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Role of calcium and magnesium cations in the interactions between kaolinite and chalcopyrite in seawater

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Abstract: A number of flotation plants around the world have increased the use of seawater due to limited sources of fresh water. The aim of this research work is to study the role that Mg^{2+} and Ca^{2+} ions play in the interactions between kaolinite and chalcopyrite in seawater. In order to achieve this objective, the effect of kaolinite on flotation of chalcopyrite is studied over the pH range from 8 to 11, when flotation is carried out in seawater and in a 0.01M NaCl solution. The influence of calcium, magnesium, sodium, and potassium ions on the extent of depression by kaolinite is evaluated. The micro-flotation results indicate that chalcopyrite is depressed by kaolinite in both 0.01 NaCl solution and seawater. In the 0.01 NaCl solution, the depressing effect of kaolinite decreases as the pH increases from 8 to 11. However, the results obtained using seawater show that the depressing effect of kaolinite is similar to what is observed in a 0.01 NaCl solution only at pH values below 9, but above this pH kaolinite significantly affects the recovery of chalcopyrite. The results from experiments with using solutions containing individual cations show that the depressing action of kaolinite in the presence of Mg^{2+} and Ca^{2+} is more obvious at pH values of 9 and 10, respectively, which correlates with the pH values at which the first hydroxy-complexes of these divalent cations start forming. This seems to indicate that depressing effect of kaolinite on chalcopyrite in seawater may be related to formation of hydrolyzed species of calcium and magnesium. These species can induce heterocoagulation between kaolinite and chalcopyrite. The trends observed in the micro-flotation experiments are in good agreement with the results of the induction time measurements and slime coating tests.

***Keywords**: froth flotation, chalcopyrite, chalcopyrite flotation, clay minerals, kaolinite, seawater, slime coating*

Introduction

One of the main challenges today in the field of mineral processing is the need to process ores containing high levels of phyllosilicates. In case of copper mining, phyllosilicates are commonly present in low grade copper ores. Because of their

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softness, they generate high levels of slimes that affect froth flotation. In particular, clay minerals are the most common phyllosilicates found in copper ores, and kaolinite is quite frequent (Kelm et al., 2013). Kaolinite plate-like particles have two different surfaces generated during particle breakage, i.e., the basal silica-like and the alumina-like edges (Johnson et al., 2000; Laskowski, 2012). The silica-like faces carry a negative charge, while the alumina-like edges display a pH dependent surface charge resulting from protonation/deprotonation of exposed aluminum hydroxyl groups with iep values around 7.0-8.0 (Ran and Melton, 1977). The adverse effect of the presence of clay minerals on the process of flotation of copper sulfide ores has been explained by combination of several phenomena, i.e., slime coatings, coating of bubbles with clay particles, high reagent consumption (reagents uptake), changes in the froth stability and pulp rheology. In particular, slime coating has been proposed to be one of the main mechanisms that negatively affects the efficiency of froth flotation.

Nowadays, the use of seawater to process copper ores by flotation seems to be the only sustainable solution in many zones with limited resources of fresh water (Castro and Laskowski, 2011; Castro et al., 2012). Seawater contains significant amount of different ions (Na^+, K^+, Mg^{2+}, Ca^{2+}, SO_4^{2-}, Cl^-) which could potentially induce heterocoagulation between mineral particles. James and Healy (1972 a, b, c) showed that adsorption of hydrolysable metal ions depend on the pH of their hydrolysis when the substrate is strongly hydrated such as in the case of SiO_2. However, in the case of TiO_2 adsorption responds to differences of electrical charges between the substrate and ions. This is important in the case of kaolinite because the faces of kaolinite particles are usually described as the surfaces that have a silica-like behavior. Adsorption of monovalent cations, and their effect on the zeta potential and yield stress of silica was also studied by Franks (2002). They found that at high pH the least hydrated ions generated the largest yield stresses, which increased in the order $Li^+ < Na^+ < K^+ < Cs^+$. Adsorption of poorly hydrated ions such as K^+ and Cs^+ even generated reversal of the zeta potential at high concentrations, which is in agreement with the adsorption sequence of monovalent cations on the silica surface that was suggested by the Hofmeister series ($Cs^+ > K^+ > Na^+ > Li^+$) with Cs^+ adsorbing in higher amount than Li^+ (Sonnefeld et al., 1995). Raghavan and Hsu (1984) showed that the presence of calcium ions in solution induces heterocoagulation between silica and molybdenite. Liu et al. (2002) showed that calcium enhanced heterocoagulation between montmorillonite and bitumen leading to low bitumen recoveries. Castro et al. (2014) showed that molybdenite flotation can be severely depressed by magnesium hydrolysis products, and that in the case of Ca^{2+} the depressing action could be related to the action of $Ca(OH)^+$. The effect of hydrolyzed species of magnesium and calcium ions on the degree of interactions between clay minerals and chalcopyrite is particularly important in the case of flotation plants that need to process ores containing high levels of clays using seawater as a process water.

The objective of this research work is to evaluate the depressing effect of kaolinite on flotation of chalcopyrite using *i*) 0.01 M NaCl solutions in distilled water, *ii*) solutions containing Ca^{2+}, Mg^{2+}, Na^+, and K^+ at the concentrations at which they appear in seawater, over the pH range from 8 to 11, *iii*) and seawater.

Materials and methods

Samples and reagents

The kaolinite sample was provided by the Clay Minerals Society. According to Chipera and Bish (2001) the mineralogical composition of this sample is 96 % kaolinite, 3% anatase, and 1% of other impurities The measured mean particle size for kaolinite was 8.9 micrometers, with 100 % of the particles below 21 micrometers. According to Kelm and Helle (2005) the measured specific surface area was 180 m^2/g. The chalcopyrite sample was of a high purity and was prepared from the mineralized rock specimens obtained from Ward`s Natural Science Establishment. This sample was prepared by hand-grinding pure crystals of this mineral in a ceramic mortar and pestle to obtain particles in the size range between 63 and 210 micrometers. Further purification was attempted with the use of a magnetic separator to remove some magnetic impurities. Desliming was carried out to remove ultra-fines from the sample. Washing with acetone and distilled water was carried out in order to remove some organic contaminants that could have potentially been incorporated in the sample during the process of handling and preparation. Additionally, in order to keep oxidation at minimum, the samples were stored in a freezer in sealed plastic bags previously purged with nitrogen, at a temperature of about 1 °C following the procedure of Ekmekci and Demirel (1997). The effectiveness of the procedure that was followed to avoid sample oxidation was verified by performing micro-flotation tests at different times over the 6 months experimental program. It was verified that the chalcopyrite flotation was not affected by the sample storage. The XRD chalcopyrite content of the sample was 98.9 % with minor amounts of quartz (0.8%) and pyrite (0.3%). The chemical analysis of the samples showed 34.3% Cu, 30.4% Fe, and 35.2% S.

It is important to point out that the surface properties of sulfide minerals strongly depend on the grinding conditions and these conditions determine, to a large extent, the flotation properties of sulfides (Heyes and Trahar, 1979). The type of grinding media (whether they are made of iron, steel, stainless steel or ceramic) also affects the flotation of sulfide minerals (Bruckard et al., 2011). It is because of this reason that the use of freshly ground ore samples is recommended when working with sulfides. In this work the objective was to study the effect of clay minerals on the flotation of pure chalcopyrite, using 0.01M NaCl solutions and seawater. In our tests the samples were dry crushed and ground, and were stored under nitrogen.

Potassium amyl xanthate (PAX) and methyl isobutyl carbinol (MIBC) were used as a collector and a frother, respectively. Distilled water of electrical conductivity of 21.5 μS/cm was used in all the experiments. pH was adjusted using sodium hydroxide in all the tests.

Procedures

Micro-flotation

Flotation of chalcopyrite was evaluated through micro-flotation tests carried out in a 150 cm^3 Patridge and Smith glass cell using nitrogen (N_2) at a flowrate of 20 cm^3/min. The flotation feed was first prepared mixing 1 gram of chalcopyrite (+63 –210 micrometers) with 150 mg of kaolinite (which gives 13 % of kaolinite in the feed). The solid flotation feed was then mixed with 100 cm^3 of 0.01 M NaCl solutions in distilled water, seawater, and solutions containing Ca^{2+}, Mg^{2+}, Na^+, and K^+ at concentrations of 400, 1300, 11000, and 400 ppm, respectively. The suspensions were then conditioned at the required pH for 3 minutes. These experiments were carried out at values of pH ranging from 8 to 11 (typical pH values in processing copper sulfide ores). After 3 minutes of conditioning, PAX and MIBC were added at concentrations of 40 and 25 ppm, respectively (based on the 150 cm^3 of the micro-flotation cell), and conditioned for 5 minutes more at the previously established value of pH. The additional solution was then added to maintain 150 cm^3 needed in the micro-flotation cell. Finally, the gas valve was opened to start the process of flotation which was carried out for 2 minutes, scraping the froth off every 10 seconds. The pulp level in the micro-flotation cell was kept constant by adding a background solution prepared at the same composition and pH of the original solution. Concentrates and tailings were then wet sieved using a 400 mesh sieve (38 micrometers) to remove the particles of kaolinite, and to measure the amount of chalcopyrite in each stream. Finally, the samples were dried in an oven at 105 °C for 5 hours and the solids flotation yield was calculated dividing the mass of chalcopyrite in the concentrate by the mass of chalcopyrite in concentrate plus in the tailings. All the tests were conducted in triplicates, thus the results presented in this paper are average values, with the largest standard deviation being 2 percentage points.

Induction time measurements

Induction time measurements were conducted using the procedure described by Castro et al. (2014) and the induction time meter built at the University of Alberta. According to this procedure a fresh bubble held on a capillary is pushed downward through a solution so that it contacts the bed of particles for a measured and controlled contact time. The bubble is then lifted upwards to its initial position, and observed through a microscope in order to determine the attachment occurred during the contact time. The process is repeated 10 times at different positions on the particles bed and the number/percentage of successful contacts is determined. Next, the contact time is changed to different values and the procedure is repeated again in each case. The final result of the tests is a plot of percentages of successful contacts (N_{sc}) versus the measured contact time (t_c). In this work, the induction time was obtained by determining the contact time at which 50% of the contacts were successful. The experimental data were fitted using equation:

$$N_{SC} = k_1\left[1 - \exp\left(-k_2 t_C^{K_3}\right)\right] \tag{1}$$

where k_1, k_2 and k_3 are fitting constants.

The beds of particles were prepared by mixing 3 grams of chalcopyrite (+63-210 micrometers) with 30 cm^3 of solution containing 40 ppm of PAX. This was followed by addition of kaolinite at a concentration of 13% (solid base), the pH was adjusted to the required value and the slurry was conditioned for 12 minutes, after which it was transferred to a 15 cm^3 cell in order to start the induction time measurements. It has to be pointed out that no frother was added in these experiments and that air was used to generate the bubbles. All these experiments were conducted in duplicates, thus the results presented in this paper are average values. The procedure that was used was essentially described in Oats et al. (2010).

Heterocoagulation between kaolinite and chalcopyrite

The interaction of kaolinite particles with chalcopyrite particles was evaluated in this work using the methodology explained in Figure 1 and described by Uribe et al. (2016). It is based on the assumption that if heterocoagulation between particles of chalcopyrite and kaolinite takes place, then the sedimenting chalcopyrite particles remove with them fine kaolinite. As a result, turbidity of the suspension in the presence of chalcopyrite, T_2 in Figure 1, decreases respect to the turbidity measured in the absence of chalcopyrite, T_1 in Figure 1. The extent of slime coating can be quantified by comparing the difference between T_1 and T_2. If this number is near zero then it could be concluded that aggregation of kaolinite particles with chalcopyrite is negligible.

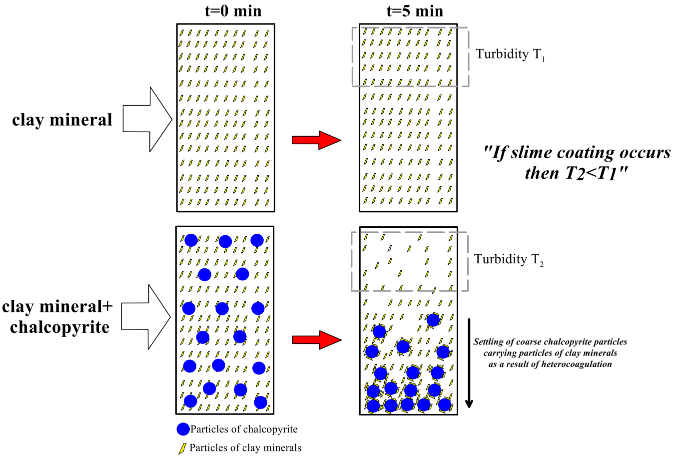

Fig. 1. Schematic of method to assess heterocoagulation between chalcopyrite and kaolinite particles

In this work suspensions were prepared by mixing 0.8 grams of chalcopyrite (+63 –210 micrometers) and 120 mg of kaolinite (13% kaolinite), with 120 cm^3 of solution containing 40 ppm of PAX and 25 ppm of MIBC. After this, they were conditioned for 3 minutes under controlled mixing conditions which was ensured by using the same magnetic stirrer and plate for all the tests. The suspensions were then placed in a 100 cm^3 graduated cylinder where they were left to settle for 5 minutes. After that, a 10 cm^3 suspension aliquot was withdrawn using a syringe from a section positioned at 2/3 the height of the cylinder and tested for turbidity. Turbidity measurements were performed using a portable turbidimeter OrbecoTB200 with the maximum reading of 999 NTU. In order to correlate this information with the flotation data, all these tests were conducted at the same conditions of the micro-flotation experiments.

Results

Micro-flotation

Figure 2A shows the effect of the presence of kaolinite on the recovery of chalcopyrite as a function of pH in 0.01 M NaCl solutions. The results indicate that the depressing effect of kaolinite on the recovery of chalcopyrite decreases as the pH of the suspension increases. Figure 2A also shows the results of experiments that were carried out to evaluate the effect of the presence of fine quartz (particle size similar to kaolinite) on the recovery of chalcopyrite in 0.01 M NaCl solutions. As it can be seen, at a pH of 8 the presence of fine quartz particles has no effect on flotation of chalcopyrite indicating that fine quartz particles do not accumulate on the surface of chalcopyrite under such conditions. Figure 2B shows the micro-flotation data obtained in seawater. It can be seen that in this case the effect of kaolinite is similar to what is observed in 0.01 M NaCl solutions only at $pH < 9$. The trend is totally different when pH is larger than 9. Flotation of chalcopyrite decreases at $pH > 9$ even in the absence of kaolinite but the effect of kaolinite on chalcopyrite flotation is seen at pH of 10. This suggests that the stronger depressing effect of kaolinite observed at $pH > 9$ is related to the formation of hydroxy-complexes of magnesium and calcium.

Additional experiments were performed in order to evaluate the effect of some important seawater cations. Figure 3 shows the depressing effect of kaolinite on flotation of chalcopyrite in solutions containing 11000 ppm Na^+, 400 ppm K^+, 400 ppm Ca^{2+}, and 1300 ppm Mg^{2+}, (approximate concentrations of these cations in seawater). It can be seen that the depressing action of kaolinite on chalcopyrite in the presence of 1300 ppm of Mg^{2+} becomes more pronounced at $pH > 9$. Besides, in the presence of 400 ppm of Ca^{2+} chalcopyrite is strongly depressed at pH values above 10. Both these pH values agree with the values at which the first hydroxy-complexes of magnesium $Mg(OH)^+$ and calcium $Ca(OH)^+$ start forming (Fuerstenau and Palmer, 1976).

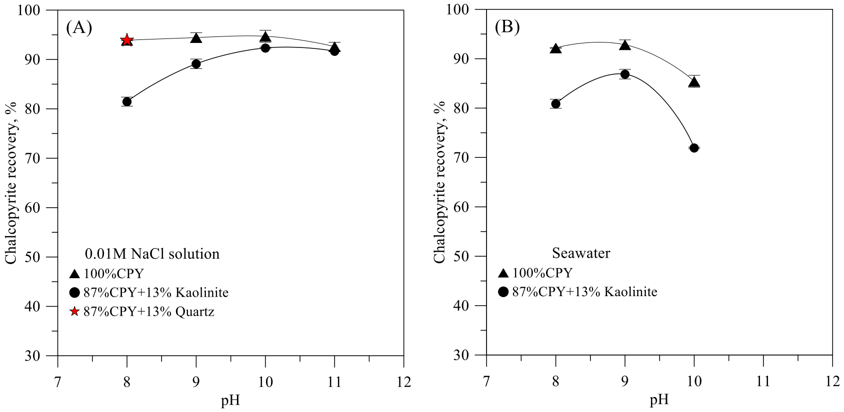

Fig. 2. Effect of the presence of kaolinite on the recovery of chalcopyrite as a function of pH in (A) 0.01 M NaCl solution and (B) seawater. Conditions: 40 ppm PAX, 25 ppm MIBC. CPY denotes chalcopyrite

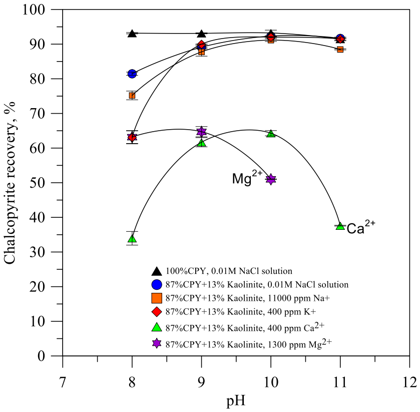

Fig. 3. Effect of the presence of kaolinite on the recovery of chalcopyrite as a function of pH in solutions that contain 11000 ppm Na^+, 400 ppm K^+, 400 ppm Ca^{2+}, and 1300 ppm Mg^{2+}. Conditions: 40 ppm PAX, 25 ppm MIBC

Induction time measurements

Induction time measurements are used in the present work to assess the effect of clays on adhesion of a bubble to a bed of hydrophobic chalcopyrite particles. In these experiments higher values of induction times indicate that the process of adhesion between bubbles and chalcopyrite particles is less effective (and this should correlate with lower recoveries). Figure 4 shows how the presence of kaolinite affects the induction time. In both aqueous media the induction time values are higher in the presence of kaolinite, which is in the agreement with the micro-flotation data presented in Figure 2, and indicates that kaolinite particles hinder the attachment of bubbles to chalcopyrite particles. It is obvious that the induction time is more affected by the presence of kaolinite in seawater (Figure 4B) especially when pH is larger than 9.

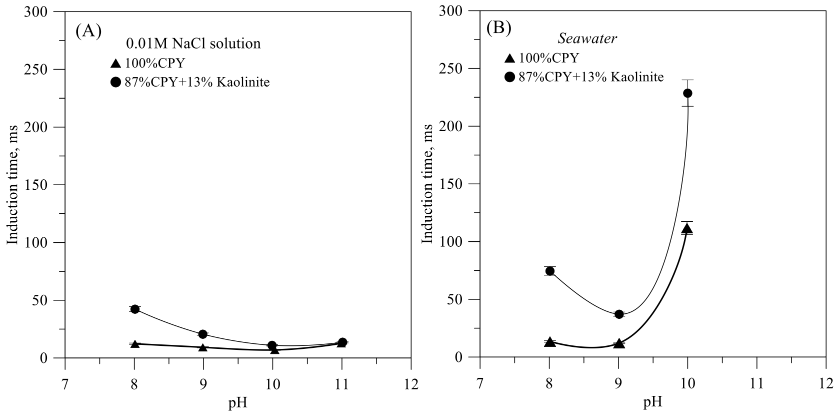

Fig. 4. Effect of the presence of kaolinite on the induction time in (A) 0.01 M NaCl solution and (B) seawater

Experiments were also carried out to assess the effect of cations present in seawater on the induction time, in the presence and absence of kaolinite. The results are shown in Figure 5. While induction times for chalcopyrite in 0.01M NaCl solutions were very short over the whole tested pH range, and the same was observed in the tests with kaolinite when the tests were carried out in solutions containing Na$^+$, ions, the effect of kaolinite was totally different when Mg^{2+} and Ca^{2+} were also present.

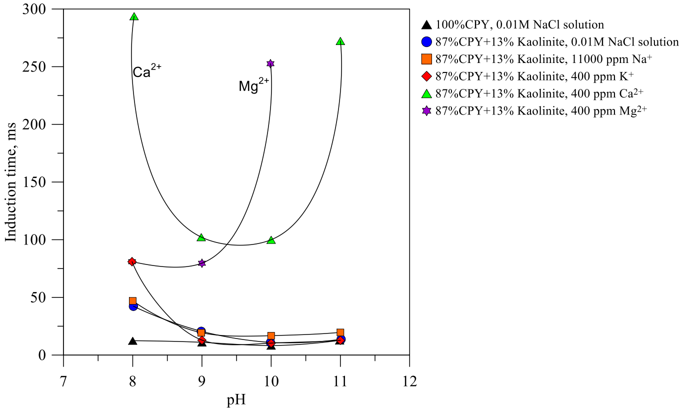

Fig. 5. Effect of the presence of kaolinite on the induction time in solutions that contain 11000 ppm Na$^+$, 400 ppm K$^+$, 400 ppm Ca^{2+}, and 1300 ppm Mg^{2+}

Heterocoagulation between kaolinite and chalcopyrite

Figure 6 indicates a totally different effect of kaolinite on turbidity in diluted NaCl solution and seawater. While in the NaCl solution turbidity increases with pH indicating better clay dispersion, this is not seen in seawater. The curves (Fig. 6B) reveal much lower stability of the kaolinite dispersion, and this is especially strong at pH of 10. Around this pH kaolinite hetero-coagulates with chalcopyrite. Additional turbidity tests were carried out with coarse quartz particles (-210 + 63 micrometers) and kaolinite and the results are plotted in Figure 6B (star). It can be seen that when quartz was used instead of chalcopyrite, the turbidity of the suspensions of kaolinite with and without quartz was the same indicating no heterocoagulation.

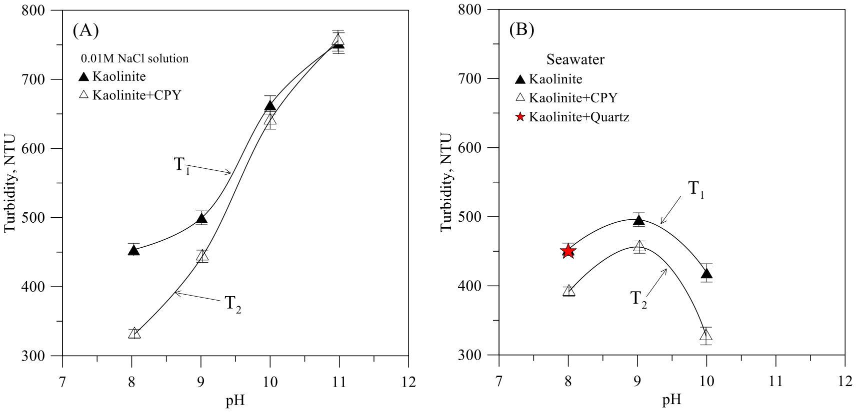

Fig. 6. Turbidity of suspensions of kaolinite, and 13% kaolinite + 87% chalcopyrite prepared with (A) 0.01 M solutions of NaCl and (B) seawater (for definitions of T_1 and T_2 see Figure 1)

Figure 7 presents the results of experiments that were performed to assess kaolinite - chalcopyrite interactions in solutions prepared with ions present in seawater (11000 ppm Na^+, 400 ppm K^+, 400 ppm Ca^{2+}, and 1300 ppm Mg^{2+}). The results indicate that there are no significant differences between the effects of Na^+ and K^+. However, in the cases of Mg^{2+}, and Ca^{2+} the situation is different. Both, Mg^{2+} and Ca^{2+} affect the properties of kaolinite suspension and the kaolinite–chalcopyrite interactions.

Discussion

It is known that Na-kaolinite forms stable dispersions in water. This stability improves with pH when the overall negative charge of the anisotropic kaolinite particles prevails. Addition of hydrolyzing cations like Mg^{2+} and Ca^{2+} destabilizes such systems. Such a destabilization stage was shown to be especially important in flocculation (Wright and Kitchener, 1976; Sworska et al., 2000). The results presented in this paper confirm the special role that multivalent cations play in the clay-containing systems.

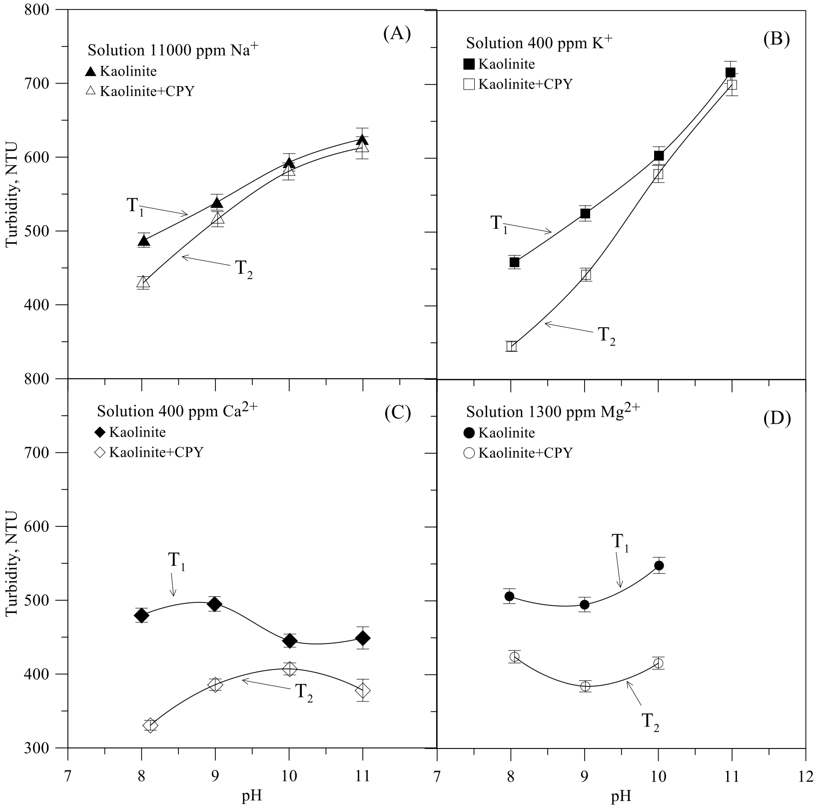

Fig. 7. Turbidity of suspensions of kaolinite, and 13% kaolinite+87%chalcopyrite suspension prepared with solutions containing 11000 ppm Na^+, 400 ppm K^+, 400 ppm Ca^{2+}, and 1300 ppm Mg^{2+}

In the case of inherently hydrophobic minerals, earlier publications coming from CRHIAM Center of University of Concepcion on flotation of Cu-Mo sulfide ores in seawater (Castro and Laskowski, 2011; Castro et al., 2012; Castro et al., 2014) showed that molybdenite flotation is strongly affected in seawater when pH is increased with lime to depress pyrite. This was explained by formation of Mg^{2+} hydrolysis products. The same group recently reported that flotation of molybdenite over the alkaline pH range can be restored using hexametaphosphate (Rebolledo et al., 2016).

In agreement with this line of thinking, in the tested pH range of 8 to 11, the depressing effect of kaolinite on chalcopyrite flotation decreases as the pH increases (Fig. 2A) when a 0.01M NaCl solution is used. However, the depressing effect of kaolinite at high pH values, which is negligible in diluted solutions of NaCl, re-appears again when the tests are carried out in seawater. Destabilization of the kaolinite dispersion in the seawater environment apparently also initiates coagulation of kaolinite onto chalcopyrite and this “slime coating” leads to chalcopyrite depression.

As Figure 3 indicates the depressing action of kaolinite on chalcopyrite using solutions containing 1300 ppm of Mg^{2+} and 400 ppm of Ca^{2+} becomes stronger at pH above 9 and 10, respectively. It is important to note that some tests were also performed to evaluate the effect of cations in the absence of kaolinite, and the results showed that cations alone have no effect on chalcopyrite flotation. This supports the idea that in the studied case it is kaolinite which causes depression of chalcopyrite. The induction time data obtained in seawater presented in Figure 4B are in a good agreement with the micro-flotation results as they show that the induction times sharply increase at pH > 9. The data obtained in the experiments carried out in the solutions of specific seawater cations presented in Figure 5 show that the induction time values sharply increase at pH above 9 and 10 for solutions of Mg^{2+} and Ca^{2+}.

The turbidity of kaolinite suspensions in seawater environment (Figure 6B) show significant differences between the turbidity of kaolinite suspensions (T_1) and kaolinite + chalcopyrite suspensions (T_2) especially at pH > 9. This again implies heterocoagulation between both minerals. Results of the experiments that were conducted in the solutions of seawater cations presented in Figure 7 show that the differences between T_1 and T_2 values are visible in Na^+ and K^+ solutions at low pH values. These effects disappear in the highly alkaline range. The results obtained in the experiments with solutions of Mg^{2+} and Ca^{2+} are quite different. They indicate that kaolinite suspension was destabilized in these tests and that it interacted with chalcopyrite.

Conclusions

The effect of kaolinite on flotation of chalcopyrite at different pH values, and type of water (0.01M NaCl and seawater) was studied. Micro-flotation tests reveal that chalcopyrite is depressed by kaolinite in 0.01M NaCl solution and seawater. In 0.01M NaCl solutions, the depressing effect of kaolinite decreases as pH increases from 8 to 11. In seawater, the depressing effect of kaolinite becomes significantly stronger above pH 9. Experiments that were performed using solutions containing individual cations showed that the depressing action of kaolinite in the presence of Mg^{2+} and Ca^{2+} becomes more profound at pH values of 9 and 10, respectively, which are the pH values at which the first hydroxy-complexes of these divalent cations appear in a solution. Therefore, in seawater the depressing effect of kaolinite on chalcopyrite may be related to the action of hydrolyzed species of magnesium and calcium which could induce heterocoagulation between kaolinite and chalcopyrite. The trends obtained from the micro-flotation tests correlate well with the induction time, and slime coating results. In general, these results agree very well with the conclusions reached by Forbes et al. (2014) that the effect of kaolinite on chalcopyrite flotation increases with decreasing pH. There is however one exception, in the alkaline pH ranges the depressing effect of kaolinite is again high when the tests are carried out in seawater. And this points to the role Mg^{2+} and Ca^{2+} ions play in such systems.

It must be pointed out that these results are perfectly in line with earlier publications coming from Center CRHIAM of University of Concepcion on flotation of Cu-Mo sulfide ores in seawater (Castro and Laskowski, 2011; Castro et al., 2012; Castro et al., 2014). As it was shown in those papers molybdenite flotation is strongly affected in seawater when pH is increased with lime to depress pyrite. Responsible for the depressing effect were shown to be Mg^{2+} and Ca^{2+} hydrolysis products and this agrees remarkably well with main findings of this project that point to the role of hydrolysis products in heterocoagulation of clay particles on the surface of chalcopyrite.

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