS_2 particles and $\text{Mg}(\text{OH})_2$ colloids with and without SHMP. In the absence of SHMP, both Van der Waals interaction energy V_{W1} and electrostatic interaction energy V_{E1} were negative within all particle distances examined. In addition, the total interaction energy V_T between MoS_2 and $\text{Mg}(\text{OH})_2$ colloids was negative, revealing that the attraction force dominated the interparticle aggregation between MoS_2 and $\text{Mg}(\text{OH})_2$ colloids. Specifically, the absolute value of V_{E1} was significantly greater than that of V_W , indicating that the negative V_E played a dominant role on V_T between MoS_2 and $\text{Mg}(\text{OH})_2$ colloids when no SHMP was added.

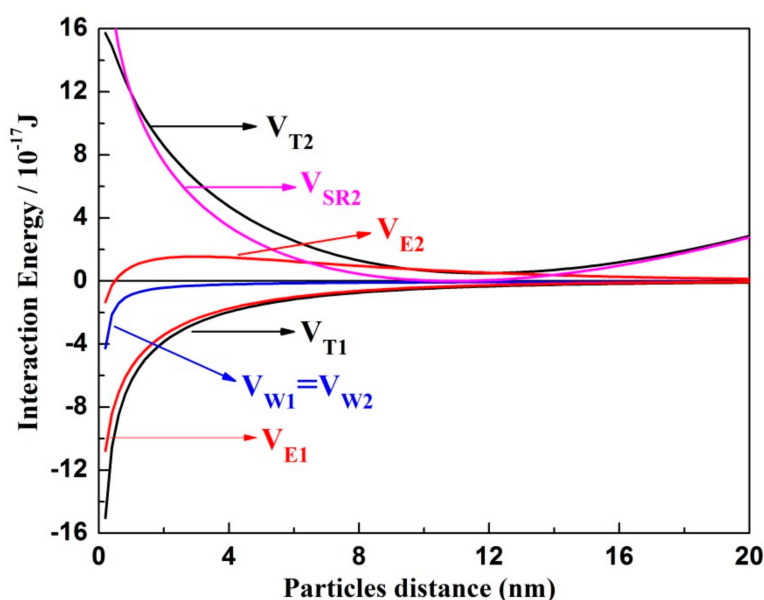


Figure 13. Interaction energy between MoS_2 and $\text{Mg}(\text{OH})_2$ at pH 10.

When 50 mg/L SHMP was added, V_{E2} was increased from negative to positive at longer particle distance. Meanwhile, the steric hindrance interaction energy V_{SR} appeared due to the increased steric repulsion force among particles when SHMP molecules with a long chain were adsorbed on the minerals surface. More importantly, the absolute value of V_{SR} was significantly greater than others within a short particle distance, indicating that the positive V_{SR} dominated the force between MoS_2 and $\text{Mg}(\text{OH})_2$ colloids when approaching each other. Accordingly, the presence of SHMP reversed V_T from negative to positive values, indicating the appearance of repulsion force among particles. Therefore, the increased MoS_2 recovery in the presence of SHMP was mainly due to the prevention of $\text{Mg}(\text{OH})_2$ attaching onto MoS_2 surface.

5. Conclusions

The flotability of MoS_2 was depressed in either 0.01 M CaCl_2 or 0.05 M MgCl_2 solution at alkaline condition, mainly due to the adsorption of complex Ca and Mg species including CaMoO_4 , CaOH^+ , $\text{Mg}(\text{OH})_2$, and MgOH^+ on the edges and micro-edges of face. The addition of SHMP had a negligible effect on MoS_2 recovery in solution without Ca^{2+} and Mg^{2+} , but eliminated the negative effects of

Ca^{2+} and Mg^{2+} on MoS_2 flotation when present. TMAFM analyses indicated that the adsorption of precipitates increased surface roughness but decreased surface homogeneity while SHMP reduced the adsorption of precipitates on the MoS_2 surface.

Two mechanisms were proposed based on various measurements and theoretical calculation, with the latter being more significant for improved MoS_2 recovery in the presence of divalent ions. Firstly, SHMP can complex with Ca^{2+} and Mg^{2+} to form dissolvable complexes in the solution, decreasing the formation of hydrophilic Ca and Mg complexes and precipitates. Secondly, EDLVO calculation indicated that the presence of SHMP in 0.05 M MgCl_2 solution changed the total interaction force between MoS_2 and $\text{Mg}(\text{OH})_2$ colloids from attraction to repulsion, thereby preventing the adsorption of hydrophilic $\text{Mg}(\text{OH})_2$ on MoS_2 surface.

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