minerals

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The Depressing Effect of Kaolinite on Molybdenite Flotation in Seawater

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Abstract: Copper-molybdenum grades of important mining deposits have progressively decayed, which is associated with high levels of clay minerals which affect froth flotation. The depressing effect of clay minerals on copper sulfides was previously reported but there are no systematic studies on the effect on molybdenite flotation in seawater. The objective of this work was to study the effect of kaolinite on molybdenite flotation in seawater and to evaluate the use of sodium hexametaphosphate (SHMP) as dispersant. The results of this work show that kaolinite depresses molybdenite flotation which is more significant in seawater at pH > 9. All the experimental data validate the hypothesis that kaolinite covers molybdenite, reducing its flotation recovery. The depressing effect of kaolinite on molybdenite flotation in seawater is enhanced by the magnesium and calcium hydroxo complexes at pH > 9, which induce heterocoagulation between kaolinite and molybdenite, thus reducing recovery. The attachment of the positively charged hydroxo complexes of magnesium and calcium to the molybdenite and kaolinite surfaces is diminished by SHMP. This reagent increases the repulsive forces between molybdenite and precipitates and as a result, molybdenite becomes more hydrophobic and recovery increases.

Keywords: molybdenite; clays; dispersants; seawater

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1. Introduction

Copper-molybdenum grades of important mining deposits around the world have progressively decayed during the last few decades, which is generally associated with high concentrations of phyllosilicates. Clay minerals are the most common phyllosilicates found in copper-molybdenum porphyry deposits [1]. These types of soft mineral species are usually dispersed in mineral slurries as fine particles generating the conditions for non-Newtonian behavior [2], which affects the entire mineral processing chain, i.e., milling, froth flotation, thickening, and dewatering [3–7]. In particular, the efficiency of flotation of copper sulfides is severely affected by clay minerals [3,4,8]. Molybdenum is a strategic metal which is commonly found associated with copper in porphyry copper deposits, and molybdenite (MoS_2) is the main molybdenum-containing mineral, which is characterized by its natural hydrophobicity, thus it readily floats together with copper sulfides. However, the effect of clay minerals on molybdenite flotation has seldom been studied.

Nowadays, seawater offers a real solution for mining operations which are in geographic zones in which the availability of continental water is limited. The Centinela (AMSA) and Sierra Gorda (KGHM) mining operations in Chile are examples of the successful use of seawater in the processing of copper-molybdenum minerals. Although seawater represents a real solution to the shortage of freshwater in mineral processing, its high ionic strength also brings up some negative effects. Seawater contains high concentrations of different ions, which induces important changes in the surface properties of copper-molybdenum sulfides, and thus strongly affects the flotation efficiency [8–13]. It was previously reported that molybdenite flotation in seawater is strongly depressed as pH is increased. This is explained by the attachment of magnesium hydroxo complexes to molybdenite, rendering it hydrophilic [14–18]. Other studies showed that the flotation of chalcopyrite and enargite is depressed in water with high salinity in the alkaline pH range and that this depression seems to depend on the prevailing pulp redox potential [11,12]. The presence of ions in seawater also affects the frothing properties of flotation by inhibiting bubble coalescence [19–21], which also improves the flotation of naturally hydrophobic particles by reducing the double layer thickness of bubbles and particles [22–24]. The presence of ions in seawater also influences the interactions between copper sulfides and clay minerals. Uribe et al. [8] studied the effect of kaolinite on chalcopyrite flotation in different aqueous media including seawater, and found that the depressing effect of kaolinite on chalcopyrite in seawater is related to the formation of hydrolyzed species of calcium and magnesium, which induce heterocoagulation between kaolinite and chalcopyrite. These authors hypothesized that the hydroxo complexes are adsorbed on chalcopyrite and kaolinite particles, which leads to heterocoagulation.

The use of dispersants was studied as an alternative to improve the recovery of valuable minerals in the presence of high concentrations of clays and ions in solution [10,12]. The dispersants' behavior was studied in different aqueous media and it was found that sodium hexametaphosphate (SHMP) has the capacity to interact with magnesium in its ionic form and when it is part of the crystalline structure, e.g., serpentine or rare earth ores [25–28]. Likewise, it was found that SHMP can be used as a dispersant to re-establish the floatability of molybdenite in seawater [10,29]. Other studies concluded that SHMP improves the flotation of chalcopyrite in the presence of kaolinite in seawater by decreasing the capacity for interaction between the two minerals [12]. However, to the best of our knowledge, there have been no studies on the effect of dispersants on molybdenite flotation performed using seawater and in the presence of clay minerals.

The objective of this work was to study the effect of kaolinite on molybdenite flotation in seawater and to evaluate the effect of SHMP under these conditions.

2. Experimental

2.1. Samples and Reagents

The molybdenite sample (size range −88 + 44 µm) used in this work was obtained from an industrial molybdenum concentrate, which was initially washed with sodium hydrosulfide (NaSH) and acetone to remove flotation collectors and other organic compounds. Then, it was further purified through 3 stages of collectorless flotation to remove the remaining impurities, such as pyrite. The removal of organic reagents was checked by analyzing the total organic carbon (TOC) content of liquid extracts obtained at different pH values, which showed no presence of TOC, thus no presence of flotation reagents [29]. The molybdenite samples showed 99.34% purity, with a chemical composition of 59.6% Mo and 39.8% S. The kaolinite sample (100% −15 µm) was provided by the Clay Minerals Society Source Clays. X-ray diffraction analysis indicated a composition of 96% kaolinite, 3% anatase, and 1% impurities. Molybdenite was stored in a freezer in sealed plastic bags previously blown with nitrogen, at 1 °C, to reduce oxidation [29–31]. Methyl isobutyl carbinol (MIBC) was used as frother, sodium hexametaphosphate (SHMP) obtained from Sigma Aldrich (97% purity) was used as dispersant, and diesel as collector. Sodium hydroxide was used to adjust the pH and solutions of different ions were prepared using the chloride salts of sodium, potassium, calcium, and magnesium. Seawater was obtained from the coast of Concepción, Chile. A 0.01 M NaCl solution prepared using Milli-Q water of 18.2 MΩ·cm at 25 °C was considered as freshwater.

2.2. Microflotation Tests

Molybdenite flotation was assessed using a 150 mL Partridge and Smith glass cell with nitrogen gas at 80 mL/min. The experiments were done using 1 g of molybdenite, either pure or in mixtures of 1 g molybdenite plus 0.18 g of kaolinite (15%), which was initially conditioned for 2 min in 100 mL of solution (freshwater, Mg^{2+}, Ca^{2+}, or seawater) at the required pH. After the initial conditioning stage, reagents were added to obtain a final concentration of 25 ppm of MIBC, 100 ppm of diesel, and 0, 20, 50 or 100 ppm of SHMP (depending on the condition). The reagents were added first in 50 mL of solution, then added to the 100 mL of the conditioned suspension to complete the volume of the microflotation cell, and lastly mixed for an additional 3 min. Then, the gas valve was opened to start the process of flotation for 2 min, removing the froth every 10 s. The pulp level in the microflotation cell was kept constant by adding a background solution prepared with the same composition, and at the same pH value as the original solution. Finally, after the experiments, molybdenite and kaolinite particles were separated in the concentrate and tailings stream using a 38 µm mesh screen (400#) and dried in an oven set at 105 °C for 5 h. The recovery was calculated as the ratio between the mass of molybdenite in the concentrate, and the mass in the concentrate plus the mass in the tailings. All tests were done in triplicate.

2.3. Induction Time Measurements

Induction time was measured using a device built at the University of Alberta and following a procedure described elsewhere [18]. In this type of measurement, a bubble produced in a capillary is pushed through a solution against a bed of particles for a measured and controlled contact time. Then, the bubble is detached from the particle bed and observed through a microscope to determine the occurrence of bubble–particles adhesion. The procedure is repeated 10 times at different positions over the particle bed, and the percentage of successful contact is determined. Different contact times are tested and a curve of percentages of successful contact (N_{sc}) versus the measured contact time (t_c) is plotted. Induction time is the time at which 50% of the contacts are effective. The experimental data were fitted using Equation (1):

$$N_{sc} = a_1\left(1 - exp\left(-a_2 t_c^{a_3}\right)\right) \quad (1)$$

where a_1, a_2 and a_3 are fitting constants.

The beds of mineral particles were prepared by mixing 3 g of either pure molybdenite or mixtures of 3 g of pure molybdenite plus 0.54 g of kaolinite (15%) with 30 mL of solution. The pH was adjusted and the slurry was conditioned for 12 min after which it was transferred to a 15 mL cell in order to start the induction time measurements. No collector was added in the experiments and air was used to generate the bubbles. All these experiments were conducted in triplicate and the results presented in this paper are averaged values.

2.4. Turbidity Measurements

Turbidity tests were used to follow the aggregation/dispersion phenomena of molybdenite and molybdenite/kaolinite suspensions in the absence and presence of SHMP; thus, differences of turbidity indicate changes in coagulation/heterocoagulation. Suspensions were prepared by mixing either 1 g of pure molybdenite or mixtures of 1 g of pure molybdenite plus 0.18 g of kaolinite, with 120 mL of the different aqueous solutions tested in this work. The dosages of collector and dispersant were the same as those used in the microflotation tests. Afterwards, the suspensions were conditioned for 5 min. Then, suspensions were left to settle in 100 mL graduated cylinders for 5 min, after which 10 mL aliquots were taken from a section positioned at 2/3 the height of the cylinder which were tested for turbidity. Turbidity measurements were performed using a HACH 2100N turbidimeter, whose maximum reading is 4000 NTU. In order to correlate this information with the floatability data, all the tests were performed at the same conditions used during the microflotation experiments.

2.5. Electrophoretic Mobility Measurements

Electrophoretic mobility measurements were done using a Zetacompact Z9000 from CAD Instruments. Suspensions were prepared mixing 0.07 g of either pure molybdenite or mixtures of molybdenite and kaolinite with different solutions. These suspensions were conditioned for 3 min using a magnetic stirrer to disperse fine particles while the pH was adjusted to 8 or 10 using sodium hydroxide.

3. Results

3.1. Microflotation

Figure 1a shows the recovery of molybdenite in the absence and presence of kaolinite (15%) as a function of pH, in fresh and seawater. The experimental data ratify the previously reported observations that molybdenite flotation is strongly depressed in seawater at pH > 9 [10]. These data also indicate that molybdenite recovery decreases in the presence of kaolinite in both types of water but to a stronger extent in seawater. Figure 1b shows the recovery of molybdenite in the presence of kaolinite in solutions of 10,752 mg/L Na, 390 mg/L K, 416 mg/L Ca, 1295 mg/L Mg (seawater concentrations). It can be seen that magnesium and calcium ions have the most significant depressing effects on molybdenite flotation. The results show that neither sodium nor potassium enhances the depressing effect of kaolinite.

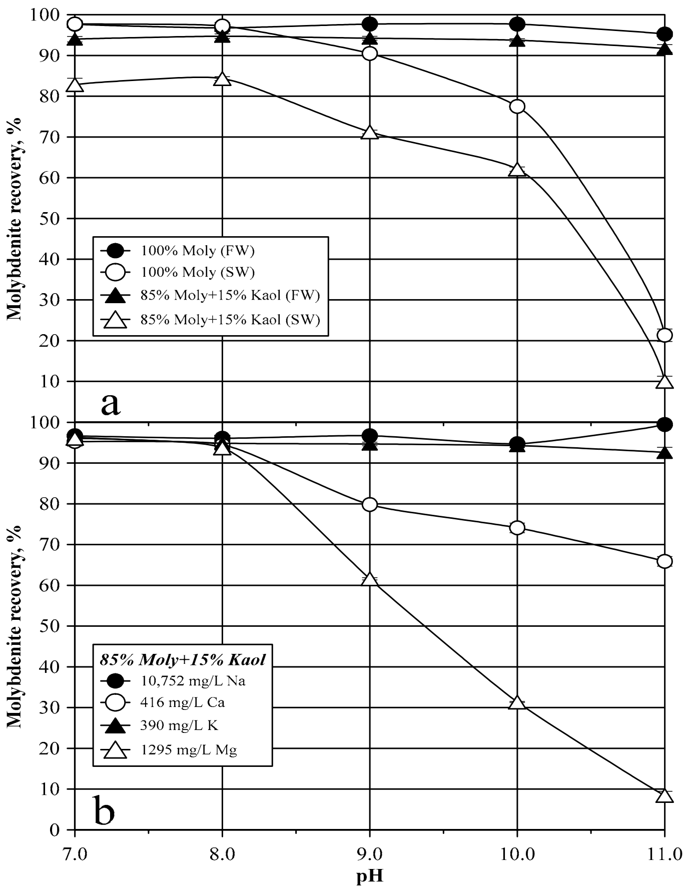

Figure 1. Recovery of molybdenite in the absence and presence of 15% kaolinite as a function of pH in different aqueous solutions, i.e., (**a**) fresh (FW) and seawater (SW), and (**b**) solutions of 10,752 mg/L Na, 390 mg/L K, 416 mg/L Ca, 1295 mg/L Mg. Moly: molybdenite; kaol: kaolinite.

Figure 2 shows the recovery of molybdenite in the presence of kaolinite, with and without SHMP, and in different aqueous solutions, i.e., (a) seawater, (b) 416 mg/L Ca, and (c) 1295 mg/L Mg. The results obtained in seawater (a) show that molybdenite recovery is increased in up to 35 percentage points as SHMP is added, which is more significant at pH > 9. This effect can be observed from a dose of 20 mg/L SHMP. Figure 2b,c shows that SHMP strongly increases molybdenite recovery, an effect that is more significant in the case of tests done in magnesium solutions.

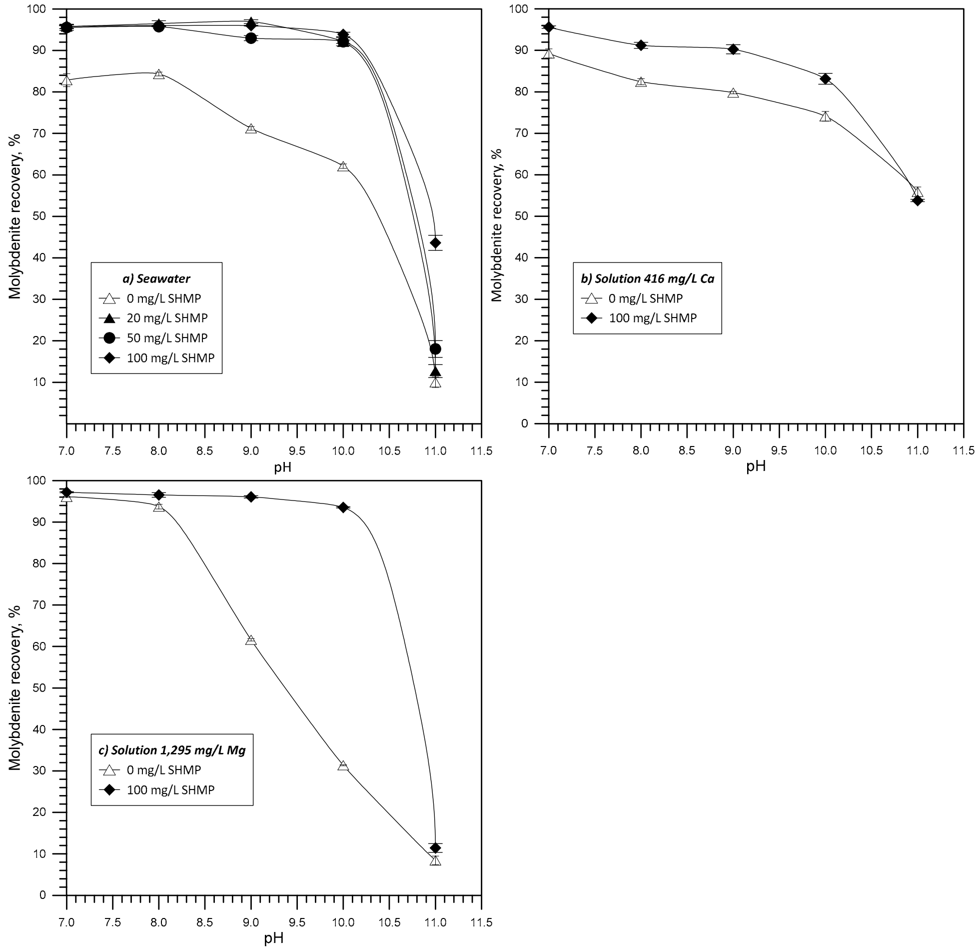

Figure 2. Recovery of molybdenite in the presence of 15% kaolinite, with and without sodium hexametaphosphate (SHMP), and in different aqueous solutions, i.e., (**a**) seawater, (**b**) 416 mg/L Ca, and (**c**) 1295 mg/L Mg.

3.2. Induction Times

Figure 3 shows the induction times obtained at different pH in freshwater, seawater, and in solutions of 10,752 mg/L Na, 390 mg/L K, 416 mg/L Ca, and 1295 mg/L Mg. Induction times were measured using particle beds of molybdenite and molybdenite + kaolinite. It is important to mention that values higher than 10,000 ms were not registered as they are out of the measuring range of the equipment. In the measurements with pure molybdenite (Figure 3a), the results indicate that induction times increase with pH in all the tested solutions, and that they reach the highest values in seawater. The monovalent cations have a slight effect of increasing induction times at the whole range of pH, while divalent cations have a significantly stronger effect with magnesium being the seawater cation that explains the strong effect of seawater on induction time, in particular at pH > 9. These results are in agreement with the microflotation data presented in Figures 1 and 2. In the measurements with beds of particles of mixtures of molybdenite + kaolinite (Figure 3b), the results indicate that induction times increase with pH in all the solutions, and that the highest values are obtained in seawater. Kaolinite increases the induction time, which agrees with the lower molybdenite recoveries obtained in the presence of this clay mineral. Figure 3b also shows that calcium and magnesium have a strong effect on induction time in the presence of kaolinite, which agrees with the microflotation data. Monovalent cations also seem to enhance the effect of kaolinite of increasing induction time but to a weaker extent compared to divalent cations.

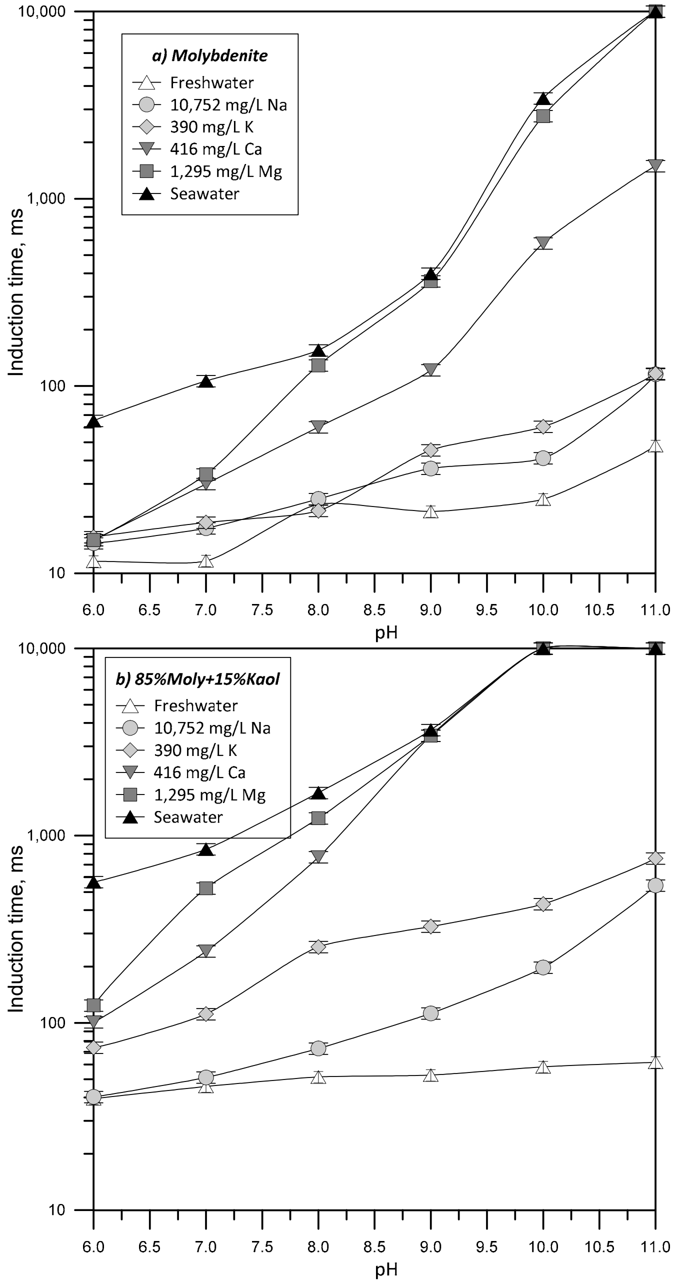

Figure 3. Induction times obtained at different pH in freshwater, seawater and in solutions of 10,752 mg/L Na, 390 mg/L K, 416 mg/L Ca, 1295 mg/L Mg. The measurements were done using particle beds of (**a**) molybdenite and (**b**) 85% molybdenite + 15% kaolinite. Moly: molybdenite; kaol: kaolinite.

Figure 4 shows the induction times obtained at different pH in seawater, using particle beds of pure molybdenite and molybdenite+kaolinite, in the absence and presence of 100 mg/L of SHMP. The induction times are reduced with SHMP in the whole range of pH to values even lower than those observed for pure molybdenite particles. These results correlate with the high molybdenite recoveries observed in the presence of SHMP.

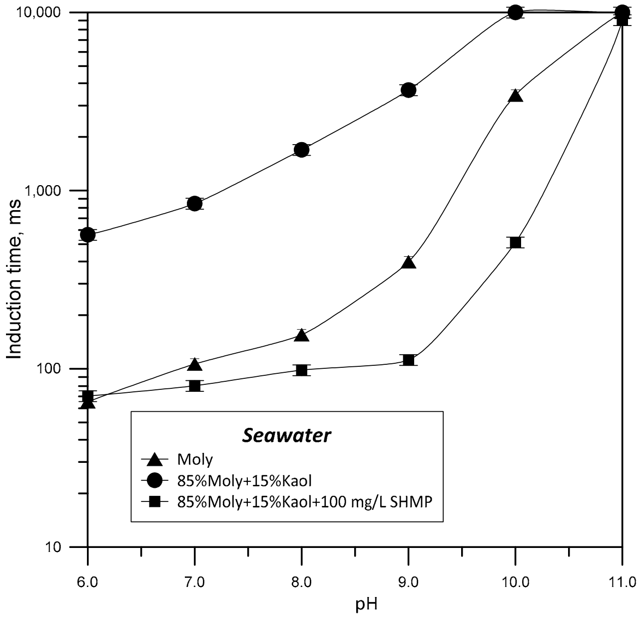

Figure 4. Induction times obtained at different pH in seawater, using particle beds of molybdenite, 85% molybdenite + 15% kaolinite without SHMP, and 85% molybdenite + 15% kaolinite in the presence of 100 mg/L of SHMP. Moly: molybdenite; kaol: kaolinite.

3.3. Turbidity

Figure 5 shows the results obtained in fresh and seawater for suspensions of pure molybdenite particles at pH 8 and 10. Turbidity increases with pH in both aqueous media, and the use of SHMP produces an increase in the turbidity in fresh and seawater. These results indicate that SHMP interacts with both molybdenite and the hydroxo complexes of magnesium (further information about these compounds can be found in [14]) (at pH 10), which leads to cleaner molybdenite surfaces, thus improving recovery.

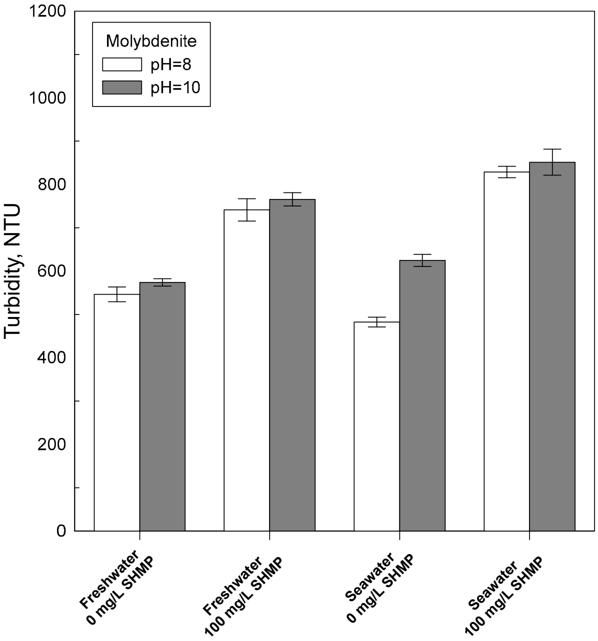

Figure 5. Turbidity results of molybdenite suspensions at pH 8 and 10, in freshwater and seawater, with and without SHMP as a dispersant.

Figure 6 shows the results obtained in fresh and seawater for suspensions of molybdenite + kaolinite mixtures at pH 8 and 10. The results show that turbidity values are substantially higher than for suspensions of pure molybdenite (Figure 5) which is explained by the presence of fine kaolinite particles. In the absence of SHMP, turbidity decreases in seawater with respect to freshwater, which can be correlated to more coagulation/heterocoagulation. In the presence of SHMP, turbidity substantially increases in seawater, which is related to the dispersion of the three types of solid particles, i.e., molybdenite, kaolinite and hydroxo complexes of magnesium/calcium produced from seawater.

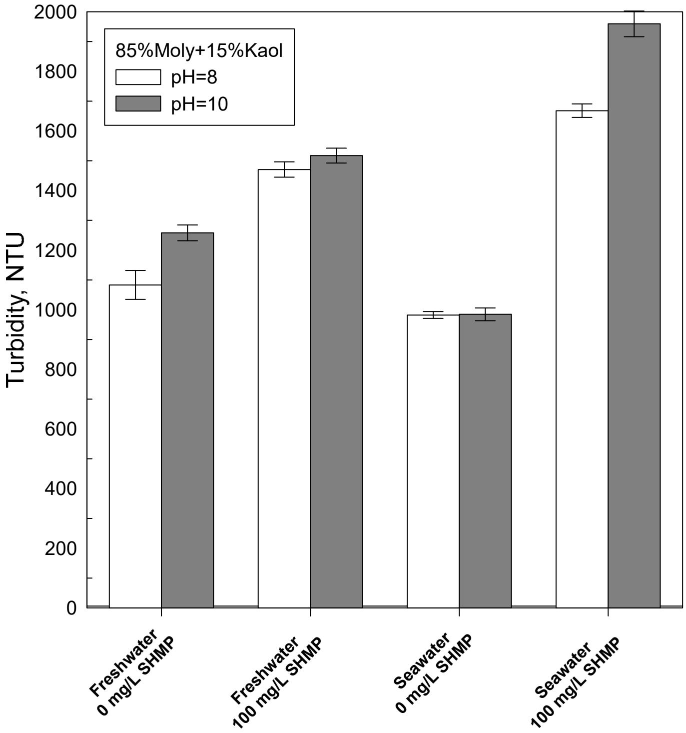

Figure 6. Turbidity results of suspensions of 85% molybdenite + 15% kaolinite at pH 8 and 10, in freshwater and seawater, with and without SHMP as a dispersant. Moly: molybdenite; kaol: kaolinite.

3.4. Electrophoretic Mobility

Figure 7 shows the electrophoretic mobility distributions measured for particles of molybdenite, kaolinite, and molybdenite+kaolinite mixtures with and without SHMP in freshwater at pH 8 (a) and 10 (b). The results obtained at both pH show that the electrophoretic mobilities for molybdenite display a unimodal distribution, while they are bimodal for kaolinite; this might be due to the potential difference between the edges and faces in kaolinite. The results obtained when molybdenite and kaolinite are added together (85%moly + 15%kaol) show a unimodal distribution, which indicates interaction between the two minerals. When the dispersant is added (85%moly + 15%kaol + 100 g/mL SHMP) the interaction between molybdenite and kaolinite seems to be reduced in the presence of SHMP, as in this case a bimodal distribution is observed.

Figure 8 shows the electrophoretic mobility distributions obtained at pH 10 for particles of molybdenite, kaolinite, and molybdenite + kaolinite mixtures with and without SHMP in a solution of 647 mg/L Mg. The results show that the electrophoretic mobilities move towards more positive values in the magnesium solution which indicates the adsorption of these cations on all the minerals tested in this work. Molybdenite and kaolinite distributions display a sort of unimodal distribution; when both minerals are mixed, the resulting distribution tends to resemble the kaolinite electrophoretic mobility distribution. The addition of SHMP generates a bimodal distribution, located at more negative values of electrophoretic mobilities, which indicates that this reagent renders the particles more negatively charged.

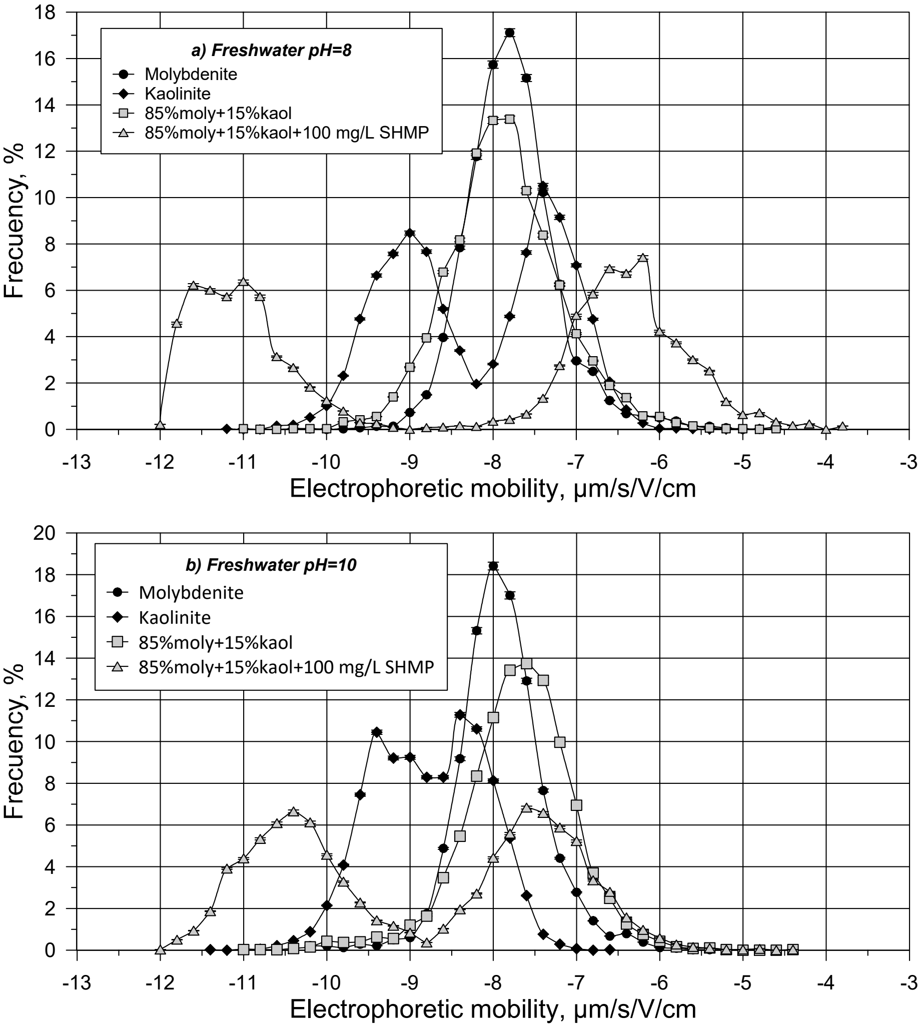

Figure 7. Electrophoretic mobility distributions of particles of molybdenite, kaolinite, and 85% molybdenite + 15% kaolinite with and without SHMP in freshwater at pH 8 (**a**) and 10 (**b**). Moly: molybdenite; kaol: kaolinite.

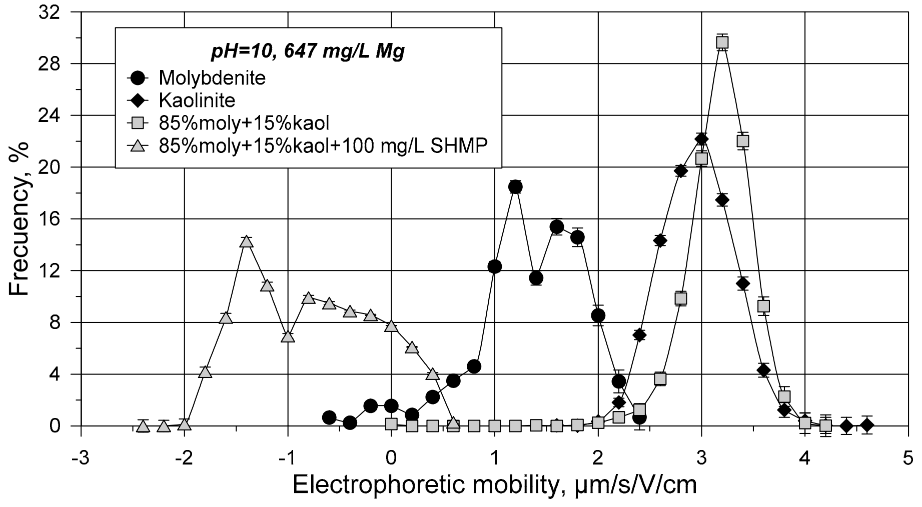

Figure 8. Electrophoretic mobility distributions obtained at pH 10 of particles of molybdenite, kaolinite, and 85% molybdenite + 15% kaolinite with and without SHMP in a solution of 647 mg/L Mg. Moly: molybdenite; kaol: kaolinite.

4. Discussion

As was previously mentioned, seawater contains high concentrations of different ions which are expected to induce aggregation between mineral particles. This was already reported by Uribe et al. [8], who showed that the depressing effect of kaolinite on chalcopyrite was significant in seawater as the pH is raised to values above 9–9.5. These authors related this depressing effect to the formation of hydrolyzed species of magnesium (further information about these compounds can be found in [14]) that induce heterocoagulation between kaolinite and chalcopyrite, thus reducing recovery. Ramirez et al. [12] studied the flotation of chalcopyrite in the presence of kaolinites of different crystallinity in fresh and seawater at pH 7–12 and evaluated the effect of SHMP as a slime dispersant. They showed that chalcopyrite flotation in freshwater was only depressed at pH 7, and that chalcopyrite flotation was restored with SHMP. When these authors used seawater, chalcopyrite was depressed at $pH > 9$ which was explained by the compression of the electrical double layer (EDL) and by the action of magnesium precipitates (further information about these compounds can be found in [14]) that induce a strong interaction between kaolinite and chalcopyrite. In seawater, chalcopyrite flotation in the presence of kaolinite was improved using SHMP, an effect which was stronger using a poorly crystallized type of kaolinite [12]. The use of dispersants to remove precipitating/coagulating hydroxides from the molybdenite surface in the absence of clays was tested and the results were reported by Rebolledo et al. [10], who showed that SHMP restores molybdenite flotation over the alkaline pH range without affecting pyrite flotation. The results presented in this work show that kaolinite affects molybdenite flotation which is more significant in seawater at $pH > 9$, and that SHMP reduces this depressing effect, results which are in line with the previously cited studies.

Molybdenite (MoS_2) is a molybdenum mineral which has a crystal structure formed by S–Mo–S layers in which sulfur and molybdenum atoms are connected by covalent bonds while the S–Mo–S layers are linked together by van der Walls interactions [32,33]. This type of crystalline structure explains how molybdenite particles are formed by non-polar and highly hydrophobic surfaces, which are usually referred to as faces, and polar and highly hydrophilic surfaces, called edges. Thus, molybdenite is usually described as an anisotropic mineral with different surface properties on the edges and faces [32,34]. Molybdenite faces are chemically less active than the edges with a point of zero charge (PZC) at around pH 4 [34] while the edges are more active and negatively charged over a wide range of pH which results from the reactions of molybdenum with water and/or oxygen, which leads to the formation of negatively charged adsorption sites at the solid/liquid interface of $HMoO_4^-/MoO_4^{2-}$ ions [32]. The edges and faces of molybdenite become more negatively charged as the pH increases, which can be observed in Figure 7, which shows that the electrophoretic mobility distribution of molybdenite moves to more negative values as the pH is increased from 8 to 10. Lopez-Valdivieso et al. [35] proposed that the hydrophobic faces of molybdenite are heterogeneous with imperfections such as polar nano-edges and nano-faces, which can also be associated with a high level of roughness. The presence of nano-edges generates polar sites that enhance the adsorption of organic and inorganic molecules such as organic polymers, inorganic polyelectrolytes, and hydroxides [34,36]. The nano-edges are chemically active and negatively charged as chemical species such as $HMoO_4^-/MoO_4^{2-}$ can be formed at high pH. The microflotation data presented in Figure 1a shows that molybdenite flotation is strongly depressed in seawater at $pH > 9$ which correlates with the induction times presented in Figure 3a, which shows higher induction times at alkaline pH in seawater. The induction time data (Figure 3a) show that divalent cations have a stronger effect, with magnesium being the seawater cation that affects these parameters more. The depression of molybdenite flotation in seawater at $pH > 9$ was previously explained by the attachment of the positively charged hydroxo complexes of magnesium to the molybdenite faces, which occurs most probably on the nano-edges of these basal planes [17]. The presence of magnesium precipitates is evidenced in Figure 5. It shows that turbidity increases in seawater at pH 10 compared to freshwater, which is explained by the presence of these colloidal particles dispersed in suspension. At pH 8 turbidity decreases as more coagulation of molybdenite particles takes place.

The results presented in this manuscript show that molybdenite flotation is depressed by kaolinite, an effect which is significantly stronger in seawater. Kaolinite is a clay mineral usually found associated with copper sulfides in porphyry-type deposits [1], and it is a two-layer silicate consisting of alternating layers of silica tetrahedra and octahedral aluminum hydroxide (T–O), which are held tightly together by hydrogen bonding and low isomorphous substitution which explains why kaolinite swelling in water is minor [37]. It was proposed that kaolinite particles have two different surfaces, i.e., the basal silica-like faces, and the alumina-like edges [38–41]. Previous results showed that the silica-like faces are negatively charged at $pH > 4$, and that the alumina-like edges are positively charged at $pH < 6$, and negatively charged at $pH > 8$ [42]. The microflotation results shown in Figure 1a indicate that the depressing effect of kaolinite on molybdenite is more pronounced in seawater. Figure 1b shows that calcium and magnesium ions have the largest depressing effects from pH 9, and that neither sodium nor potassium affects the interactions between kaolinite and molybdenite flotation. These results indicate that, as in the case of chalcopyrite flotation in the presence of kaolinite [12], the depressing effect of kaolinite on molybdenite is strongly enhanced by hydrolyzed species of magnesium which induce heterocoagulation between kaolinite and molybdenite, thus reducing recovery. The microflotation data correlate with the induction time measurements, as these indicate that kaolinite increases the induction time and that calcium and magnesium have a strong effect in the presence of kaolinite (Figure 3b). Monovalent cations increase induction time, but significantly less than divalent cations. The turbidity data presented in Figure 6 also show lower values in seawater, which can be explained by more heterocoagulation between the two minerals. Moreover, the electrophoretic mobility distributions presented in Figures 7 and 8 indicate that when molybdenite and kaolinite are added together, unimodal distributions are obtained, which evidences the occurrence of interactions between the two minerals. All the experimental data validate the hypothesis that kaolinite covers molybdenite and thus its flotation recovery is reduced, and that this depressing effect is improved by magnesium and calcium hydroxo complexes.

The results presented in this work indicate that SHMP has a strong effect on the extent of the interactions between kaolinite and molybdenite in seawater, as well as on the depression of molybdenite in seawater at $pH > 9$. Dispersants are chemical reagents that generate stable suspensions as a result of the increase of repulsive forces existing between the colloidal particles [43]. Polyphosphate-type dispersants such as SHMP have been widely used in the kaolin industry [44,45]. Equation (2) shows the dissociation of the SHMP ($(NaPO_3)_6$) into the $Na_4P_6O_{18}{}^{2-}$ anion, which is the active part of the molecule.

$$(NaPO_3)_6 = Na_4P_6O_{18}{}^{2-} + 2Na^+ \tag{2}$$

Ma [46] studied the interaction of Mg^{2+} and Ca^{2+} ions with kaolinite using SHMP as a dispersant, concluding that this reagent has a complexing capacity on these ions, which was also proposed by Li et al. [47,48] who reported that SHMP has a modifying effect on hydroxo complexes, which is described in Equations (3) and (4).

$$Na_4P_6O_{18}{}^{2-} + Ca^{2+} = CaNa_4P_6O_{18} \tag{3}$$

$$Na_4P_6O_{18}{}^{2-} + Mg^{2+} = MgNa_4P_6O_{18} \tag{4}$$

Consequently, the attachment of the positively charged hydroxo complexes of magnesium and calcium to the molybdenite faces and kaolinite, which improves heterocoagulation between these minerals and reduces molybdenite recovery, should be diminished by SHMP as this reagent changes the surface properties of the colloidal precipitates. Besides, the turbidity results presented in Figure 5 show that the dispersion of molybdenite particles in freshwater is affected by the presence of SHMP, which is an indication that this dispersant also adsorbs onto molybdenite faces. Then, if SHMP adsorbs on molybdenite and on the hydroxo complexes of magnesium and calcium, the repulsive forces between the molybdenum mineral and precipitates increase and molybdenite becomes cleaner and more hydrophobic which explains the increase in recovery as can be seen in Figure 2. This explanation also applies to the flotation of molybdenite in the presence of kaolinite. The induction time data presented in Figure 4 show that SHMP reduces induction time, which correlates with the better molybdenite recoveries and with the turbidity values presented in Figures 5 and 6, which indicate more dispersion in the presence of SHMP. The electrophoretic mobility distributions for molybdenite, and molybdenite in the presence of kaolinite (Figures 7 and 8), show that the addition of SHMP generates a bimodal distribution which is located at more negative values of electrophoretic mobilities which validates the proposed mechanism.

5. Conclusions

The results presented in this work show that kaolinite depresses molybdenite flotation in fresh and seawater, but that this depressing effect is more significant in seawater at $pH > 9$. All the experimental data validate the hypothesis that kaolinite covers molybdenite, reducing its flotation recovery.

The depressing effect of kaolinite on molybdenite flotation in seawater is enhanced by magnesium and calcium hydroxo complexes at $pH > 9$ which indicates that hydrolyzed species of these cations strongly induce heterocoagulation between kaolinite and molybdenite, thus reducing recovery.

The attachment of the positively charged hydroxo complexes of magnesium and calcium to the molybdenite and kaolinite surfaces is diminished by SHMP. This dispersant renders the molybdenite and hydroxo complexes of magnesium and calcium more negatively charged, increasing the repulsive forces; thus, molybdenite becomes more hydrophobic and recovery increases.

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