



Understanding the roles of high salinity in inhibiting the molybdenite flotation



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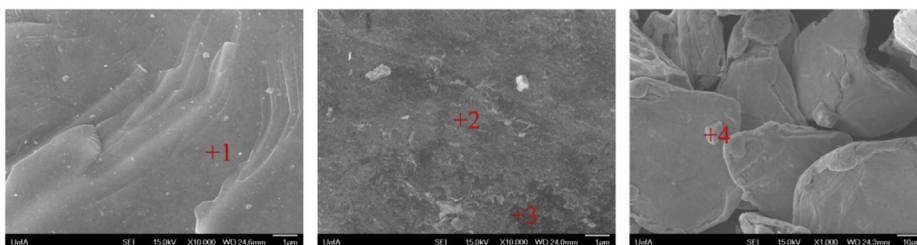
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HIGHLIGHTS

- Molybdenite was depressed in sea water flotation at pH above 9.5.
- SEM-AES, XPS and ToF-SIMS were used to study the depression mechanism.
- $\text{Mg}(\text{OH})_2$ and CaCO_3 deposited on the surface of molybdenite in sea water at pH 11.
- Colloidal precipitates $\text{Mg}(\text{OH})_2$ depressed molybdenite more than crystallized CaCO_3 .

GRAPHICAL ABSTRACT

Molybdenite is depressed by the colloidal precipitates $\text{Mg}(\text{OH})_2$ deposited on the surfaces at pH above 9.5 in sea water flotation.



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ABSTRACT

De-ionized water (DI water) and simulated sea water were applied to float molybdenite in this study. Results showed that the flotation recovery of molybdenite was sharply reduced in simulated sea water at pH above 9.5. To find out the exact mechanisms of depression, several advanced apparatuses were applied for surface characterization. Based on the measurements by the scanning electron microscopy (SEM), two kinds of precipitates (colloidal precipitates and crystallized precipitates) were observed on the molybdenite surface which was immersed in the simulated sea water during flotation. It was found that the colloidal precipitates overspread on the surface while the crystallized precipitates randomly scattered on the surface. With the detection by auger electron spectrum (AES), it was found that magnesium and calcium were the main components in the colloidal precipitates and crystallized precipitates, respectively. According to the X-ray photoelectron spectrum (XPS) tests, it was testified that the colloidal precipitates were $\text{Mg}(\text{OH})_2$ and the crystallized precipitates were CaCO_3 , which was confirmed by ToF-SIMS results. These precipitated $\text{Mg}(\text{OH})_2$ and CaCO_3 particles on the molybdenite surfaces play an important role in inhibiting the flotation of molybdenite in the simulated sea water.

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1. Introduction

Flotation in sea water became a very important issue as sea water is the only available water resource in some arid areas where some large deposits of Cu-Mo sulfide ores (e.g., Atacama Desert, Chile) are located [1–3].

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Molybdenite (MoS_2) as the most important molybdenum source is a sulfide mineral that consists of S–Mo–S crystal like sandwiches that are bonded to each other by van de Waals forces. Within these crystals, S and Mo atoms are held together by covalent bonds [4–6]. Characterized by the anisotropic crystal structure of molybdenite, hydrophobic faces and hydrophilic edges can be formed by the rupture of the van de Waals interactions and the rupture of the covalent Mo–S bonds, respectively. Since the faces are hydrophobic and the edges are not, the natural floatability of molybdenite depends highly on the faces to edges ratio.

Water is a media for mineral processing and the flotation efficiency is highly dependent on the quality of water [7]. Fresh water is the ideally water resource for froth flotation, but to meet the demands to reduce fresh water extraction and save fresh water, increasing water reuse and accessing multiple water sources are inevitable [8]. The use of sea water could be a sustainable solution for many dry zones located close to sea [7].

Sea water as one of the most important high salinity water resources covers 97% of the whole water resources on earth. The direct use of sea water in mining industry will greatly alleviate the pressure of water shortage. Compared to fresh water, sea water has a high salinity of 3.5% with salts dissolved in water. It consists of the primary ions of Na^+ and Cl^- , and the secondary ions of Ca^{2+} , Mg^{2+} , SO_4^{2-} , HCO_3^- , etc. [9,10]. NaCl improves natural hydrophobic mineral flotation because of the reduced bubble size and the reduced energy barrier between hydrophobic surfaces and bubbles. Although the flotation recovery of molybdenite was not so good as that of bituminous coal in salt flotation, it can be explained by the anisotropic properties of molybdenite and heterogeneous nature of the plane surfaces, as revealed by AFM studies [4,7]. Castro et al. also demonstrated NaCl solution improves molybdenite flotation compared with the fresh water. SO_4^{2-} and HCO_3^- showed no inhibition for molybdenite flotation, while Ca^{2+} , Mg^{2+} depressed molybdenite heavily starting at pH around 9.5 due to the hydrolysis of Ca^{2+} , Mg^{2+} ions. The effect of Mg^{2+} is significantly higher than that of Ca^{2+} considering the molar concentration of Mg^{2+} in sea water is about four times higher than that of Ca^{2+} and the value of K_{sp} for $\text{Mg}(\text{OH})_2$ is lower than that for $\text{Ca}(\text{OH})_2$ [1]. However, the effect of Mg^{2+} on flotation was rarely studied while the depression effect of Ca^{2+} has been well studied [1,11,12]. Meanwhile, it is not found in literature that surface characteristics of molybdenite were investigated to find out the changes on mineral surfaces after being conditioned in sea water at alkaline conditions.

In this study, flotation performances of molybdenite in deionized water (DI water) and simulated sea water were investigated from pH 2–12. Scanning electron microscopy (SEM) [13], auger electron spectrum (AES), X-ray photoelectron spectrum (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) [14] were used to analysis the molybdenite surfaces that conditioned in DI water and simulated sea water at pH 11. The purpose of this study is to understand the roles of high salinity in inhibiting the molybdenite flotation.

2. Material and methods

2.1. Materials

2.1.1. Molybdenite samples

Molybdenite concentrates obtained from a concentrate of Teck Highland Valley Copper were used as experimental samples in this study. The residual organic reagents and thio-collectors adsorbed onto the concentrates were removed by diethyl ether and 10^{-4} M sodium sulfide solution, respectively [1]. The samples were then washed profusely with DI water and dried at low temperature (below 60°C). The FTIR and total carbon analysis results of washed

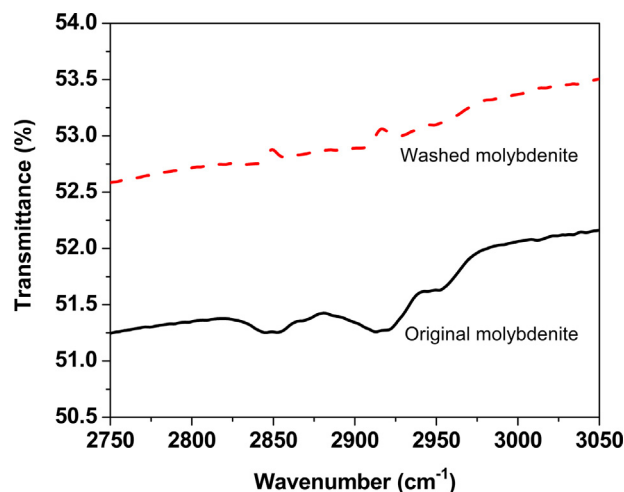


Fig. 1. FTIR detection of original molybdenite (concentrate not washed) and washed molybdenite.

molybdenite are shown in Fig. 1 and Table 1. The dried washed samples were then sieved and 38–75 μm particles were collected for use.

From Fig. 1, it can be observed that the absorption bands in the 2800–3000 cm^{-1} region due to C–H stretching appears in the original molybdenite sample (the molybdenite sample without washing with diethyl ether and sodium sulfide) which indicates organic reagents existing, while no absorption bands in the same region was found in the washed molybdenite sample. So the organic reagents adsorbed onto the molybdenite concentrates during the flotation process are thought to be washed away after dealing with diethyl ether and sodium sulfide solution.

Total carbon analysis was also used to investigate if the organic reagents were cleaned from the concentrates after the washing procedure. From Table 1, it can be seen that the carbon content (indicates C–H compounds/organic reagents existing in molybdenite concentrates) is reduced from 2.3832% in original molybdenite sample to 0.4899% in washed molybdenite sample. The result indicates that almost all the organic reagents were removed from the molybdenite concentrates by the washing operation, so the washed molybdenite samples can be used in the following flotation experiments.

2.1.2. Reagents

Simulated sea water was prepared according to the formula provided by Kester et al. [10] and the composition was shown in Table 2. All inorganic salts used for sea water preparation from Fisher Scientific were A.C.S grade and used as supplied. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) from Fisher Scientific were utilized for pH adjustment. All aqueous solutions were prepared with DI water generated by water purification system from Millipore Inc. unless otherwise stated.

The commercial potassium amyl xanthate (PAX, $\text{CH}_3-(\text{CH}_2)_4-\text{O}-\text{CS}_2\text{K}$) from Prospec Chemicals, Canada was employed as the collector. It was purified [15] by dissolving it in acetone, followed by recrystallization and washing with petroleum ether.

Table 1
Total carbon analysis of molybdenite.

Sample	Weight (mg)	% C
CaCO_3 (test)	24.6	11.8118
Original Molybdenite	21.2	2.3832
Washed Molybdenite	19.3	0.4899

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