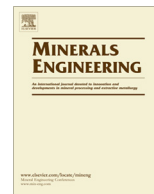




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## Effect of $Mg^{2+}$ and $Ca^{2+}$ as divalent seawater cations on the floatability of molybdenite and chalcopyrite

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### ABSTRACT

Seawater flotation has been applied to mineral processing in areas located far from fresh water resources. However, as seawater has a detrimental effect on molybdenite floatability under alkaline conditions ( $pH > 9.5$ ), its application in the conventional copper and molybdenum (Cu–Mo) flotation circuit is hindered. A fundamental study of the effect of two divalent cations in seawater,  $Mg^{2+}$  and  $Ca^{2+}$ , on the floatability of chalcopyrite and molybdenite is presented in this paper. Floatability tests showed that both  $MgCl_2$  and  $CaCl_2$  solutions depress the floatability of chalcopyrite and molybdenite at pH values higher than 9. Furthermore,  $Mg^{2+}$  exerts a stronger effect than  $Ca^{2+}$  owing to the adsorption of  $Mg(OH)_2$  precipitates on the mineral surfaces, as indicated by dynamic force microscopy images. The floatability of chalcopyrite was significantly depressed compared with that of molybdenite in a  $10^{-2}$  M  $MgCl_2$  aqueous solution at pH 11. This phenomenon is likely due to the adsorption of hydrophilic complexes on the mineral surface, which reduces the surface hydrophobicity. A reversal of the zeta potential of chalcopyrite in  $MgCl_2$  and  $CaCl_2$  solutions at pH 11 and 8, respectively, indicated the adsorption of precipitates onto the surface. In contrast, the zeta potential of molybdenite decreased continuously under the same conditions. The floatability test of chalcopyrite and molybdenite in mixed systems showed that selective separation of both minerals should be possible with the addition of emulsified kerosene to a  $10^{-2}$  M  $MgCl_2$  solution at pH 11. A mechanism is proposed to explain this phenomenon.

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## 1. Introduction

Flotation is a water-intensive process; however, due to the scarcity of fresh water resources, increasing social demand for fresh water access, and stringent regulation of industrial water use, flotation units need to use groundwater, recycled water, or seawater, which have high electrolyte concentrations (Wang and Peng, 2014). Moreover, the use of seawater for flotation is more suitable for mining operations located near the seashore or in areas that lack access to ground and fresh water. However, from an economic perspective, seawater flotation is only feasible if the production output (i.e., concentrate grades and mineral recoveries) is comparable to those of conventional fresh water flotation units.

Flotation is a physicochemical mineral separation process that utilizes the differences in the surface properties of valuable minerals and unwanted gangue minerals (Wills and Napier-Munn, 2006). In froth flotation, bubbles are used to separate hydrophobic mineral particles, as the hydrophobic particles stick to the bubbles, float to the surface, and are recovered as a froth. The main challenges facing the use of seawater in copper–molybdenum sulfide flotation are achieving a high recovery of not only copper but also its valuable by-products (Mo and Au), managing pyrite depression in seawater at lower pH, reducing the excess of lime consumption in seawater, and obtaining a high copper concentrate grade for high-pyrite copper ores (Castro, 2012). Moreover, seawater and saline water are usually considered detrimental for the flotation of copper–molybdenum ores.

However, the presence of some inorganic salts (e.g., KCl, NaCl,  $Na_2SO_4$ ,  $MgCl_2$ ,  $MgSO_4$ , and  $CaCl_2$ ) in solutions and seawater is reported to inhibit bubble coalescence and reduce bubble size, thus improving bubble stability and providing adequate frothing

Abbreviations: DFM, dynamic force microscopy; PAX, potassium amyl xanthate; DTP, sodium diisobutyl dithiophosphate; EK, emulsified kerosene.

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characteristics (Craig et al., 1993a, 1993b; Laskowski et al., 2013; Quinn et al., 2014). For example, the flotation circuit in the Raglan concentrator (Xstrata Nickel) in northern Quebec, Canada, can be operated without the addition of frothers because the high salt content of the process water reduces the bubble size and stabilizes the froth layer (Quinn et al., 2007). Similar results were obtained by Laskowski et al. (2013) and Castro et al. (2013), who showed that fine bubbles can be obtained in seawater, even without the addition of frothers.

Several sulfide minerals are processed in flotation plants using saline water and seawater (Drelich and Miller, 2012; Moreno et al., 2011; Wang and Peng, 2014). Bore water with high ionic strength is used in nickel flotation plants (Mt Keith mine, Leinster mine, and Kambalda nickel concentrator operated by BHP Billiton) in Western Australia. In Chile, the Las Luces concentrator (Las Cenizas Mining Group) employs seawater in a copper-molybdenum plant in Taltal. Furthermore, the Batu Hijau concentrator (Newmont) in Sumbawa Island, Indonesia, utilizes seawater to process a gold-rich porphyry copper ore (chalcopyrite-bornite) (Castro, 2012).

In addition, seawater has been used to separate copper minerals (e.g., chalcopyrite) from molybdenum minerals (e.g., molybdenite) in copper-molybdenum (Cu-Mo) flotation units. Sodium hydrosulfide (NaHS) is employed to depress chalcopyrite in this process, allowing molybdenite to be collected in the froth layer (Moreno et al., 2011). However, NaHS produces toxic hydrogen sulfide gas ( $H_2S$ ) at low pH values. Therefore, safer methods are needed to separate chalcopyrite and molybdenite.

In the absence of chalcopyrite depressants, molybdenite exhibits poor floatability in seawater at high pH values, whereas chalcopyrite recovery is slightly lower under the same conditions (Castro, 2012; Laskowski et al., 2013; Ramos et al., 2013). This behavior limits the application of seawater in conventional Cu-Mo flotation circuits at high pH values. It was suggested that this phenomenon might be caused by the precipitation of  $Mg(OH)_2$  on the bubble surface, which strongly affects bubble-particle interactions. Moreover, the precipitation of  $Mg(OH)_2$  on the molybdenite surface may account for the depression of molybdenite floatability. However, these studies employed ore samples containing various minerals (e.g., chalcopyrite, bornite, chalcocite, pyrite, and molybdenite) and flotation reagents (e.g., collectors and frothers), which, to some extent, may affect mineral floatability and the mechanism involved during the flotation process. In addition, calcium and magnesium ions in seawater can form colloidal hydroxides, carbonates, and sulfates, which can depress some mineral species, such as molybdenite (Castro, 2012). Therefore, a fundamental study of the effect of divalent cations in seawater (e.g.,  $Mg^{2+}$  and  $Ca^{2+}$ ) on the floatability of pure chalcopyrite and molybdenite in the absence of flotation reagents is needed to understand the basic mechanism of this process.

On the other hand, the floatability of molybdenite significantly increases with increasing NaCl concentration due to the effect of inorganic electrolytes on the compression of electrical double layers. Thus, the zeta potentials of the bubbles and particles are reduced, and repulsive interactions are decreased (Lucay et al., 2015). Furthermore, the increase in the floatability of molybdenite was found to be independent of pH above 0.5 M ionic strength. Similar results were obtained by Zhao and Peng (2014), who studied the effect of electrolytes (e.g., NaCl, LiCl, NaF, KCl, and NaI) on the flotation of secondary copper minerals, such as chalcocite, in the presence of clay minerals (e.g., kaolinite). An increase in chalcocite floatability with an increase in the electrolyte concentration was attributed to the electrolytes reducing the electrostatic attraction between kaolinite and chalcocite, thus preventing the coating of kaolinite on the chalcocite surface. Similarly, Raghavan and Hsu (1984) demonstrated that  $CaCl_2$  improves the floatability of molybdenite in the presence of fuel oil as a molybdenite collector by

decreasing the surface potential of the molybdenite. Moreover, Kurniawan et al. (2011) reported that inorganic electrolytes enhance coal flotation performance, depending on the type and concentration of the salts.

The enhancement of mineral floatability may be associated with the effect of salt on destabilizing the hydration layer on the mineral surface and improving the surface hydrophobicity (Wang and Peng, 2014). Troncoso et al. (2014) showed that the contact angle of silica increases with an increase in the concentration of various electrolytes (e.g., NaCl,  $CaCl_2$ , and  $AlCl_3$ ), which indicates that the mineral surface may become more hydrophobic in saline solution. However, the stability of the hydration layer on chalcopyrite and molybdenite surfaces in  $MgCl_2$  solution improves at higher pH values (Suyantara et al., 2016). A bubble-particle interaction study demonstrated that the increase in the hydration layer stability lengthens the bubble-particle induction time in a  $MgCl_2$  aqueous solution at pH 11 owing to the adsorption of  $Mg(OH)_2$  precipitates on the mineral surface, which reduces the surface hydrophobicity.

Seawater contains cations (e.g.,  $Na^+$ ,  $Mg^{2+}$ ,  $Ca^{2+}$ , and  $K^+$ ) and anions (e.g.,  $Cl^-$ ,  $SO_4^{2-}$ ,  $HCO_3^-$ , and  $Br^-$ ), which affect the electric charge at the bubble/aqueous solution and particle/aqueous solution interfaces. The mineral surface charge is affected by the electrolyte type and solution ionic strength or concentration. At constant surface charge density, the surface potential decreases continuously as the electrolyte concentration increases (Israelachvili, 2011). Li and Somasundaran (1991) and Han et al. (2004) showed that the bubble/aqueous solution interface is negatively charged in  $10^{-2}$  M NaCl and  $10^{-2}$  M  $CaCl_2$  solutions at all pH values and positively charged in a  $10^{-2}$  M  $MgCl_2$  solution in the pH range of 9.5–10.5. In addition, Israelachvili (2011) demonstrated that relatively small amounts of divalent ions substantially lower the magnitude of the surface potential. On particle/aqueous interfaces,  $Ca^{2+}$  and  $Mg^{2+}$  ions are reported to increase the magnitude of the original positive surface charge of aged dolomite particles and alter the original negative surface charge of aged calcite particles (Kasha et al., 2015). Moreover, the surface of sulfide minerals (e.g., chalcopyrite, tennantite, and molybdenite) are negatively charged in  $10^{-3}$  M KCl and  $5 \times 10^{-3}$  M  $KNO_3$  solutions in the pH range of 3–10 (Hirajima et al., 2014; Petrus et al., 2012; Raghavan and Hsu, 1984).

In the flotation process, collectors physically adsorb on mineral surfaces and alter the surface hydrophobicity. However, collectors and inorganic ions may compete for adsorption sites on mineral surfaces, affecting the flotation recovery in seawater or electrolyte solutions. This effect can be seen in corundum flotation using sodium dodecyl sulfate as a collector in sodium chloride and sodium sulfate solutions. Fuerstenau and Pradip (2005) demonstrated that corundum depression is greater at higher salt concentrations. On the other hand, an activation effect was observed when sulfate ions were added to a solution containing sodium dodecyl chloride. These results indicate the complexity of the interaction between collectors and electrolyte solutions on a mineral surface. In addition, the presence of inorganic electrolytes might affect the adsorption of collectors on the mineral surface. Wang et al. (2015) showed that the contact angle of sphalerite treated with potassium amyl xanthate (PAX) decreases with increasing NaCl concentration, which indicates a decrease in the adsorption of PAX on the sphalerite surface owing to the competitive adsorption of salt ions. The adsorption mechanism of collectors and inorganic ions on mineral surfaces is driven by the mineral surface charge. Therefore, it is important to understand the mineral surface charge in electrolyte solutions or in the presence of collectors.

In the present work, the effect of divalent cations in seawater ( $Ca^{2+}$  and  $Mg^{2+}$ ) on the flotation of pure molybdenite and chalcopyrite was intensively investigated. The effect of these ions on the zeta potentials of molybdenite and chalcopyrite was also studied.

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