Floatability of molybdenite and chalcopyrite in artificial seawater

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ABSTRACT

Seawater has been reported to depress the floatability of molybdenum in copper-molybdenum (Cu-Mo) flotation circuits under alkaline conditions (pH > 9.5). However, the seawater used in the process contains various minerals and flotation reagents, which make it difficult to investigate the depression mechanism. This paper presents a fundamental study into the effect of artificial seawater as a seawater model solution on the floatability of molybdenite and chalcopyrite, which are the main minerals in the Cu-Mo flotation process. Floatability tests in the absence of flotation reagents (i.e., frothers and collectors) reveal that artificial seawater adversely affects the floatability of molybdenite and chalcopyrite at pH > 9. This phenomenon can be attributed to the adsorption of hydrophilic $Mg(OH)_2$ precipitates formed under alkaline conditions on the mineral surfaces, which increases the surface wettability of the mineral particles, as shown by contact angle measurements and atomic force microscopy (AFM) images. The effect of kerosene as a molybdenite collector has also been investigated to assess its potential in the selective flotation of molybdenite and chalcopyrite in artificial seawater.

1. Introduction

Flotation is a water-intensive process; thus, to minimize the use of freshwater, most mining operations use recycled water, underground water, saline water, or seawater, which contain various inorganic electrolytes (Wang and Peng, 2014). Seawater is used in the Las Luces copper-molybdenum (Cu-Mo) beneficiation plant in Taltal, Chile (Moreno et al., 2011), in which the copper ores are depressed by adding sodium hydrosulfide (NaHS) and molybdenum ores are collected as froth products. Other flotation plants use saline or seawater to process sulfide minerals (Drelich and Miller, 2012; Wang and Peng, 2014), such as the Michilla Project (Antofagasta), Chile, and the KCGM Project (Barrack/Newmont), Australia. The Batu Hijau concentrator (Newmont) in Sumbawa Island, Indonesia (Castro, 2012) also uses seawater to process gold-rich porphyry copper ore. Bore water is used in the nickel flotation plants operated by BHP Billiton in Mt Keith mine, Leinster mine, and Kambalda Nickel Concentrator, Australia.

Flotation units are controlled at an alkaline pH using lime (CaO or $Ca(OH)_2$) because this is cost effective. Moreover, lime can act as a strong depressant for pyrite and arsenopyrite when xanthate collectors are used (Wills and Napier-Munn, 2006) because the hydroxyl and calcium ions form Fe(OH), FeO(OH), $CaSO_4$, and $CaCO_3$ on the mineral particle surfaces. In freshwater, pyrite is traditionally depressed at pH 11.5–12.0 (Castro, 2012). However, in seawater, pyrite should be depressed at a lower pH (pH < 9.5) to avoid the depression of

molybdenum and minimize excessive lime consumption. Alkaline conditions are also beneficial in preventing the generation of toxic hydrogen sulfide gas (H_2S) from the added NaHS.

The typical electrolyte composition of seawater is listed in Table 1 (U. S. Department of Energy, 1994). Seawater exerts a buffering effect, which increases the lime consumption at pH values traditionally used for Cu-Mo flotation in freshwater (Castro, 2012; Jeldres et al., 2015b, 2015a). The buffering effect is caused by the presence of bicarbonate/carbonate ions (HCO_3^-/CO_3^{2-}) and boric acid and borate ions ($B(OH)_3/B(OH)_4^-$) (Pytkowicz and Atlas, 1975). As shown in Table 1, seawater contains secondary ions (i.e., Ca^{2+}, Mg^{2+}, SO_4^{2-}, and CO_3^{2-}), which can form colloidal precipitates. For example, calcium and magnesium ions can form colloidal hydroxides, carbonates, and sulfates based on the following reactions (Castro, 2012; Hirajima et al., 2016; Jeldres et al., 2016):

Speciation of CO_2

$$CO_{2(g)} + H_2O \leftrightarrow H_2CO_{3(aq)} \tag{1}$$

$$H_2CO_{3(aq)} \leftrightarrow HCO_{3(aq)}^- + H_{(aq)}^+ \tag{2}$$

$$HCO_{3(aq)}^- \leftrightarrow CO_{3(aq)}^{2-} + H_{(aq)}^+ \tag{3}$$

Speciation of Mg and Ca

$$Ca_{(aq)}^{2+} + HCO_{3(aq)}^- \leftrightarrow CaHCO_{3(aq)}^+ \tag{4}$$

Table 1
The composition of major chemical species in seawater and artificial seawater.

Species	Seawater (U. S. Department of Energy, 1994), g/L	Artificial seawater, g/L
Cl^-	19.35	17.87
Na^+	10.78	10.01
SO_4^{2-}	2.71	2.64
Mg^{2+}	1.28	1.18
Ca^{2+}	0.41	0.41
K^+	0.40	0.35
HCO_3^-	0.11	0.14
Br^-	0.07	0.06
Total	35.12	32.66

$$Ca^{2+}_{(aq)} + OH^-_{(aq)} \leftrightarrow CaOH^+_{(aq)} \tag{5}$$

$$CaOH^+_{(aq)} + OH^-_{(aq)} \leftrightarrow Ca(OH)_{2(aq)} \tag{6}$$

$$Mg^{2+}_{(aq)} + OH^-_{(aq)} \leftrightarrow MgOH^+_{(aq)} \tag{7}$$

$$Mg^{2+}_{(aq)} + 2OH^-_{(aq)} \leftrightarrow Mg(OH)_{2(aq)} \tag{8}$$

Salt precipitation

$$Mg^{2+}_{(aq)} + 2OH^-_{(aq)} \leftrightarrow Mg(OH)_{2(s)} \tag{9}$$

$$Ca^{2+}_{(aq)} + CO_3^{2-}_{(aq)} \leftrightarrow CaCO_{3(s)} \tag{10}$$

$$Ca^{2+}_{(aq)} + 2OH^-_{(aq)} \leftrightarrow Ca(OH)_{2(s)} \tag{11}$$

$$Ca(OH)_2 + SO_4^{2-}_{(aq)} + 2H_2O \leftrightarrow CaSO_4 \cdot 2H_2O_{(s)} + 2OH^-_{(aq)} \tag{12}$$

$$Ca(OH)_2 + CO_3^{2-}_{(aq)} \leftrightarrow CaCO_{3(s)} + 2OH^-_{(aq)} \tag{13}$$

$$Mg(OH)_2 + SO_4^{2-}_{(aq)} \leftrightarrow MgSO_{4(s)} + 2OH^-_{(aq)} \tag{14}$$

$$Mg(OH)_2 + CO_3^{2-}_{(aq)} \leftrightarrow MgCO_{3(s)} + 2OH^-_{(aq)} \tag{15}$$
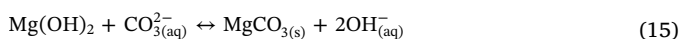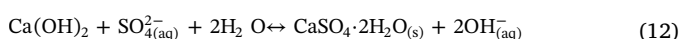
The solubility product constants (K_{sp}) of $Mg(OH)_2$, $Ca(OH)_2$, and $CaCO_3$ are 1.2×10^{-11}, 4.1×10^{-6}, and 6.7×10^{-7}, respectively.

There are several benefits of using electrolyte solutions instead of freshwater in the flotation process. The presence of various inorganic electrolytes (e.g., KCl, NaCl, CaCl₂, MgSO₄, MgCl₂, and Na₂SO₄) in concentrations higher than the critical coalescence concentration (CCC) can inhibit bubble coalescence (Craig et al., 1993a, 1993b; Lessard and Zieminski, 1971; Quinn et al., 2014b) and stabilize the froth layer. Moreover, increasing the electrolyte concentration can reduce bubble size and bubble rise velocity and increase the gas holdup to values comparable to those obtained in the presence of the methyl isobutyl carbinol (MIBC) frother (Quinn et al., 2014a, 2007), which improves the flotation recovery. For these reasons, the flotation circuit in the Raglan concentrator (Xstrata Nickel) in Northern Quebec, Canada, can operate without the addition of frothers because the high electrolyte concentration of the process water provides adequate frothing (Quinn et al., 2007).

Frothers are required to produce fine bubbles in the flotation process. However, Castro et al. (2013, 2010) reported that fine bubbles could be obtained in seawater in the absence of a frother, although smaller bubbles can be produced by the addition of a frother. In addition, the froth layer thickness is more stable in seawater and independent of pH (Laskowski et al., 2013). However, they also reported that the frothability was higher in freshwater, having a maximum froth layer thickness at pH ~ 10.5, than in seawater and that the frothability decreased over the pH range of 9.0–11.5 in electrolyte solutions with high ionic strength (i.e., 0.6 M NaCl solution, seawater, or divalent cations).

Furthermore, the floatability of minerals improved in the presence of inorganic electrolytes and at high electrolyte concentrations. Jeldres

et al. (2016) suggested that seawater might be beneficial for mineral flotation because the effects of slime coatings are reduced. Seawater also improves the floatability of pentlandite, possibly because of the mitigation of slime coating effects caused by the compression of the electrical double layer around both the particles and bubbles. Zhao and Peng (2014) reported that chalcocite floatability increased with increasing concentration of electrolytes (e.g., NaCl, LiCl, NaF, KCl, and NaI) in the presence of kaolinite. This phenomenon is attributed to the reduction of electrostatic attraction between kaolinite and chalcocite, which prevent kaolinite from coating the chalcocite surface in the presence of electrolytes. However, saline waters (brackish water, seawater, and hypersaline water) containing various cations (i.e., Ca^{2+}, K^+, Mg^{2+}, Na^+) depressed chalcocite floatability in the presence of potassium ethyl xanthate (KeX) at pH 8 (Smith et al., 2014). These results indicate the complexity of the effect of electrolyte solutions on the floatability of minerals.

The effect of various electrolytes on mineral floatability has been reported by Uribe et al. (2017). They found that the depressing effect of kaolinite on chalcopyrite floatability decreased with increasing pH, from 8 to 11, in 0.01 M NaCl solution. However, the results obtained using seawater show that the depressing effect of kaolinite is similar to that observed in 0.01 M NaCl solution but at pH values lower than 9; above this pH, kaolinite significantly depressed the recovery of chalcopyrite. This phenomenon may be related to the action of the hydrolyzed magnesium and calcium species in seawater, which could induce heterocoagulation between the kaolinite and chalcopyrite. Indeed, kaolinite strongly depressed chalcopyrite floatability in solutions containing 1300 ppm Mg^{2+} and 400 ppm Ca^{2+}.

The floatability of molybdenite in saline solutions has been investigated by Lucay et al. (2015). They reported that the floatability of molybdenite fines significantly increased with increasing ionic strength of the NaCl solution and is independent of pH when the concentration of the NaCl solution is greater than 0.5 mol/L. This is because of the low electrostatic repulsion between the bubbles and the edges of molybdenite particles, which is exceeded by the interactions arising from van der Waals and hydrophobic forces. Similarly, the floatability of molybdenite increased in an aqueous solution containing Ca^{2+} ions (Raghavan and Hsu, 1984). This improvement may be attributed to the decrease in the electrical double-layer repulsion between the bubbles and the molybdenite particles, which are less negatively charged due to the adsorption of calcium ions. Calcium ions have also been reported to activate sphalerite (ZnS), improving the adsorption of sodium isopropyl xanthate (SIPX) on sphalerite at pH 9, thus increasing its flotation recovery (Dávila-Pulido et al., 2015). They suggested that the sphalerite was activated by the specific adsorption of calcium species (presumably the hydroxo complex CaOH⁺).

On the other hand, there is no consensus on the effect of calcium ions on molybdenite floatability, as listed in Table 2. Nagaraj and Farinato (2014) showed that calcium ions have no effect on copper or molybdenum recovery in the pH range of 9–11. In contrast, Hirajima et al. (2016) reported the depressing effect of Ca^{2+} ions on the natural floatability of molybdenite at pH > 9, which is possibly due to the adsorption of $CaCO_3$ precipitates on the molybdenite surface. However, Qiu et al. (2016) found that crystallized $CaCO_3$ has little effect on molybdenite depression in seawater. A similar detrimental effect of Ca^{2+} on molybdenite floatability was reported by Lucay et al. (2015). They found that Ca^{2+} ions could reduce the natural floatability of molybdenite fines in the presence of various concentrations of sulfate (SO_4^{2-}) ions. According to Lopez-Valdivieso et al. (2012, 2006), the low floatability of molybdenite fines at low concentrations of sulfate ions is caused by the adsorption of Ca^{2+} ions at the molybdenite edges and micro-edges on the faces of molybdenite particles. Moreover, calcium ions can react with sulfate ions forming gypsum ($CaSO_4 \cdot 2H_2O$), which further reduces the floatability of molybdenite (Lucay et al., 2015). These contradictions regarding the effect of calcium ions on the floatability of molybdenite may have emerged because of the different