

# Sodium hexametaphosphate and sodium silicate as dispersants to reduce the negative effect of kaolinite on the flotation of chalcopyrite in seawater



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## ABSTRACT

The interactions between chalcopyrite and kaolinites of different crystallinity, over the pH range from 7 to 12, are studied. The tests were carried out in seawater, and in a 0.01 M NaCl solution. The effect of the dispersants, sodium hexametaphosphate (SHMP) and sodium silicate (SS) was evaluated. The results show that both tested dispersants are able to restore chalcopyrite flotation in the presence of kaolinite in seawater over the pH range from 7 to 11.

## 1. Introduction

Depletion of major copper deposits forces mining industry to rely more on the ore bodies of progressively lower content of valuable components. Currently more complex and finely disseminated ores are processed in Chile. Low grade ores commonly contain difficult-to-treat gangue such as phyllosilicates and at the same time shortage of water forces industry to process copper ores in seawater. In many parts of the world this is the only sustainable solution (Castro, 2010, 2012; Castro et al., 2012, 2014). Phyllosilicates affect mineral processing in grinding, froth flotation, thickening, dewatering and final disposal stages (Zhao and Peng, 2012). The soft nature of phyllosilicates leads to high levels of ultra-fine particles generated in the grinding stage, which generates highly non-Newtonian slurries. Mechanisms related to slime coating (Uribe et al., 2017, 2016; Zhao and Peng, 2012; Forbes et al., 2014), changes in the rheological pattern increasing slurry viscosity, coating of air bubbles with fine clay particles which reduces the available hydrophobic surface for particle-bubble attachment (Uribe et al., 2016), reagent uptake, and changes in froth stability were proposed to explain the negative effect of phyllosilicates in the process of flotation. However, the behavior of phyllosilicates, and in particular the behavior of clay minerals is still unknown when seawater is used to float copper ores.

Seawater can be treated as 0.6 M NaCl solution with a high content of  $Mg^{2+}$  and  $Ca^{2+}$  ions. In our previous publication on flotation of Cu-Mo sulfide ores in seawater (Uribe et al., 2017), the effect of kaolinite

on flotation of chalcopyrite was studied at different pH values, and in fresh and seawater. The results indicated that in seawater the depressing effect of kaolinite becomes significantly more pronounced 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 harmful at pH values of 9 and 10, respectively, which are the pH values at which the first hydroxy-complexes of these divalent cations appear. It was, therefore, concluded that in seawater the depressing effect of kaolinite on chalcopyrite may be related to the action of the products of hydrolysis of magnesium and calcium. Such species can induce heterocoagulation of kaolinite on chalcopyrite. These conclusions were validated through flotation tests, induction time measurements, and slime coating tests. It is to be pointed out that these results are perfectly in line with previous publications coming from CRHIAM that showed that molybdenite flotation is strongly affected in seawater when pH is raised using lime to depress pyrite, and that responsible for the depressing effect are mostly  $Mg^{2+}$  hydrolysis products. The use of dispersants to disperse precipitating/coagulating hydroxides from the molybdenite surface was tested, and the results were reported in the paper by Rebolledo et al. (2016).

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## 2. Materials and methods

### 2.1. Samples and reagents

Two different samples of kaolinite provided by the Clay Minerals Society were used in this work, i.e., a well crystallized (kaolinite 1) and a less crystallized sample (kaolinite 2). XRD analyses indicated that both samples had more than 97% of kaolinite with minor amounts of anatase, and other impurities. According to the supplier, kaolinite 1 is well crystallized with a cation exchange capacity (cec) of 2.0 meq/100 g and a BET surface area of 10.05 m<sup>2</sup>/g. Kaolinite 2 is a less crystallized kaolinite with a cation exchange capacity (cec) of 3.3 meq/100 g and a BET surface area of 23.5 m<sup>2</sup>/g. The measured mean particle sizes for kaolinites 1 and 2 were 8.9 and 8.5 μm, respectively, with 100% of the particles below 21 and 20 μm, respectively.

The chalcopyrite sample was of a high purity and was prepared from the mineralized rock specimens obtained from Ward's Natural Science Establishment. 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 gave 34.3% Cu, 30.4% Fe, and 35.2% S. For micro-flotation tests, chalcopyrite was prepared by hand-grinding pure crystals in a ceramic mortar and pestle to obtain particles in the size range between 63 and 210 μm. Purification was carried out by using a magnetic separator to remove some magnetic impurities, and by desliming to remove ultra-fines. Washing with acetone and distilled water was carried out in order to remove some organic contaminants that potentially could have been incorporated in the sample during the process of handling and preparation. As an attempt to reduce sample oxidation, chalcopyrite was stored in a freezer in sealed in plastic bags 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 5 months experimental program. It was verified that the chalcopyrite flotation was not affected by the sample storage.

Flotation tests were conducted using an artificial copper ore (1% of Cu) that was prepared by mixing pure chalcopyrite with quartz. This mixture was first crushed in a cone crusher down to a particle size of ~2 mm, and then wet ground before flotation tests to a particle size P<sub>80</sub> = 150 μm, in a laboratory ball mill, using mild steel balls. The sample of coarse quartz used to generate the artificial copper ore was obtained from Wards Natural Science Establishment. XRD indicated that this was a nearly pure quartz sample. Potassium amyl xanthate (PAX) and methyl isobutyl carbinol (MIBC) were used as collector and 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. Sodium hexametaphosphate (SHMP) dispersant was obtained from Sigma Aldrich (97% purity). We used sodium silicate (SS), Na<sub>2</sub>SiO<sub>3</sub>, obtained from Milipore Sigma as sodium silicate extra pure solution (catalog number 105621).

### 2.2. Procedures

Micro-flotation tests were carried out in a 150 cm<sup>3</sup> Patridge and Smith glass cell using nitrogen at a flowrate of 20 cm<sup>3</sup>/min. The flotation feed was prepared mixing 1 g of chalcopyrite (+ 63–210 μm) with 150 mg of kaolinite 1 or 2 (which gives 13% of kaolinite in the feed). The solid flotation feed was then mixed with 100 cm<sup>3</sup> of 0.01 M NaCl solutions in distilled water, or seawater. The suspensions were conditioned at the required pH for 3 min. These experiments were carried out at values of pH ranging from 7 to 12 (representative for the processed copper sulfide ores). Following 3 min of conditioning, PAX and MIBC were added at concentrations of 40 and 25 ppm, respectively (based on the 150 cm<sup>3</sup> of the micro-flotation cell), and conditioned for 5 more minutes at the previously established value of pH. Finally, the gas valve was opened to start the process of flotation which was carried out for

2 min, scraping the froth off every 10 s. 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 μm) to remove the particles of kaolinite, and to measure the amount of chalcopyrite in each stream. Finally, samples were dried in an oven at 105 °C for 5 h and recovery 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 and thus the results presented in this paper are average values, with the largest standard deviation being 1.4 percentage points.

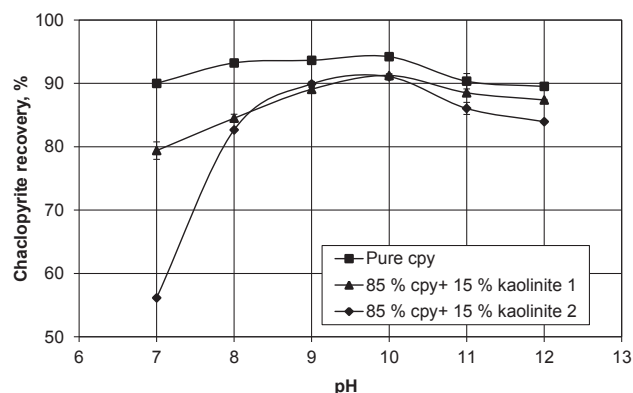
Additional micro-flotation tests were carried out to study the effect of Mg<sup>2+</sup> hydrolysis products on the floatability of chalcopyrite at different redox potential conditions. In these tests 1 g of chalcopyrite was initially conditioned for 20 min in a beaker with 100 cm<sup>3</sup> of solution (with and without 1300 ppm of Mg<sup>2+</sup> as a chloride salt), and at a given redox potential adjusted using hydrogen peroxide or sodium sulfite (Na<sub>2</sub>SO<sub>3</sub>). Once redox conditions reached equilibrium, pH is adjusted to 10.5 and PAX and MIBC are added to obtain concentrations of 40 and 25 ppm, respectively. The suspension was then conditioned for additional 3 min after which micro-flotation tests are performed as described in the preceding paragraph.

The batch flotation tests were carried out in a 2.7 L EDEMET Automated flotation cell. The flotation feed for every test corresponded to the artificial copper ore containing 1% of Cu that was prepared by mixing pure chalcopyrite with quartz, and that was wet ground to a particle size P<sub>80</sub> = 150 μm. Kaolinite 1 was added in replacement of quartz at different percentages of the total mass of artificial ore, i.e., 0, 5, 10 and 15%. 1 kg samples were ground in a laboratory ball mill to a P<sub>80</sub> of 150 μm, and then placed in the flotation cell where the solids content was adjusted to 32% by weight. The pH was adjusted to 10 using lime and the slurry was conditioned for 2 min at 900 rpm with 30 g/t PAX, 20 ppm MIBC. The flotation tests were conducted at an air flowrate of 12 L/min with collection of the concentrate every 10 s over a 10 min period. Concentrates and tailings were analyzed for Cu to determine the recoveries and grades. All the tests were performed in duplicates with an average standard deviation of 0.5 percentage points.

## 3. Results

### 3.1. Micro-flotation results in a 0.01 M NaCl solution

As [Figs. 1–3](#) indicate, over alkaline pH ranges kaolinite does not really affect flotation of chalcopyrite. Depressing effect is clearly visible around pH of 7. Both tested dispersing agents, sodium hexametaphosphate and sodium silicate, restore floatability depressed by kaolinite around pH 7.



**Fig. 1.** Effect of kaolinite 1 and kaolinite 2 on flotation of chalcopyrite in a 0.01 M NaCl solution as a function of pH.

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