

Article

# A New Concept on High-Calcium Flotation Wastewater Reuse

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**Abstract:** Calcium ions are a kind of unavoidable ions in water. It has the deleterious effect on molybdenite flotation. High-calcium flotation wastewater (HCFW) was reused for flotation circuits after the pretreatment removing  $\text{Ca}^{2+}$  in from HCFW. The high cost of wastewater treatment limits HCFW reuse. In this paper, an efficient, innovative, low-cost and environmental-friendly flotation wastewater reuse technology was introduced. XLM, as a composite collector for molybdenite, is a mixture of diesel oil (DO) and polycyclic aromatic hydrocarbons (PAHs). It could reduce the deleterious effects of  $\text{Ca}^{2+}$  on the flotation of molybdenite in HCFW. Therefore, this was used to replace the pretreatment removing  $\text{Ca}^{2+}$  in from high  $\text{Ca}^{2+}$  wastewater and saved the cost of wastewater treatment. When XLM consists of 4 wt % PAHs and 96 wt % DO, it has better adaptability than DO in the different  $\text{Ca}^{2+}$  concentration of flotation water. The contact angle measurements indicated that PAHs, as a synergistic component of a composite collector, could adsorb on the edges of molybdenite in the presence of  $\text{Ca}^{2+}$  by forming PAHs- $\text{Ca}^{2+}$ - $\text{MoO}_4^{2-}$  structure to increase the contact angle of fine molybdenite particle and reduce the deleterious effects of  $\text{Ca}^{2+}$  on the flotation of molybdenite. The industrial-scale test further that demonstrated XLM can improve the molybdenite roughing recovery and grade by 1.8% and 3.46% compared with DO as the collector in high  $\text{Ca}^{2+}$  flotation wastewater. It is feasible and effective to replace high-cost wastewater treatment for molybdenum plants.

**Keywords:** molybdenite; flotation; wastewater treatment; calcium ion; composite collector

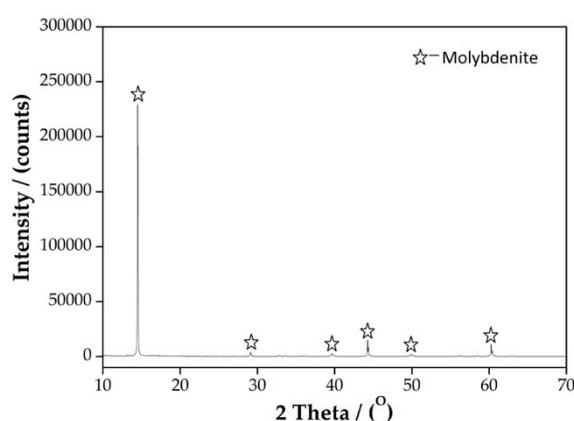
## 1. Introduction

With the rapid development of society and economy, the demand for metal material has increased dramatically all over the world. This resulted in the overexploitation of mineral resources and producing large amounts of wastewater in mineral processing. Massive volumes of wastewater will pose a great threat to the surrounding environment and public health because it contains various pollutants, such as metal ions, suspended solids, and organic compounds [1]. Due to the shortage of fresh water and increasingly stringent regulations on the quality of discharged water, most flotation wastewater is recycled and used in the flotation process after natural sedimentation in a tailing dam or simple treatment. This can lead to several environmental improvements since it decreases discharge of pollutants and saves high-quality water from ground and surface aquifers [2].

Water is an important flotation medium. Water quality will have a great impact on mineral flotation [3–6]. However, along with continual recycling of wastewater, the residual reagents and unavoidable ions will be enriched [7,8]. When the concentrations of residual reagents or unavoidable

ions reach a certain level, the chemistry of water will change [9]. This will lead to some negative effect on minerals flotation [10].

The molybdenum (Molybdenite,  $\text{MoS}_2$ )–tungsten (scheelite,  $\text{CaWO}_4$ ) flotation plant is owned and operated by China Molybdenum Co. Ltd. (CMOC). It is one of the global largest producers of molybdenum and tungsten. Currently, 50,000 t/d of ore is mined and processed to obtain molybdenum and tungsten concentrates with sequential selective flotation [11]. A simplified production process is shown in Figure 1. About 230,000  $\text{m}^3$ /d of flotation wastewater will be reused after sedimentation in a tailing dam. However, the underutilized water glass ( $\text{Na}_2\text{SiO}_3$ ) as depressor (the dosage is 80–100 kg/t) in the cleaning flotation process of scheelite, will make flotation wastewater difficult for the tailings to settle. The residual water glass in the flotation wastewater will have a serious influence on the roughing flotation process of scheelite and wastewater recycling efficiency. Therefore, lime (as a coagulant, 30–50 t/d) is used to remove the residual water glass, reducing wastewater sedimentation time in a tailing dam. Then, the water in the tailings dam is reused in the molybdenum flotation.



**Figure 1.** The result of XRD analysis of the purified molybdenite sample.

However, excess lime or  $\text{Ca}^{2+}$  ions enriched in recycled water significantly depresses molybdenite flotation [12–14]. When the concentration of  $\text{Ca}^{2+}$  in processed water exceeds 600 mg/L, the flotation recovery of molybdenite decreases by 3–5% in comparison with water tap [15]. The adverse effect of  $\text{Ca}^{2+}$  in the process water on the molybdenite flotation has been reported in the numerous studies [14–17]. This might be explained by (1) the bridging role of calcium ions that promoted heterocoagulation between fine gangue particles (e.g., quartz) and molybdenite particles in Cu-Mo ores [14]; (2) gypsum precipitation from  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  in saline water, that could adsorb on the edges of molybdenite particles and the micro-edges of the micro-crystals, composing the faces of molybdenite particles in copper-molybdenite flotation circuits [16]; (3) the interaction of  $\text{Ca}^{2+}$  with molybdenite edges, forming the precipitates of calcium molybdate ( $\text{CaMoO}_4$ ) responsible for the depressing effect of  $\text{Ca}^{2+}$  on the flotation of molybdenite, that preventing the adsorption of diesel on molybdenite surface [15]. This is also an agreement with Zanin et al. (2009) [17]. His study reported that  $\text{Ca}^{2+}$  can directly depress the flotation of molybdenite even in the absence of fine quartz particles.

To solve this problem, some studies on using other flocculants instead of lime or Ca-containing flocculants were carried out. Castro and Laskowski (1997, 2004, 2013, and 2015) studied the depressing effect of organic flocculants on molybdenum flotation [18–21]. In their studies, polyacrylamide flocculants (PAM) and non-ionic flocculants (e.g., poly ethylene oxide) have a strong depression on molybdenite flotation. Some scholars studied the depressing effect of inorganic salt flocculants on molybdenum flotation [22–24]. Their studies showed that  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$  and other metal salt flocculants have also a strong depression on molybdenite flotation. These indicated that the method of using other flocculants instead of lime or Ca-containing flocculants was not feasible. Therefore, Jeldres et al. (2017) studied the impact of seawater with calcium and magnesium removal for the flotation of copper-molybdenum sulphide ores [25]. In their studies, the pretreatment was conducted by the

$\text{Na}_2\text{CO}_3/\text{CaO}$  method, which could promote the precipitation of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . They found that high copper and molybdenum recoveries can be achieved at a high alkaline condition for Cu-Mo ores when the seawater was pre-treated. This indicated the method is feasible with the pretreatment removing  $\text{Ca}^{2+}$  in from high-calcium wastewater. However, all of the methods of removing  $\text{Ca}^{2+}$  in from high-calcium wastewater have high cost and complex processing on the pretreatment of high-calcium water. Therefore, it is an important issue to know how CMOC can recycle flotation wastewater, on the premise of both a low cost of flotation wastewater reuse (without removing calcium ions) and reducing Mo metal loss.

In this paper, we provide an efficient, innovative, low-cost and environmentally friendly flotation wastewater reuse technology. XLM, as a composite collector for molybdenite, is a mixture of diesel oil (DO) and polycyclic aromatic hydrocarbons (PAHs). It could reduce the deleterious effect of  $\text{Ca}^{2+}$  on molybdenite flotation in HCFW. Therefore, it was used to replace the pretreatment removing  $\text{Ca}^{2+}$  in from HCFW and saved the cost of HCFW treatment. The optimum composition of XLM and the adaptability of XLM in flotation water with different calcium ion concentrations at  $\text{pH} = 8$  is studied. The mechanism of XLM reducing the deleterious effect of  $\text{Ca}^{2+}$  on molybdenite flotation in HCFW is analyzed by contact angle measurements. The technical feasibility of wastewater reuse was also studied by an industrial-scale test.

## 2. Materials and Methods

### 2.1. Materials and Reagents

The Mo samples used in the bench-scale flotation experiment were supplied by CMOC. These ores were first crushed to below 2 mm, then put into a ceramic ball mill. The fines, which have a particle size from 0 to 76  $\mu\text{m}$ , consisting of 65% of the mass. The chemical analysis of this sample with inductively coupled plasma mass spectrometry (ICP-MS) and X-ray fluorescence analysis indicated the main composition of 0.12% Mo, 0.07%  $\text{WO}_3$ , 0.007% Cu, and 10.12% Fe. The mineralogical composition of this sample with X-ray diffraction analysis indicated a main valuable mineral composition of 0.19% molybdenite, 0.09% scheelite and the main gangue composition of 25.70% garnet, 18.70% diopside, 16.30% wollastonite, 14.60% quartz, 10.10% biotite and 9.10% feldspar.

The pure molybdenite sample used for contact angle measurements was supplied by CMOC. The high-grade molybdenite was first selected by hand. Then, they were crushed and ground in a ceramic ball mill. The grinding products were further enriched with collectorless flotation. Finally, the purified molybdenite was screened to obtain the  $-38 \mu\text{m}$  fraction for powder contact angle measurements. The purified molybdenite sample with X-ray diffraction analysis shows 99 wt % molybdenite. The XRD analysis result of this sample is shown in Figure 1.

Diesel oil (DO) is the nonpolar oil collector for molybdenite. DO only adsorbs on the faces of molybdenite by hydrophobic forces and van der Waals forces, and does not adsorb on the edges of molybdenite. The typical addition rate of DO is 180 g/t in bench-scale and industrial-scale tests, respectively.

Polycyclic aromatic hydrocarbons (PAHs) may adsorb on the edges of molybdenite. It has a general chemical formula of  $\text{C}_n\text{H}_{2n-12}$  ( $14 \geq n \geq 10$ ,  $n = 11$  in this study). Figure 2 shows the typical molecule structure of PAHs.

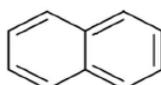


Figure 2. The typical molecule structure of PAHs.

XLM is a composite collector for molybdenite, consisting of 4 wt % PAHs and 96 wt % DO. The typical addition rate of XLM is also 180 g/t in bench-scale and industrial-scale tests, respectively. Pine oil is a conventional frother. The typical addition rate of pine oil is 100 g/t. Sodium silicate

( $\text{Na}_2\text{O}\cdot n\text{SiO}_2$ ,  $n = 2.4$ ) is used as a dispersing agent. The typical addition rate of sodium silicate is 200 g/t in bench-scale and industrial-scale tests. Calcium chloride is used for adjusting calcium concentrations of flotation water. Sodium hydroxide is used for adjusting the pH of pulp. Diesel, PAHs, pine oil and sodium silicate were industrial grade chemicals. Sodium hydroxide and calcium chloride were of analytical grade.

Flotation water is deionized water, synthetic water and high-calcium water. Synthetic water is prepared by dissolving  $\text{CaCl}_2$  and  $\text{NaOH}$  in distilled water. High calcium water was from the tailings dam of China Molybdenum Co., Ltd., in China. It is the tungsten-molybdenum flotation wastewater in which the main factor is 800 mg/L  $\text{Ca}^{2+}$  and pH = 8–9. It was used as process water during the production.

## 2.2. Flotation Experiments

The bench-scale flotation was conducted in an RK/FGC 3 L hitch groove flotation machine. The rotating speed of flotation impeller was 1700 r/min; 1000 g Mo sample was first added into a flotation cell. Then, dispersing agent, collector and frother were added in sequence. The conditioning times for dispersing agent, collector and frother were 1 min, 2 min and 1 min, respectively. The flotation time was 7 min. Three repeat flotation experiments were conducted and the average value of recovery and grade was reported.

An industrial-scale test was conducted in the workshop of the Second Dressing Company of China Molybdenum Co., Ltd. There are three sets of the same flotation system. The industrial-scale tests were conducted on two flotation system, using XLM and DO as collectors, respectively. The feed was 1800 t/d in each flotation system. The Mo ore used in the industrial-scale test was from Mo ore for daily production. The industrial-scale tests flow-sheet and reagent conditions are shown in Figure 3.

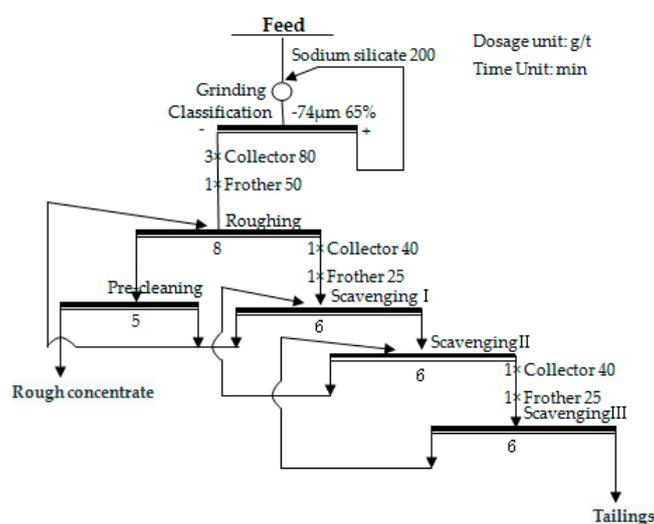


Figure 3. Industrial-scale tests flow-sheet and reagent conditions.

## 2.3. Powder Contact Angle Measurements

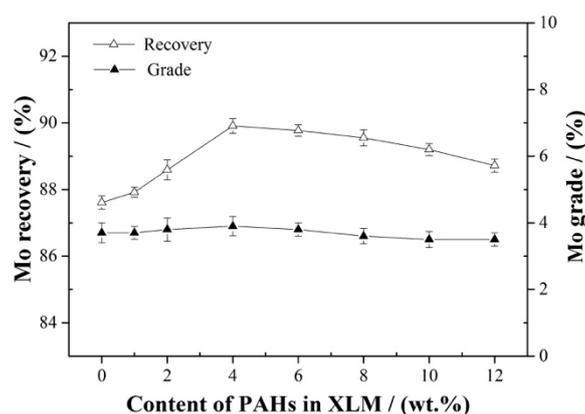
Base on Washburn equation [26,27], powder contact angle was measured with JF99A powder contact angle measuring instrument [28,29] from Xiamen McLaren jingruike instrument co. Ltd. Firstly, molybdenite crystals 50 g was mixed in a  $\text{Ca}^{2+}$  solution of 0 mg/L or  $\text{Ca}^{2+}$  solution of 800 mg/L for 10 min, respectively. Secondly, XLM or DO as the collectors at a concentration of 20 mg/L were added after dispersing by a thermostatic oscillator for 3 min. The solids were filtered and dried at 45 °C. Thirdly, a filter paper is first wet, then put into the bottom of the tube sleeve. Fifthly, the quartz tube was loaded into the sleeve. Sixthly, a dry powder sample was put into the quartz tube and compressed. Finally, when the sample was packed to 7 cm of the quartz tube, it was put into a JF99A

powder contact angle measuring instrument after weighing for contact angle measurement at room temperature (20 °C). Five repeat measurements were conducted and the average contact angle value was reported.

### 3. Results and Discussion

#### 3.1. Bench-Scale Flotation Tests

Figure 4 show the influence of the content of PAHs in XLM on molybdenite flotation in HCFW (800 mg/L  $\text{Ca}^{2+}$ , pH = 8–9). The results show that the molybdenum recovery first increases with increasing the content of PAHs in XLM. Then, the recovery decreases gradually after the content of PAHs is greater than 4 wt %. The reason that the recovery increased first and then decreased, maybe that PAHs can mainly adsorb on the edges of molybdenite, not on the faces of molybdenite when PAHs is below 4%. The 4% may be the maximum adsorption of PAHs on the edges of molybdenite. Then, with PAHs increasing, the adsorption of diesel oil on the faces of molybdenite will be reduced because the redundant PAHs start to adsorb on the faces of molybdenite. Figure 4 also shows that PAHs only had a slight effect on Mo grade ranging from 3.0% to 4.0%. This indicates the optimum content of PAHs in XLM as the synergistic component of composite collector for the molybdenite sample is 4 wt % in HCFW. When XLM consists of 4 wt % PAHs and 96 wt % DO, molybdenum recovery is 89.9%. Compared to DO, the molybdenum recovery was increased by approximately 2.3%.



**Figure 4.** Influence of the content of PAHs in XLM on molybdenite flotation in HCFW (800 mg/L  $\text{Ca}^{2+}$ , pH = 8–9).

Figure 5 shows the adaptability of XLM in flotation water with different calcium ion concentrations at pH = 8. The data shows that firstly, two molybdenum recovery curves become flat before the concentration of calcium ion in flotation water is under 60 mg/L. Then, the molybdenum recovery decreases with increasing the concentration of calcium ion in flotation water. Finally, the recovery curve becomes flat again after the concentration of calcium ion is greater than 600 mg/L. Obviously, XLM as the collector has higher Mo flotation recovery than that of that of DO after  $\text{Ca}^{2+}$  concentration is over 100 mg/L. This further indicates that XLM has better adaptability than DO in the different  $\text{Ca}^{2+}$  concentration of flotation water.

Figure 6 shows the flotation recovery of different size molybdenite particle in high-calcium water (pH = 8–9,  $\text{Ca}^{2+}$  = 800 mg/L) from screening product of flotation test. The data shows that the molybdenum recovery of –97~+74 micrometer fraction is better than another size of molybdenite particle in XLM and DO as collectors. Then, the molybdenum recovery decreases with declining/rising molybdenite particle sizes when molybdenite particle sizes are under/over –97~+74 micrometer fraction. Obviously, XLM had a greater improvement effect on the molybdenite flotation from a fine size fraction than from intermediate, medium and coarse-size fraction. For example, from –38-micrometer size fraction, molybdenite recovery increased from about 79.2% in DO as the collector to about

88.8% in XLM as the collector when flotation water is a high-calcium flotation wastewater (pH = 8–9,  $\text{Ca}^{2+}$  = 800 mg/L). However, that recovery is similar, within experimental errors, with DO or with XLM to the medium and large size fractions when flotation water is a high calcium flotation wastewater (pH= 8–9,  $\text{Ca}^{2+}$  = 800 mg/L). It is clear that the improvement effect of XLM on the flotation of molybdenite shown in Figure 5 is mainly attributed to the improvement of fine-size fractions. Wan et al. (2017) reported that the PAHs in XLM may absorb on the edges of molybdenite in the presence of  $\text{Ca}^{2+}$ , hence reducing the deleterious effect of  $\text{Ca}^{2+}$  on the flotation of fine molybdenite. This indicates PAHs played a significant role to improve fine molybdenite particle recovery in HCFW.

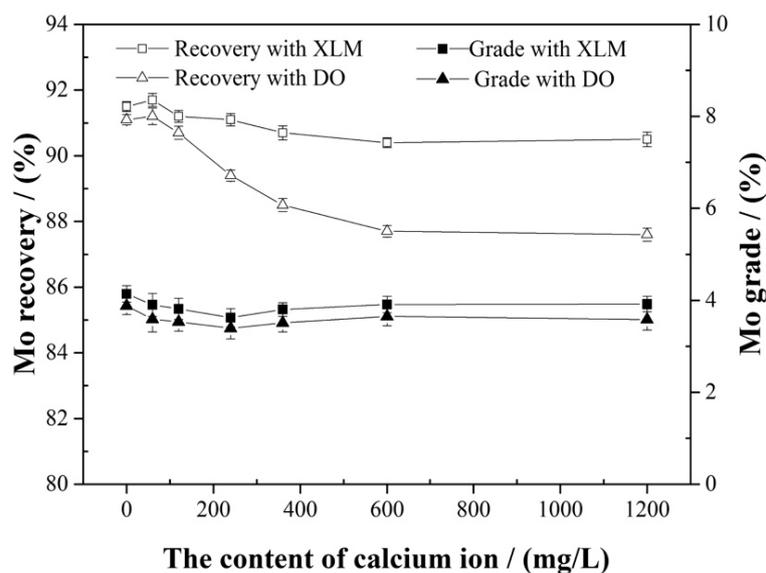


Figure 5. Comparison study between XLM and DO as the collector as a function of  $\text{Ca}^{2+}$  concentration at pH = 8.

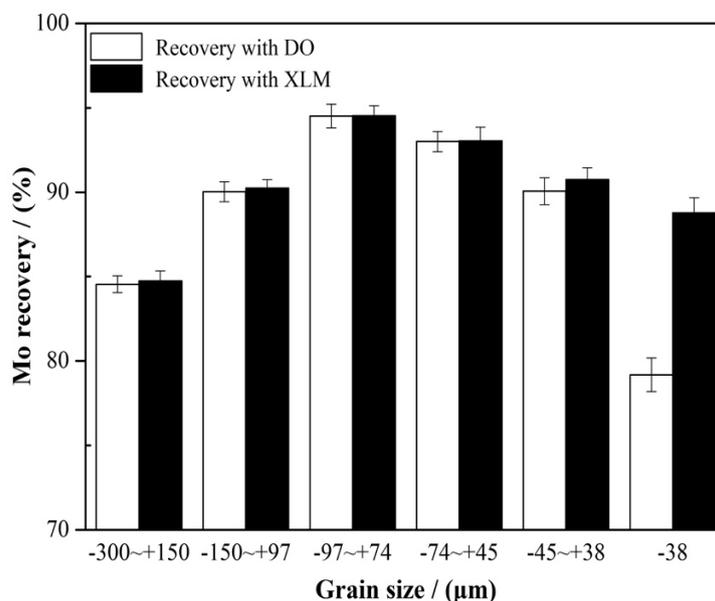
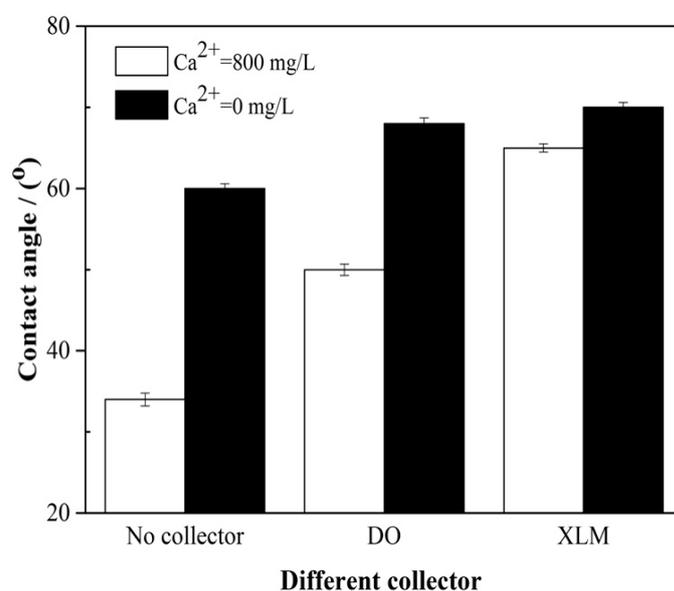
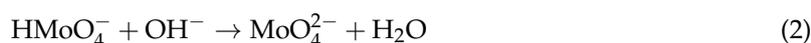
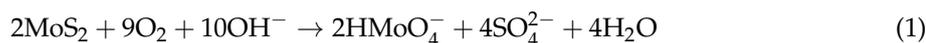


Figure 6. The flotation recovery of different size molybdenite particle in high calcium process water (pH = 8–9,  $\text{Ca}^{2+}$  = 800 mg/L) from screening product of flotation test.

### 3.2. Contact Angle Measurements

The contact angle of molybdenite in the absence and presence of XLM and DO as a function of  $\text{Ca}^{2+}$  concentration at pH 8 was studied. The result is shown in Figure 7. As can be seen, the contact

angle of molybdenite in the presence 800 mg/L  $\text{Ca}^{2+}$  at pH 8 is lower than that of the absence  $\text{Ca}^{2+}$  at pH 8. Obviously,  $\text{Ca}^{2+}$  could decrease the hydrophobicity of molybdenite. This is in agreement with Zanin et al. (2009) who has also reported that  $\text{Ca}^{2+}$  did not affect the contact angle on the faces of molybdenite but reduced the contact angle on the edges of molybdenite at pH 8 [17]. Wan et al. (2017) also reported that the deleterious effect of  $\text{Ca}^{2+}$  on the flotation of molybdenite resulted from the interaction between  $\text{Ca}^{2+}$  and molybdenite edges [15]. The preferential oxidation of molybdenite edges produced  $\text{MoO}_4^{2-}$  which made molybdenite edges negatively charged and attractive to  $\text{Ca}^{2+}$ , leading to the formation of  $\text{CaMoO}_4$  precipitates responsible for depressing molybdenite flotation. The reaction equation governing the process is given by:



**Figure 7.** The contact angle of molybdenite in the absence and presence of XLM and diesel oil as a function of  $\text{Ca}^{2+}$  concentration at pH 8.

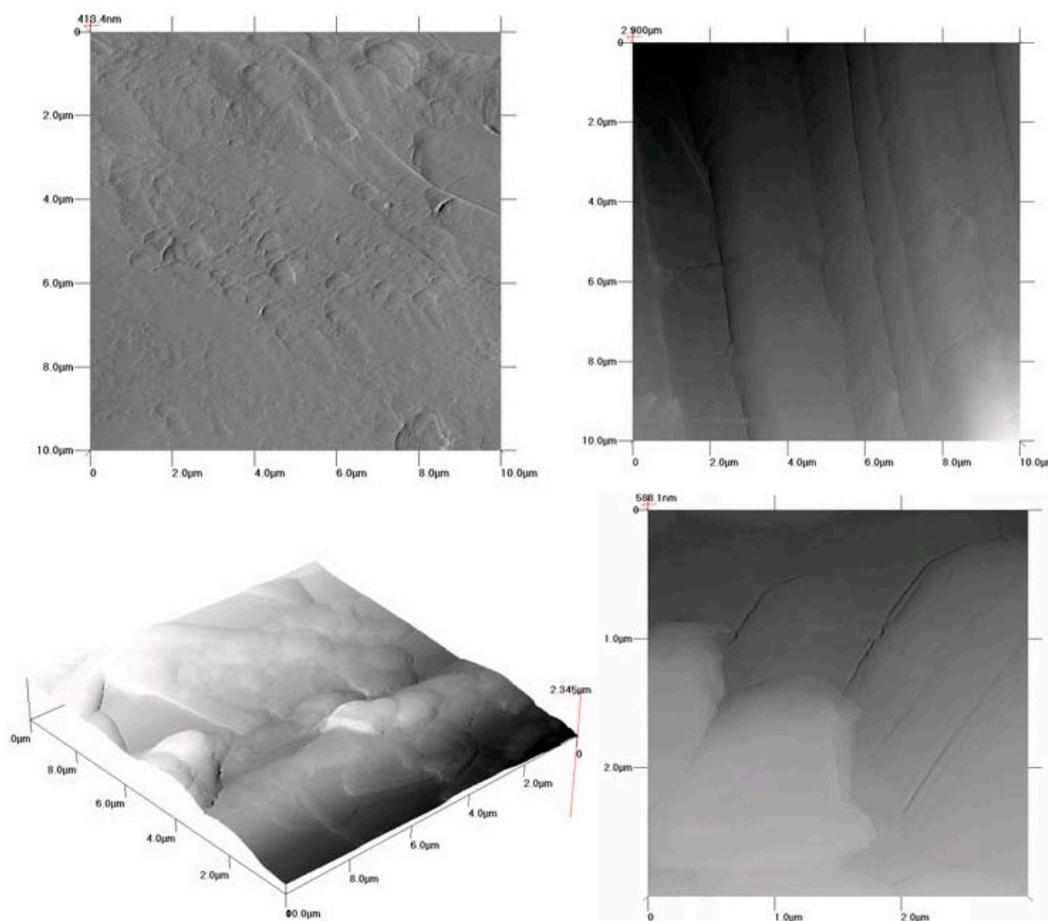
The reaction Equation (1) + (2) + (3) could obtain Equation (4). The reaction equation governing the process is given by:



Meanwhile, the formation of calcium molybdate ( $\text{CaMoO}_4$ ) precipitates on the edges of molybdenite and can increase the area of molybdenite edges but has little effect on the area of molybdenite faces [15]. Therefore, this increases the edge/face ratio of molybdenite particle. Gontijo et al. (2007) reported that a small coverage of hydrophilic species on the mineral surface may have a significant depression on the mineral flotation [30]. This indicates that the formation of  $\text{CaMoO}_4$  on the edges of molybdenite may prevent the adsorption of DO on molybdenite surface leading to the depression of molybdenite floatability.

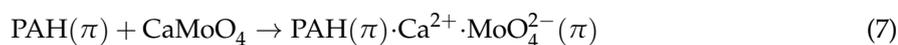
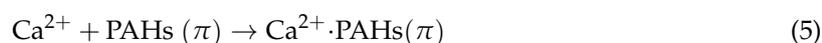
Ornelas Tabares et al. (2006) and Hirajim et al. (2016) reported that the face presents defects and are heterogeneous, and constituted by micro-crystal bands with micro-faces as shown in Figure 8 [31,32]. The face of the molybdenite particle is formed by micro-faces and micro-edges. Although the micro-edges are on the faces of molybdenite, they behave similarly as the edges of molybdenite.

Therefore, the micro-edges on the faces of molybdenite and the edges of molybdenite may be to prevent the adsorption of DO on molybdenite surface leading to a stronger depressing effect than that of only molybdenite edges.



**Figure 8.** AFM Images of faces of molybdenite particles used for contact angle measurements [31,32].

Figure 7 also shows that the contact angle of molybdenite using XLM as the collector in the presence of 800 mg/L  $\text{Ca}^{2+}$  at pH 8 is higher than that of DO as the collector in the presence 800 mg/L  $\text{Ca}^{2+}$  at pH 8. This also indicates that PAHs played a significant role to improve the contact angle of fine molybdenite particle recovery in the presence 800 mg/L  $\text{Ca}^{2+}$  at pH 8. Wan et al. (2017) explained that PAHs may adsorb on the edges of molybdenite in the presence of  $\text{Ca}^{2+}$  [33] due to the  $\pi$  bonds. The  $\pi$  bonds are covalent chemical bonds where two lobes of one involved atomic orbital overlap two lobes of the other involved atomic orbital [34]. Meanwhile, molybdate ions also having  $\pi$  bonds was reported by some studies [35,36]. Therefore, PAHs may adsorb on the edges of molybdenite by (1) the cation- $\pi$  interaction between adsorbed  $\text{Ca}^{2+}$  on molybdenite edge and PAHs, (2) the  $\pi$ - $\pi$  interaction between  $\text{MoO}_4^{2-}$  on molybdenite edge and PAHs, and (3) the electrostatic interaction between adsorbed  $\text{Ca}^{2+}$  molybdenite edge and PAHs. In fact, the cation- $\pi$  interaction and the  $\pi$ - $\pi$  interaction have been widely observed in biological systems [37]. The reactions responsible for the adsorption of PAHs on molybdenite edges were proposed as follows:



### 3.3. Industrial-Scale Tests

To further demonstrate the technical feasibility of the composite collector (XLM), instead of the pretreatment removing  $\text{Ca}^{2+}$  in from high  $\text{Ca}^{2+}$  wastewater to reduce the deleterious effect of  $\text{Ca}^{2+}$  on the flotation of molybdenite in the HCFW, industrial-scale tests were conducted. The results are shown in Table 1. The data shows the average recovery of Mo rough concentrate using XLM/ DO as the collector during industrial-scale tests, is 87.9% and 86.1% respectively. The average recovery of XLM is 1.8% more than that of DO. Table 1 also shows the average grade of Mo rough concentrate using XLM/ DO as the collector during industrial-scale tests, is 11.94%/8.48% respectively. The average grade of XLM is 3.46% more than that of DO. This also indicates that XLM being used to replace the pretreatment removing  $\text{Ca}^{2+}$  in from high  $\text{Ca}^{2+}$  wastewater is feasible and effective in CMOC.

**Table 1.** Results analysis of comparison study between XLM and DO as the collector in Industrial-scale tests.

Serial Number	Collector	Mo Rough Concentrate		$\beta_1 - \beta_2$ (%)	$\varepsilon_1 - \varepsilon_2$ (%)
		Average Grade $\beta$ (%)	Average Recovery $\varepsilon$ (%)		
1	XLM	11.94	87.9	3.46	1.8
2	DO	8.48	86.1		

The research which uses XLM as the collector has improved the flotation recovery by about 1.8% per day and solved the difficult problem about the high treatment cost of flotation wastewater. This has significant improvements in technology and economy by improving the flotation recovery by about 1.8% and saving the cost of  $\text{Na}_2\text{CO}_3/\text{CaO}$  method. The economic analysis of XLM as the collector in HCFW, DO as the collector in HCFW and flotation wastewater with  $\text{Na}_2\text{CO}_3/\text{CaO}$  method is described by Equations (8)–(16). The net profit of XLM as the collector in HCFW, DO as the collector in HCFW and flotation wastewater with  $\text{Na}_2\text{CO}_3/\text{CaO}$  method reach about 80,424 RMB/d, −79,200 RMB/d and −470,100 RMB/d. Obviously, the economic benefit of XLM is more 159,624 RMB/d and 550,524 RMB/d than that of DO and  $\text{Na}_2\text{CO}_3/\text{CaO}$  method.

$$\text{The cost of} = (8800 \text{ RMB/d} \times 96\% + 6400 \text{ RMB/t} \times 4\%) \times 180 \text{ g/t} \times 50,000 \text{ t/d} = 78,336 \text{ RMB/d} \quad (8)$$

$$\text{The profit of molybdenite using XLM as collector} = (50,000 \text{ t/d} \times 0.12\% \times 1.8\% \times 98\%) / 50\% \times 75,000 \text{ RMB/t} = 158,760 \text{ RMB/d} \quad (9)$$

$$\text{The net profit of XLM} = 158,760 \text{ RMB/d} - 78,336 \text{ RMB/d} = 80,424 \text{ RMB/d} \quad (10)$$

$$\text{The cost of DO} = 8800 \text{ RMB/d} \times 180 \text{ g/t} \times 50,000 \text{ t/d} = 79,200 \text{ RMB/d} \quad (11)$$

$$\text{The profit of molybdenite using DO as collector} = 0 \quad (12)$$

$$\text{The net profit of DO} = 0 - 79,200 \text{ RMB/d} = -79,200 \text{ RMB/d} \quad (13)$$

$$\text{The cost of } \text{Na}_2\text{CO}_3 = 150,000 \text{ t/d} \times 2.12 \text{ kg/t} \times 2200 \text{ RMB/t} = 699,600 \text{ RMB/d} \quad (14)$$

$$\text{The profit of molybdenite using } \text{Na}_2\text{CO}_3/\text{CaO} \text{ method} = (50,000 \text{ t/d} \times 0.12\% \times 3.5\% \times 98\%) / 50\% \times 75,000 \text{ RMB/t} = 308,700 \text{ RMB/d} \quad (15)$$

$$\text{The net profit compares with } \text{Na}_2\text{CO}_3/\text{CaO} \text{ method} = 308,700 \text{ RMB/d} - 699,600 \text{ RMB/d} - 79,200 \text{ RMB/d} = -470,100 \text{ RMB/d} \quad (16)$$

where 8800 RMB/t and 6400 RMB/t are the prices of DO and PAHs, the 96% and 4% are the contents of DO and PAHs in XLM, the 180 g/t is the dosage of the collector, 50,000 t/d is the throughput of molybdenite flotation in Equation (8); 0.12%, 50% and 98% are the ore grade, the grade of molybdenite concentrate and the recovery of the cleaning process, 75,000 RMB/t is the current price of molybdenum

concentrate whose molybdenum grade is 50% in Equation (9); 150,000 t/d is the flotation wastewater production, 2.12 kg/t is the dosage of  $\text{Na}_2\text{CO}_3$ , 2200 RMB/t is the price of  $\text{Na}_2\text{CO}_3$  in Equation (14); 3.5 is the recovery improved with the  $\text{Na}_2\text{CO}_3/\text{CaO}$  method in Equation (15).

#### 4. Conclusions

This study showed that an efficient, innovative, low-cost and environmentally friendly flotation wastewater reuse technology. XLM, as a composite collector for molybdenite, is a mixture of DO and PAHs. It could reduce the deleterious effect of  $\text{Ca}^{2+}$  on the flotation of molybdenite HCFW. Therefore, this was used to replace the pretreatment removing  $\text{Ca}^{2+}$  in from HCFW. In addition, it also saves the cost of wastewater treatment and avoids the loss of molybdenum resources. It can maximize the utilization and reduce the discharge of flotation wastewater to realize the sustainable development of resources and environment. The following conclusions were drawn:

- (1) When XLM consists of 96 wt % DO and 4 wt % PAHs, XLM has better adaptability than DO in different  $\text{Ca}^{2+}$  concentrations of flotation water.
- (2) PAHs, as synergistic components of the composite collector, could adsorb on the edges of molybdenite in the presence of a  $\text{Ca}^{2+}$  by forming PAHs- $\text{Ca}^{2+}$ - $\text{MoO}_4^{2-}$  structure to increase the contact angle of fine molybdenite particle and reduce the deleterious effect of  $\text{Ca}^{2+}$  on the flotation of molybdenite.
- (3) The industrial-scale tests showed that XLM can improve the molybdenite roughing recovery and grade by 1.8% and 3.46% compared with DO in HCFW, respectively. It is feasible and effective to replace high-cost wastewater treatment for molybdenum plants.

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