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

Wanqing Li 1, Yubiao Li 1,2,*, Zhenlun Wei 1, Qing Xiao 2 and Shaoxian Song 1

1 School of Resources and Environmental Engineering, Wuhan University of Technology, Wuhan 430070, Hubei, China; wanqing280@163.com (W.L.); erebus@whut.edu.cn (Z.W.); ssx851215@whut.edu.cn (S.S.)
2 School of Natural and Built Environments, University of South Australia, Mawson Lakes, SA 5095, Australia; qing.xiao@mymail.unisa.edu.au
* Corresponding author: Yubiao.Li@whut.edu.cn

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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 (MoS₂), with the depressing mechanisms being insufficiently understood. In this study, the influence of divalent ions (e.g., Ca²⁺ and Mg²⁺) and dispersant on MoS₂ flotation was systematically investigated. It was found that the detrimental effects of Ca²⁺ and Mg²⁺ on the natural flotability of MoS₂ were mainly due to the attachment of formed CaMoO₄ precipitates and Mg(OH)₂ colloids onto MoS₂ 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 MoS₂ flotation. In addition, the Extended Derjguin–Landau–Verwey–Overbeek (EDLVO) theory was applied to investigate the total interaction energy between MoS₂ particles and formed colloids, revealing that the reduced attraction force between MoS₂ and Mg(OH)₂ colloids in the presence of SHMP primarily resulted in the increased MoS₂ recovery. In addition, SHMP combined with Mg²⁺ and Ca²⁺ to form dissolvable complexes, thereby reducing insoluble Mg²⁺ and Ca²⁺ compounds or precipitation. Thus, this study demonstrated for the first time two influencing mechanisms of SHMP in improving MoS₂ recovery in the presence of Ca²⁺ and Mg²⁺.

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

1. Introduction

Molybdenite (MoS₂) 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]. MoS₂ 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 MoS₂ particle surface via atomic force microscopy (AFM). In addition, the face/edge aspect influences MoS₂ 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 MoS₂ particle is normally deformed during grinding, resulting in a high exposure of edges and micro-edges on the MoS₂ surface [5].

MoS₂ is usually recovered with copper minerals from Cu-Mo ores [8,9], followed by selective flotation of MoS₂ 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\(^+\), Mg\(^+\), 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\(_2\)CO\(_3\) 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

MoS$_2$ 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 MoS$_2$.

![Figure 1. X-ray Diffraction pattern (XRD) of MoS$_2$.](image)

The elemental composition of the MoS$_2$ sample is given in Table 1, indicating a high Mo concentration with a small portion of impurities, consistent with the XRD results.

<table>
<thead>
<tr>
<th>Element</th>
<th>Mo</th>
<th>S</th>
<th>Si</th>
<th>Bi</th>
<th>Cl</th>
<th>Ca</th>
<th>Al</th>
<th>Fe</th>
<th>Ba</th>
<th>K</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (%)</td>
<td>53.10</td>
<td>43.25</td>
<td>1.07</td>
<td>0.72</td>
<td>0.53</td>
<td>0.35</td>
<td>0.26</td>
<td>0.25</td>
<td>0.22</td>
<td>0.18</td>
<td>0.07</td>
</tr>
</tbody>
</table>

In addition, Figure 2 shows the cumulative size distribution of the MoS$_2$ 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 MoS$_2$ sample when its cumulative size distribution reaches 10%, 50%, 90%, respectively) were 48, 66 and 74 µm, respectively.

![Figure 2. Cumulative size distribution of MoS$_2$.](image)
Reagents including SHMP, anhydrous calcium chloride (CaCl$_2$) and magnesium chloride hexahydrate (MgCl$_2$·6H$_2$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 MΩ·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.

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 −38 µm 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 Mg(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 Kα 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 × 256 pixel resolution) of MoS$_2$ surfaces, thereby providing the layer thickness and roughness. ScanAsyst-Air Si$_3$N$_4$ 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) \cite{31,38–40}.

$$V_T = V_W + V_E + V_{SR} \tag{1}$$

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

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

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

The Hamaker constant of MoS$_2$ ($A_{11}$) in vacuum is $9.38 \times 10^{-20}$ J \cite{41}. As Hamaker constant of Mg(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 \cite{42}. The Hamaker constant of water $A_{33}$ is $3.7 \times 10^{-20}$ J \cite{42,43}. $H$ (nm) refers to the distance between particles.
The electrostatic interaction energy $V_E$ between MoS$_2$ particles and Mg(OH)$_2$ colloids can be expressed by Equation (4) [42].

$$V_E = \frac{\pi \varepsilon_0 \varepsilon_r R_1 R_2}{R_1 + R_2} \left( \psi_1^2 + \psi_2^2 \right) \left\{ \frac{2 \psi_1 \psi_2}{\psi_1^2 + \psi_2^2} \ln \left[ \frac{1 + \exp(-\kappa H)}{1 - \exp(-\kappa H)} \right] + \ln[1 - \exp(-2\kappa H)] \right\}$$  \hspace{1cm} (4)

where $\varepsilon_0$ and $\varepsilon_r$ are the vacuum dielectric constant and the relative dielectric constant of the continuous phase and the value of $\varepsilon_0 \varepsilon_r$ is $6.95 \times 10^{-10}$ C$^2$/(J·m) [31]. $\psi_1$ and $\psi_2$ refer to the surface potentials of MoS$_2$ particles and Mg(OH)$_2$ colloids, respectively, usually represented by zeta potentials [39]. $\kappa^{-1}$ is the thickness of electric double-layer, $\kappa = 0.180$ 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].

$$V_{SR} = \frac{4\pi R^2 \left( \delta - \frac{H}{2} \right)^2}{Z (R + \delta)} kT \ln \left( \frac{2\delta}{H} \right)$$  \hspace{1cm} (5)

where $R$ represents the radius of particles. $\delta$ 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, $1.9 \times 10^{-16}$ m$^2$ [31]. $k$ refers to the Boltzmann constant, $k = 1.381 \times 10^{-23}$ 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 Ca$^{2+}$/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.
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 MoS₂ flotation was consistent with many other studies [22,47–49].

Figure 5 shows the MoS₂ flotation in 0.05 M MgCl₂ solution as a function of SHMP dosage. With the increase of SHMP dosage from 0 to 40 mg/L, MoS₂ 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. MoS₂ recovery as a function of SHMP dosage at pH 10.](image)

Figure 6 shows the effects of SHMP (50 mg/L) on MoS₂ flotation at pH 10. Insignificant difference was observed for MoS₂ recovery without Ca²⁺ and Mg²⁺, regardless of SHMP addition, suggesting that SHMP had a negligible impact on MoS₂ recovery in the absence of flotation reagents and salts. In addition, MoS₂ recovery was increased dramatically within the first 3 min, achieving a recovery of more than 70%. Afterwards, MoS₂ recovery was increased slowly and eventually achieved approximately 91% at 10 min. This indicates fast flotation kinetics and a high recovery of MoS₂.

![Figure 6. MoS₂ recovery at pH 10.](image)

When 50 mg/L SHMP was added, MoS₂ recovery in CaCl₂ solution was increased from 73% to 79% while a more significant increase from 25% to 79% was observed when MoS₂ was exposed to MgCl₂ solutions. This means that the increase of MoS₂ recovery in MgCl₂ solution due to SHMP was 54% while that in CaCl₂ solution was only 6% within 10 min, indicating that SHMP played a more beneficial role on MoS₂ flotation in the presence of MgCl₂ as compared to CaCl₂.
3.2. Contact Angle Analyses

Figure 7 shows that the contact angle of the MoS\textsubscript{2} 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 MoS\textsubscript{2} surface was decreased from 88° to 82° from pH 4 to 12 without divalent ions, exhibiting the inherent hydrophobicity of MoS\textsubscript{2} and the insignificant role of pH. Tabares et al. [1] also reported that higher pH resulted in a slightly lower hydrophobicity of the MoS\textsubscript{2} surface. More significant declines from 88° to 75° and 48° were found in the presence of 0.01 M CaCl\textsubscript{2} and 0.05 M MgCl\textsubscript{2}, respectively when pH was increased from 4 to 12, indicating that both Ca\textsuperscript{2+} and Mg\textsuperscript{2+} ions reduced MoS\textsubscript{2} hydrophobicity, consistent with flotation results, e.g., MgCl\textsubscript{2} increased MoS\textsubscript{2} wettability more significantly than that of CaCl\textsubscript{2}.

![Figure 7](image-url)

Figure 7. Contact angle of MoS\textsubscript{2} surface at different pH.

Figure 8 shows that the contact angle of the MoS\textsubscript{2} surface treated without Ca\textsuperscript{2+} and Mg\textsuperscript{2+} was not obviously changed after the addition of SHMP. A slight increase in contact angle was observed in 0.01 M CaCl\textsubscript{2} solutions when 50 mg/L SHMP was added into the solution, indicating that the addition of SHMP reduced the negative effects of Ca\textsuperscript{2+} on MoS\textsubscript{2} surface. A more apparent increase in contact angle was found for MoS\textsubscript{2} treated in 0.05 M MgCl\textsubscript{2} solution when SHMP was present.

![Figure 8](image-url)

Figure 8. Contact angle of MoS\textsubscript{2} treated in various solutions at pH 10.
3.3. Zeta Potential Analyses

Figure 9 shows the zeta potentials of MoS$_2$ in the absence of SHMP. Without Ca$^{2+}$ and Mg$^{2+}$, 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 MgCl$_2$ 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.

Table 2 indicates that the zeta potentials of MoS$_2$ treated without Ca$^{2+}$/Mg$^{2+}$ or in CaCl$_2$ 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 MgCl$_2$ solution, which might be due to the reduced formation or adsorption of Mg precipitation on MoS$_2$ surface.

Table 2. Zeta potential of MoS$_2$ treated in various solutions at pH 10.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Without Ca$^{2+}$/Mg$^{2+}$</th>
<th>0.01 M CaCl$_2$</th>
<th>0.05 M MgCl$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoS$_2$</td>
<td>−57.5</td>
<td>−6.0</td>
<td>18.2</td>
</tr>
<tr>
<td>MoS$_2$ + SHMP</td>
<td>−71.9</td>
<td>−16.9</td>
<td>−5.1</td>
</tr>
</tbody>
</table>

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)$_{2(aq)}$) was formed at pH greater than 12.4 and 9.3 in 0.01 M CaCl$_2$ and 0.05 M MgCl$_2$ solution, respectively. When pulp was controlled at pH 10, three Mg complexes, namely MgOH$^+$, Mg(OH)$_2$$_{(aq)}$ and (Mg(OH)$_2$$_{(s)}$), were present in 0.05 M MgCl$_2$ solution while two Ca complexes, namely CaOH$^+$ and Ca(OH)$_2$$_{(aq)}$, were present in 0.01 M CaCl$_2$ 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 MoS$_2$ surface [23,50,51]. The broad survey spectra of untreated and treated MoS$_2$ 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 MoS$_2$ surfaces. Table 3 shows that only approximately 1% Ca was found on the surface when MoS$_2$ was treated in 0.01 M CaCl$_2$ solution, indicating same adsorption of Ca
species on MoS$_2$ surface. However, Ca was removed after 50 mg/L SHMP was added, suggesting that SHMP prevented the formation of Ca species on the MoS$_2$ surface.

![Figure 10. XPS survey spectra of MoS$_2$ treated in different solution at pH 10.](image)

**Table 3.** Elemental quantification (at %) of MoS$_2$ surface.

<table>
<thead>
<tr>
<th>Element</th>
<th>BE (eV)</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Untreated</td>
</tr>
<tr>
<td>S 2p</td>
<td>162.4</td>
<td>57</td>
</tr>
<tr>
<td>O 1s</td>
<td>533.2</td>
<td>7</td>
</tr>
<tr>
<td>Mo 3d</td>
<td>230.0</td>
<td>35</td>
</tr>
<tr>
<td>Ca 2p</td>
<td>351.0</td>
<td>0</td>
</tr>
<tr>
<td>Mg 2s</td>
<td>89.5</td>
<td>1</td>
</tr>
</tbody>
</table>

Note: BE represents Binding Energy while Untreated refers to untreated MoS$_2$.

In addition, Figure 10 shows that untreated MoS$_2$ presented a relatively weak peak for Mg 2s at 89.5 eV, while a relatively stronger Mg 2s peak was observed on MoS$_2$ surface treated in MgCl$_2$ solution, indicating the adsorption of Mg precipitate on MoS$_2$. However, SHMP prevented Mg precipitation on the MoS$_2$ 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 MgCl$_2$ 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 MoS$_2$ 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 MoO$_3$, MoS$_2$ and S 2s components [2,51,52], respectively. The Mo 3d spectra indicate that both untreated MoS$_2$ and MoS$_2$ treated in various solutions experienced slight oxidation.
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 2p3/2) being double that of the peak (S 2p1/2) 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 SO42−, 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−/SO42−), 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.**

<table>
<thead>
<tr>
<th>Species</th>
<th>BE (eV)</th>
<th>FWHM (eV)</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Untreated</td>
</tr>
<tr>
<td>Mo 3d</td>
<td>229.8</td>
<td>0.7–0.8</td>
<td>78.9</td>
</tr>
<tr>
<td>MoO3</td>
<td>232.7</td>
<td>0.8–1.0</td>
<td>3.6</td>
</tr>
<tr>
<td>S 2s</td>
<td>227.0</td>
<td>1.8–1.9</td>
<td>17.5</td>
</tr>
<tr>
<td>MoS2</td>
<td>162.6</td>
<td>0.7–0.8</td>
<td>95.4</td>
</tr>
<tr>
<td>SO42−</td>
<td>172.7</td>
<td>2.4–2.6</td>
<td>4.6</td>
</tr>
<tr>
<td>O2/MoS2</td>
<td>533.3</td>
<td>2.0–2.2</td>
<td>46.9</td>
</tr>
<tr>
<td>MoO3</td>
<td>531.9</td>
<td>2.0–2.2</td>
<td>45.2</td>
</tr>
<tr>
<td>OH−/SO42−</td>
<td>530.9</td>
<td>2.5–2.6</td>
<td>7.9</td>
</tr>
</tbody>
</table>

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 SO42− 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 SO42− was further reduced to 3.3% S and 3.9% S in CaCl2 and MgCl2 solution, respectively, possibly due to the dissolution of SO42− 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 SO42− 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−/SO42− 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 OH$^-$/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](image-url)

Figure 12. Typical 2D and 3D AFM images (5 µm × 5 µm) 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 Mg(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 Mg(OH)$_2$ 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 Mg(OH)$_2$ precipitates on the MoS$_2$ surface, thereby increasing the contact angle and improving MoS$_2$ flotation.
4.3. Mechanisms

The variation in MoS$_2$ recovery might be attributed to different mechanisms. The crystal structure of MoS$_2$ consists of hydrophobic faces and hydrophilic edges with the face consisting of micro-faces and micro-edges [3]. Generally, MoS$_2$ edges and micro-edges are easily oxidized to form molybdate ions (MoO$_4^{2-}$) or hydromolybdate ions (HMoO$_4^{-}$) (Equations (6) and (7)):

$$2\text{MoS}_2 + 9\text{O}_2 + 10\text{OH}^- \rightarrow 2\text{HMoO}_4^- + 4\text{SO}_4^{2-} + 4\text{H}_2\text{O}$$ (6)

$$\text{HMoO}_4^- + \text{OH}^- \rightarrow \text{MoO}_4^{2-} + \text{H}_2\text{O}$$ (7)

HMoO$_4^-$ is the main oxidation product when pH is lower than 6 while the main oxidation product is MoO$_4^{2-}$ under neutral and alkaline conditions [3,55]. With increased solution pH, more negative MoO$_4^{2-}$ can be formed on the edge and micro-edge of the face, causing a more negatively charged MoS$_2$ surface [55], as shown in Figure 9. Moreover, the increased electric charge due to the formation of MoO$_4^{2-}$ ions on the micro-edges of the face, decreases MoS$_2$ hydrophobicity due to oxidation [1]. Tabares et al. [1] also reported that the oxidation occurring on the micro-edges adjacent to the face of MoS$_2$ enhanced the surface hydration layer, thereby decreasing surface hydrophobicity and MoS$_2$ recovery. Therefore, the slightly reduced recovery and contact angle in solution without Ca$^{2+}$ and Mg$^{2+}$ was highly likely due to the oxidation of the MoS$_2$ surface.

When MoS$_2$ was treated in either CaCl$_2$ or MgCl$_2$ solution, the metal ions were easily adsorbed on the MoS$_2$ edge, reducing the hydrophobicity of MoS$_2$ particles [5,57]. Specifically, the adsorbed Ca$^{2+}$ onto the edges spontaneously reacts with MoO$_4^{2-}$ to form CaMoO$_4$ 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 CaCl$_2$ solution when solution pH was increased from 4 to 12. Therefore, in addition to the adsorption of CaMoO$_4$, the adsorption of positive CaOH$^+$ on the edges of negative MoS$_2$ particles by electrostatic interaction contributes to the increased zeta potential [1]. Therefore, the CaMoO$_4$ precipitate depositing on both the edges and micro-edges of the faces reduced MoS$_2$ hydrophobicity and further deteriorated MoS$_2$ flotation [1].

$$\text{MoO}_4^{2-} + \text{Ca}^{2+} \rightarrow \text{CaMoO}_4(s)$$ (8)

In 0.05 M MgCl$_2$ 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, MoS$_2$ 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 MoS$_2$ 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 Ca$^{2+}$ from the minerals surface was selectively dissolved into solution due to the complexation of SHMP. In other words, SHMP can react with Ca$^{2+}$ or Mg$^{2+}$ 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 MoS$_2$ flotation.

$$\text{(NaPO}_3\text{)}_6 \rightarrow \text{Na}_4\text{P}_6\text{O}_{18}^{2-} + 2\text{Na}^+$$ (9)

$$\text{Na}_4\text{P}_6\text{O}_{18}^{2-} + 2\text{Ca}^{2+} \rightarrow \text{CaNa}_4\text{P}_6\text{O}_{18}$$ (10)

$$\text{Na}_4\text{P}_6\text{O}_{18}^{2-} + 2\text{Mg}^{2+} \rightarrow \text{MgNa}_4\text{P}_6\text{O}_{18}$$ (11)

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 Mg(OH)$_2$ colloids attaching onto the MoS$_2$ surface via its dispersing role. Therefore, the interaction energy between MoS$_2$ particles and Mg(OH)$_2$ colloids were investigated based on EDLVO theory model.

In the absence of SHMP, the zeta potentials of MoS$_2$ and Mg(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 $\mu$m and that of Mg(OH)$_2$ colloids was 7.6 $\mu$m. Consequently, the radius of MoS$_2$ particle ($R_1$) and Mg(OH)$_2$ particle $R_2$ were 33 $\mu$m and 3.8 $\mu$m, respectively.

Figure 13 shows the interaction energy between MoS$_2$ particles and Mg(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 Mg(OH)$_2$ colloids was negative, revealing that the attraction force dominated the interparticle aggregation between MoS$_2$ and Mg(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 Mg(OH)$_2$ colloids when no SHMP was added.

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 Mg(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 Mg(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$^+$, Mg(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 Mg(OH)\(_2\) colloids from attraction to repulsion, thereby preventing the adsorption of hydrophilic Mg(OH)\(_2\) on MoS\(_2\) surface.

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**References**


23. Li, W.; Li, Y.; Xiao, Q.; Wei, Z.; Song, S. The influencing mechanisms of sodium hexametaphosphate on chalcopyrite flotation in the presence of MgCl$_2$ and CaCl$_2$. Minerals 2018, 8, 150. [CrossRef]


49. Li, Y.; Lartey, C.; Song, S.; Li, Y.; Gerson, A. The fundamental roles of monovalent and divalent cations with sulfates on molybdenite flotation in the absence of flotation reagents. *RSC Adv.* 2018, 8, 23364–23371. [CrossRef]
52. Yin, Z.; Sun, W.; Yuehua, H.; Zhang, C.; Guan, Q.; Zhang, C. Separation of molybdenite from chalcopyrite in the presence of novel depressant 4-amino-3-thioxo-3,4-dihydro-1,2,4-triazin-5(2h)-one. *Minerals* 2017, 7, 146.

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