



## Elimination of adverse effects of seawater on molybdenite flotation using sodium silicate



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### ABSTRACT

Seawater has been increasingly applied in mineral flotation process due to the scarcity of freshwater. However, seawater plays an adverse effect on molybdenite (MoS<sub>2</sub>) flotation under alkaline condition, but the influencing mechanisms were still unclear, limiting its application in flotation plants. In this study, seawater, and the ions with the most influence of Ca<sup>2+</sup> and Mg<sup>2+</sup> were applied in MoS<sub>2</sub> flotation, with the addition of sodium silicate (SS). As compared to that in freshwater, MoS<sub>2</sub> flotation recovery was significantly decreased in seawater. In addition, MoS<sub>2</sub> recovery in 0.05 M MgCl<sub>2</sub> solution was significantly lower than that in the 0.01 M CaCl<sub>2</sub> solution (these concentrations being consistent with seawater), indicating that Mg<sup>2+</sup> plays a more detrimental role than that of CaCl<sub>2</sub>. The addition of SS increased MoS<sub>2</sub> recovery to different contents, with the most apparent being for that in 0.05 M MgCl<sub>2</sub> solution. Various measurements including contact angle, zeta potential, species calculation, and XPS analysis indicate that the decreased flotation recovery is primary due to the adsorption of Ca and Mg complexes and precipitates onto MoS<sub>2</sub> surface. Moreover, the DLVO theory calculation suggests that SS prevents the adsorption of positively charged Mg precipitates onto negatively charged MoS<sub>2</sub> surface by reversing the interaction force between MoS<sub>2</sub> particles and Mg(OH)<sub>2</sub> colloids from attraction to repulsion. This study therefore provides a new insight into utilizing seawater for MoS<sub>2</sub> flotation.

### 1. Introduction

Molybdenite (MoS<sub>2</sub>), the predominant Mo-containing mineral, is generally recovered from Cu-Mo sulfides through froth flotation which is a water-intensive process and requires high volumes of water resources (Lucay et al., 2015). The flotation process of valuable sulfide ores involves the use of air bubbles to adhere to hydrophobic particles which are carried to the surface, forming a froth layer which can be removed from the liquid media. During this process, freshwater has been extensively used as the ideal flotation media (Rao et al., 2016). However, the use of freshwater in floatation has often been limited by many factors such as the availability of local freshwater resources, competing water use for growing population and other industries, and stringent environment regulations. Alternative water resources, such as underground water, recycled water and seawater, are therefore utilized in flotation to alleviate the pressure of freshwater usage. Among which, seawater, accounting for 97% of the Earth's water resource (Jeldres et al., 2016), has the greatest potential to be used in mineral flotation due to its abundance and availability for many flotation plants

(Hirajima et al., 2016).

The use of seawater for mineral flotation processes has attracted increasing attention and is now considered as an environment-friendly and sustainable solution for the mining industry. Dating back to 1930s, the Tocopilla concentrator located in Chile, for the first time, applied seawater to process chalcopyrite (Jeldres et al., 2016). Since then, several plants utilized seawater to process sulfide minerals (Drelich and Miller, 2012; Jeldres et al., 2016; Moreno et al., 2011). For instance, Las Luces, a Cu-Mo plant, employed seawater together with tailing water for grinding and flotation process. In addition, the Batu Hijau Concentrator located in Indonesia applied seawater to process a gold-rich porphyry copper ore (Wang and Peng, 2014). Another large copper plant called Raglan Concentrator in northern Canada used seawater to process copper ore.

However, the application of seawater resources inevitably brings challenges for mineral processing due to the presence of high salinity. Seawater containing various ions such as Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, etc. (D1141-98, 2003; Marrucci and Nicodemo, 1967; Qiu et al., 2016) is generally detrimental to mineral flotation under

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alkaline condition (Hirajima et al., 2016; Jeldres et al., 2016; Suyantara et al., 2018), mainly due to the presence of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  affecting the surface hydrophobicity and electrical properties of mineral surface (Jeldres et al., 2017; Li et al., 2018b; Pan and Yoon, 2018; Rebolledo et al., 2017). For instance, under alkaline conditions,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  can form hydrophilic hydroxyl complexes or colloidal precipitates (e.g.  $\text{Mg}(\text{OH})_{2(s)}$  and  $\text{CaCO}_{3(s)}$ ). These species may be adsorbed on the surface of valuable minerals to form stable hydration layers and even change the physical and chemical properties of mineral surfaces, resulting in heterocoagulation and eventually reducing mineral recovery (Castro, 2012; Castro et al., 2016; Choi et al., 2016; Li et al., 2018b; Ramos et al., 2013; Yuan et al., 2016). Therefore, it is essential to investigate the interactions of these divalent ions with mineral surfaces.

Attempts have been made to add chemical reagents to mitigate or eliminate the detrimental effects due to  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in mineral flotation process. Previous studies reported that mineral flotation can be promoted in the presence of dispersant via removing fine slime that may adhere to the surface of valuable minerals (Feng et al., 2016; Lu et al., 2011; Rebolledo et al., 2017). Sodium silicate (SS) as one of the most widely used dispersants in mineral flotation, is also commonly used as a modifier to improve mineral recovery in seawater (Al-Thyabat, 2009; Tohry and Dehghani, 2016). For instance, Ramirez et al. (2018) found that SS reduced the negative effects of kaolinite on  $\text{CuFeS}_2$  flotation. Hao et al. (2018) reported that SS contributed to a more negative surface potential of siderite. The strong repulsive forces due to the addition of dispersants disperse the micro-fine siderite from hematite and quartz. However, the influencing mechanism of SS on  $\text{MoS}_2$  flotation in seawater is still unclear.

In this paper, a systematic study containing various measurements, such as contact angle, zeta potential, speciation calculation, and XPS analysis was investigated to understand the roles of SS on  $\text{MoS}_2$  flotation using seawater, 0.01 M  $\text{CaCl}_2$  and 0.05  $\text{MgCl}_2$  solutions (consistent with the concentrations of corresponding ions in seawater) (Qiu et al., 2016). Furthermore, the DLVO theory was applied to calculate the interaction force between  $\text{MoS}_2$  and colloids formed during flotation process. This study provides a promising way for  $\text{MoS}_2$  flotation using seawater in the future.

## 2. Materials and methods

### 2.1. $\text{MoS}_2$ samples and reagents

The bulk  $\text{MoS}_2$  samples (approximately 2 cm × 5 cm × 0.5 cm) were obtained from Guilin city, Guangxi province, China. After crushing and grinding in a three head grinding machine (RK/XPM, Wuhan Rock Grinding Equipment Manufacturing Co., Ltd., Wuhan, China), the prepared sample was subjected to wet screening to obtain a variety of size fractions.  $\text{MoS}_2$  particles with a size fraction of 38–75 μm was employed for flotation while the < 38 μm fraction was used in the froth layer height measurements. The resulting samples were then rinsed using ethanol and the fine slimes were removed by ultrasonication. The samples were then dried in a vacuum oven at 30 °C for 24 h. The dry material were collected and sealed in plastic tubes, and stored in a freezer for further use. The X-ray diffraction (XRD) of the sample indicates a high purity in our previous study (Li et al., 2018b).

All chemical reagents employed in this study, including SS, NaOH,  $\text{CaCl}_2$  and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  are analytical grade. NaOH was used for the adjustment of solution pH. The composition of synthetic seawater has been reported elsewhere (Li and Li, 2019). The corresponding solutions were prepared using ultrapure water with a resistivity of 18.2 MΩ·cm generated by Millipore® Inc (Billerica, MA, USA).

### 2.2. Flotation experiments

Flotation experiments were conducted using 0.25 g  $\text{MoS}_2$  of 38–75 μm fraction in 25 mL of synthetic seawater, 0.01 M  $\text{CaCl}_2$  and

0.05 M  $\text{MgCl}_2$  solution, to reveal the influence of individual  $\text{MgCl}_2$  and  $\text{CaCl}_2$  on molybdenite flotation. The obtained suspension was then transferred into a XFGII type flotation machine (Wuhan Exploration Machinery Factory, Wuhan, China). The suspension was agitated at 1200 rpm and maintained at a required pH value by adding NaOH solution during the first 6 min. The froth was then collected every 10 s in the next 10 min with an air flow rate of 1.2 cm/s. Froth and residue were collected separately before filtration, and dried at 70 °C for recovery calculation. All flotation tests were performed in triplicates and the average flotation recoveries were presented herein. Reproducibility of the experiments was evaluated by the error calculated as one standard deviation.

### 2.3. Contact angle measurements

The contact angles of  $\text{MoS}_2$  sample treated in various solutions were measured using the sessile drop method in a JC2000C contact angle meter (Shanghai Zhongchen Digital Technology Company, Shanghai, China) to estimate the surface wettability of  $\text{MoS}_2$  surface. Subsequent to peeling off the top layers of  $\text{MoS}_2$  sample by adhesive tape, the freshly cleaved  $\text{MoS}_2$  sample was exposed and then cleaned using ultrapure water. After that, the prepared slab was treated under the same solution to the flotation tests for 10 min and then dried in air. Thereafter, a 0.25 μL drop of ultrapure water was generated and attached onto  $\text{MoS}_2$  surface using a microsyringe. The formed drop shape was imaged and analyzed as the contact angle of  $\text{MoS}_2$  surface. At least three replications were performed at different spots on the slab, and the average values were reported.

### 2.4. Zeta potential measurements

50 mg of fine  $\text{MoS}_2$  powders (< 38 μm) was magnetically stirred for 10 min in 50 mL conditioned solution. The pH of suspension was maintained by adding diluted NaOH solution. Subsequently, the prepared suspension was measured by using a Nano-ZS90 zeta potential analyzer (Malvern Co., Ltd., Malvern, UK). Each measurement was repeated at least three times at room temperature (25 ± 0.1 °C) and different pH values (4.0–12.0), and the average value was presented.

### 2.5. Froth layer height experiments

Three-phase frothing stability tests of  $\text{MoS}_2$  were performed using a machine comprising a glass froth column with a diameter of 5 cm. The column height was 80 cm, equipped with a quartz sand core at the bottom. 4 g of  $\text{MoS}_2$  powders were poured into 100 mL conditioned solutions at room temperature (25 ± 0.1 °C), and then transferred into a constant temperature oscillator for 30 min for homogenization. Subsequently, the prepared pulps were added into the glass froth column with 0.88 cm/s compressed air being introduced (Li and Li, 2019). The formed froth layer height was recorded when the froth layer was equilibrated. In general, the froth stability can be quantified by measuring the froth layer height of the pulp.

### 2.6. XPS measurements

Surface chemical properties of untreated and treated samples were analyzed using an ESCALAB 250Xi spectrometer (Thermo Fisher Scientific Inc., Waltham, MA, USA), with an Al Kα monochromatic X-ray source. The survey spectra were collected from 1350 to 0 eV with a pass energy of 100 eV and a step size of 1.0 eV. The high-resolution spectra for each element was scanned with a pass energy of 30 eV and a step size of 0.1 eV. A dwell time of 0.1 s and 5 sweeps were applied in both survey and elemental spectra. The obtained data were analyzed by Shirley method using XPS Peak 4.1 software and the binding energy calibration was based on the C1s value of 284.8 eV.

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