

Short communication

The impact of seawater with calcium and magnesium removal for the flotation of copper-molybdenum sulphide ores



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ABSTRACT

The use of seawater in the flotation of copper-molybdenum sulphide ores is becoming increasingly important. However, the complex chemistry by the presence of calcium and magnesium hydroxyl-complexes interferes with the recovery of molybdenite. This study analyzes the impact of pre-treated seawater with calcium and magnesium removal on the floatability of copper-molybdenum sulphide ores. The pretreatment was carried out by a mixture of Na_2CO_3 and CaO , which promotes the precipitation of calcium and magnesium ions. Three different conditions were compared, (i) flotation in seawater at pH 11.5; (ii) flotation in pretreated seawater with calcium and magnesium removal at pH 11.5; and (iii) flotation in seawater at natural pH, i.e. $\text{pH} \approx 7.6$. While the copper recovery was similar in all cases, the recovery of molybdenum at high alkaline condition was notably increased when seawater hardness was reduced. On the other hand, a high pyrite depression was reached because the oxidizing atmosphere at pH 11.5 allows $\text{Fe}(\text{OH})_3$ formation.

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1. Introduction

Regarding the increased scarcity of water that mining companies are facing, the use of seawater in flotation processes is becoming increasingly important (Cisternas and Moreno, 2014), and its efficient use has become one of the challenges for the Chilean mining industry (Cisternas and Gálvez, 2014). The presence of a high saline environment caused by seawater inevitably brought about some adversities, including lower efficiency in flotation stages. However, it has been demonstrated that salinity is not detrimental by itself on flotation operations, but rather it is beneficial for the recovery of some minerals. Lucay et al. (2015) showed that floatability of molybdenite is significantly improved in concentrated NaCl solutions due to ions reduce the electrostatic repulsion between bubbles and the anionic edges of molybdenite. Besides, Troncoso et al. (2014) showed that the contact angle of some minerals might increase with the electrolyte concentration and ions valence. Another positive effect of saline environment is that interfacial air-liquid films may be stabilised by the presence of certain inorganic salts, owing to inhibition of bubble coalescence and the

associated increased gas hold-up in flotation systems (Quinn et al., 2007).

However, Laskowski and Castro (2012) showed that at high pH ($\text{pH} > 10$), the flotation of molybdenite is very sensitive to magnesium hydroxyl-complexes and colloidal magnesium hydroxide. It could be explained because $\text{MgOH}^+(\text{aq})$ adsorbs onto molybdenite surface and then the precipitation of colloidal $\text{Mg}(\text{OH})_2(\text{s})$ may form a hydrophilic coating that reduces its floatability.

Additionally, calcium also has negative impacts on flotation. This might be explained by: gypsum precipitation from calcium ions (Ca^{2+}) and sulphate ions (SO_4^{2-}) on the faces of particles; the contact angle of particles decreases when calcium ions are adsorbed onto the edges and micro-edges of molybdenite; the adsorption of calcium ions on molybdenite and quartz may cause heterocoagulation; and the precipitation of calcium hydroxide at $\text{pH} > 10$ seems to counteract xanthate adsorption, decreasing the mineral hydrophobicity (Lucay et al., 2015; Dávila-Pulido et al., 2015). Thus, it is expected that molybdenite recovery is sensitive to the presence of lime (CaO) which in the flotation of Cu-Mo sulphide ores is commonly used to depress pyrite where the best range has been observed between pH 10–12.

Poor floatability of molybdenite due to calcium and magnesium compound and the increased lime consumption have been claimed

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as the biggest challenges in Cu-Mo sulphide ores flotation in seawater (Castro, 2012) and new methods are required to reach high recoveries of both copper and molybdenum with an appropriated separation of gangue iron sulphides. For a complete review of the use of seawater in flotation see Jeldres et al. (2016) and for a resume of main papers see Supplementary material. In this sense, the aim of this study is to analyze the flotation of Cu-Mo sulphide minerals in seawater with calcium and magnesium removal. Seawater pretreatment is carried out by a mixture of CaO and Na₂CO₃, which promotes Ca and Mg ions precipitation. The main chemical reactions that occur in seawater include the speciation of CO₂, speciation of Mg and Ca, and salts precipitation, which are included in Supplementary material.

2. Methodology

2.1. Materials

Seawater from the coast of Antofagasta (Chile) was used (its composition in Ramos, 2013). The copper-molybdenum sulphide ores were acquired from local mining, where a chemical analysis indicated that the elemental composition was: Cu: 0.55%, Mo: 0.010%, Fe: 4.26%. Oxiqum S.A. (a chemical industry in Antofagasta) provided the reagents, as follow Oxi-2650 (primary xanthate collector, 45 gpt), Oxi-41 (secondary dithiophosphate collector, 22 gpt), and Oxi-92 (frother, 30 gpt).

2.2. Seawater pretreatment: Ca and Mg removal

The seawater pretreatment consists of Ca and Mg ions removal, promoted by the Na₂CO₃ and CaO addition. For this work, 0.05 M of each reagent was used giving a global concentration of 0.1 M. The reagents were poured into seawater and then mixed for 30 min at room temperature. Vacuum filtration separated Mg and Ca ions precipitates and then the filtered seawater was used for the flotation tests. The Ca and Mg concentration was measured by inductively coupled plasma mass spectrometry (ICP-MS).

2.3. Flotation procedure

Ores were ground in a ceramic mill for 11.9 min getting a P₈₀ < 170 μm particle size. The ground samples were transferred into a batch cell and made up to a volume of 2750 ml for each test, giving a 30 wt% flotation pulp density. All reagents were added 5 min before flotation and mixed at a constant rate. Flotation gas was air at a flow rate of 8 L/min. The froth was scraped every 10 s during the test. Adsorption atomic spectroscopy determined the composition of the flotation concentrates.

3. Results and discussion

3.1. Ca and Mg removal

The experiments were carried out by adding two reagents: CaO and Na₂CO₃. Results are shown in Fig. 1, which correspond to the average of duplicate experiments. Also, the standard deviation is incorporated.

Lime (CaO) is a promoter of magnesium precipitation since its concentration in seawater was reduced from 1280 ppm to 10 ppm after applying 0.1 M of CaO, but as it was expected, calcium concentration was vastly increased (Fig. 1a). The precipitation of magnesium happens because lime is an alkalinizing reagent that leads to the formation of calcium and magnesium hydroxides as indicated among possible salt precipitation reactions in Appendix. On the other hand, sodium carbonate (Na₂CO₃) is useful to precipitate calcium, but the reduction of magnesium is conservative (Fig. 1b). This shows that calcium carbonate is more liable to the precipitation than magnesium carbonate. Fig. 1c illustrates the effect of adding CaO-Na₂CO₃ mixtures at different proportions on the removed amount of calcium and magnesium from seawater. For the subsequent flotation testing, it was chosen a combination of both reagents (50–50%), giving a global concentration of 0.1 M. Consequently, it avoids the excess of calcium and magnesium, where their final concentrations were 176 ppm and 190 ppm respectively.

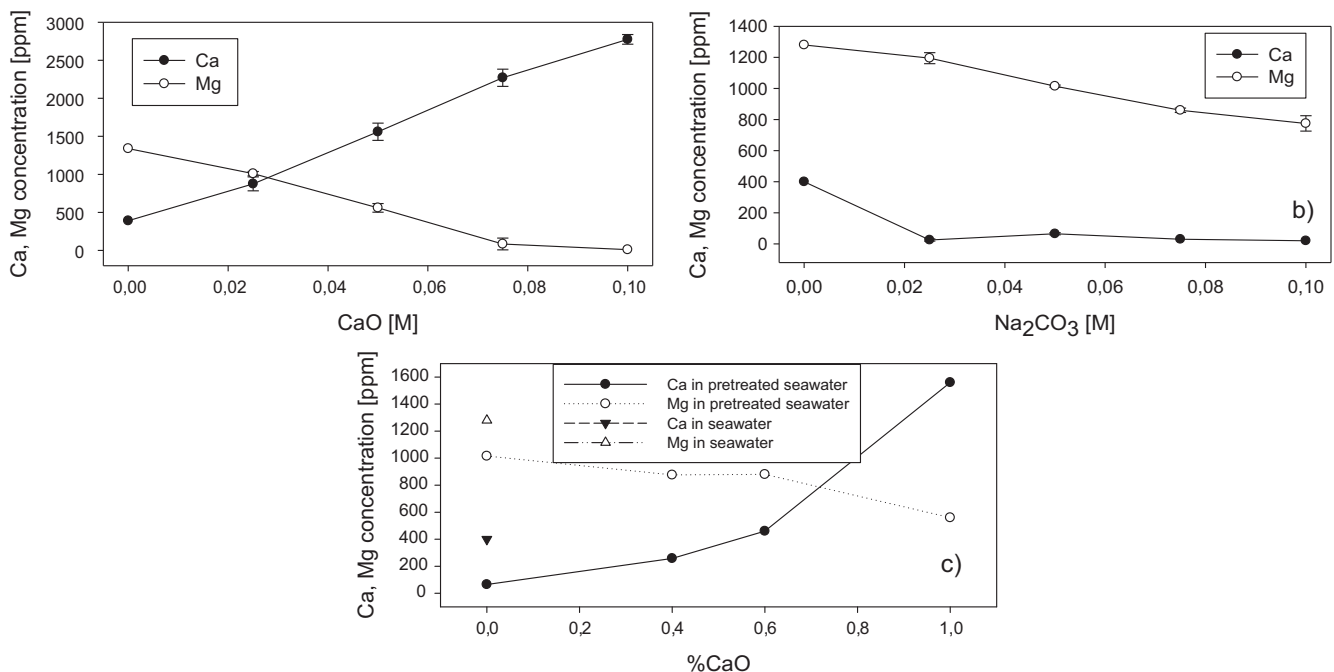


Fig. 1. Impact of different alkalinizing reagents addition on the calcium and magnesium concentration in treated seawater: (a) impact of CaO; (b) impact of Na₂CO₃; (c) impact of CaO/Na₂CO₃ ratio (global concentration: 0.05 M).

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