EFFECT OF SEAWATER MAIN COMPONENTS ON FROTHABILITY IN THE FLOTATION OF Cu-Mo SULFIDE ORE

J.S. LASKOWSKI*, S. CASTRO**, O. RAMOS**

* NB Keevil Institute of Mining Engineering, University of British Columbia, Vancouver, Canada, jsl@mining.ubc.ca
** Department of Metallurgical Engineering, University of Concepcion, Chile

Abstract: The main problem in the flotation of Cu-Mo sulfide ores in seawater is poor floatability of molybdenite at pH>9.5. Froth stability plays a very important role in determining concentrate grade and recovery in flotation operations and in this paper both floatability and frothability have been tested. The frothability have been studied by measuring froth equilibrium layer thickness in a modified laboratory flotation cell. Two chemical aspects of seawater need to be considered: the content of NaCl (around 87% of salinity), and the concentration of secondary ions (around 13%) (sulfate, magnesium, calcium, bicarbonate ions, etc.). Seawater, NaCl solutions, and seawater’s ions were found to depress frothability. The effect of pH on frothability over the pH range from 9.5 to 11, which is very strong in freshwater, becomes negligible in seawater and the tested electrolyte solutions. The analysis of the relationship between the mechanisms of molybdenite depression and the loss of frothability in seawater implies that the effects of the studied ions on molybdenite floatability and on pulp frothability are different. While depression of molybdenite floatability could be tracked down to magnesium hydroxide precipitation as a main culprit, the depression of frothability is a much more complicated issue.

Keywords: seawater, froth stability, Cu-Mo flotation, magnesium ions, molybdenite flotation

Introduction

Many large mineral deposits are located in the areas with limited resources of fresh water. The Atacama Desert, with a major portion of Chilean Copper Industry situated in this area, exemplifies such problems very well. In such cases flotation in seawater becomes an increasingly important issue. However, the use of seawater could become a sustainable solution only if it could deliver the metal recoveries and concentrate grades comparable to those that can be obtained when using freshwater.
Molybdenum recovery plays a very important role in making Cu-Mo processing plants economically viable, and the major problem in the use of seawater in flotation of Cu-Mo sulfide ores results from a poor flotation of molybdenite at pH > 10 (Castro et al., 2012c; Castro, 2012; Laskowski and Castro, 2012). This loss of Mo is particularly obvious when the ore also contains pyrite/pyrrhotite, the minerals which are conventionally depressed with lime at a high pH.

Molybdenite is a mineral with natural hydrophobicity and its anisotropic laminar crystal structure (non-polar faces and polar edges) is similar to that of talc and graphite. Along with graphite, talc, sulfur, and also coal, it belongs to a group of inherently hydrophobic solids. These minerals were shown to float very well in concentrated electrolyte solutions (e.g. 0.5 M NaCl) without any organic flotation agents in the process referred to as salt flotation (Klassen and Mokrousov, 1963; Castro and Laskowski, 2011; Castro and Laskowski, 2012). It is therefore surprising that in the flotation of Cu-Mo sulfide ores in seawater molybdenite is depressed. However, while seawater is a concentrated solution of NaCl (about 0.6 mol/dm$^3$), it also contains some secondary ions (such as, magnesium, calcium, sulfate, bicarbonate, etc.), and precipitating magnesium hydroxide was found to be the major culprit responsible for depressing molybdenite when flotation is carried out in seawater over alkaline pH range (when pH exceeds pH 9.5–10.0) (Castro et al., 2012c; Castro, 2012; Laskowski and Castro, 2012).

Flotation process requires formation of a froth layer that is to some extent stable. Frothing agents prevent bubble coalescence and reduce bubble size (Cho and Laskowski, 2002a; 2002b). It is known that foams are stabilized not only by surface-active compounds (frothers) but also by surface-inactive compounds (inorganic ions) (Quinn et al., 2007; Castro et al., 2010). Foamability of frothing agents in distilled water does not necessarily predict frothability under flotation conditions. Lekki and Laskowski (1975) showed that frothers do not have to be strongly surface active agents. For example, di-acetone alcohol, a commercial flotation frother which was used by the copper industry in Poland, is not a surface active agent but it was performing very well as a frothing agent. While there was no foam when foamability tests were carried out in the presence of this agent in distilled water, the three-phase froth was sufficiently stable. The same phenomenon has been reported for pine oil. While there was no foam when the foamability was tested with pine oil, both in fresh water and in seawater, the presence of hydrophobic particles was found to strongly stabilize the pine oil froth (Castro et al., 2012b). A strong foaming agent does not necessarily produce the most stable froths. Melo and Laskowski (2007) found that DF-1012 frother ($\text{CH}_3(\text{PO})_{6.3}\text{OH}$ where PO stands for propylene oxide group) generated the most stable foams and carried most water, but in the presence of hydrophobic bituminous coal particles produced remarkably less voluminous froth when this frother was utilized. The same phenomenon was observed by Kuan and Finch (2010) who studied the effect of hydrophobic talc particles on the properties of foams in the presence of a polyglycol frother.
Frothing agents are employed in flotation to facilitate air dispersion into fine bubbles and to stabilize the froth. Froth stability depends on the frother type and concentration, but also is a function of other variables, such as particle size, hydrophobicity, solids content, pH, airflow rate, etc. For example, as reported by Tao et al. (2000), coal particles can stabilize or destabilize the froth. This depends both on the size of these particles as well as on their concentration. The -150 µm size fraction destabilized froth at lower concentrations but stabilized it at higher concentrations, while micronized coal particles showed froth-breaking power. Kurniawan et al. (2011) found a correlation between coal recovery and bubble size and claimed that fine coal floats better in electrolyte solutions because finer bubbles are produced in such systems. Zanin et al. (2009) derived models relating the froth stability and bubble size on top of the froth to the amount of hydrophobic material present in the froth. In this work the variables affecting froth stability are extended to electrolyte concentration and ionic composition, particularly to seawater.

Replacement of fresh water with seawater in flotation pulps brings about other factors. Foaming characteristics of MIBC (methyl isobutyl carbinol) and DF-250 (CH₃(PO)₄OH) frothers in NaCl solutions and in seawater have been studied by Castro et al. (2010; 2012a). The two-phase foaming was characterized through measurements of the dynamic foamability index (DFI) for both frothers at various NaCl concentrations, and in seawater. Foamability of both, MIBC and DF-250 frothers, were much stronger in seawater than in distilled water. However, the frothability tests carried out during rougher flotation of Cu-Mo sulfide ores (Castro et al., 2012b) revealed that in the presence of polyglycol frothers (DF-250 and DF-1012) the frothability was much lower when measured in seawater as compared with that in fresh water.

To sum it up, the available evidence indicates that while depression of molybdenite in the flotation of Cu-Mo sulfide ores containing pyrite can be related to the precipitation of magnesium hydroxide, an explanation of the phenomena associated with frothing in the flotation of Cu-Mo ores is still missing.

**Experimental**

**Material and methods**

In our previous tests the samples of Cu-Mo sulfide ores from three different plants in Chile were used (Castro et al., 2012b). The experimental work described in this paper has been carried out with the use of Sample No. 3 (from the previous tests). The sample contained 0.43% Cu, 6.26% Fe and 0.008% Mo.

The laboratory flotation tests have been carried out with the use of the same reagents which are employed at the plant from which the sample was obtained and under the same conditions. The ore sample weight per one test was 1,161 g; impeller speed rate, 900 rpm; 34% solids; and air flow rate, 10 dm³/min. MX-7017 thionocarbamate (26 g/Mg); MX-945 (21 g/Mg); MIBC, methyl isobutyl carbinol (21
g/Mg) were used as reagents. Grinding test: $P_{80} = 150 \mu m$ (20% +150 µm and 60.3% – 75 µm) . The conditioning time was 5 min and flotation time 10 min.

The froth phase was studied by measuring the maximum froth layer thickness in a laboratory flotation cell so modified that it operates without discharge of concentrate. The LA-500 Agitair flotation cell with a volume of 2.7 dm$^3$ was adapted for the frothability tests, as was described elsewhere (Castro et al., 2012b). In these tests air flow rate was 10 dm$^3$/min at 900 rpm (other conditions similar to the flotation tests). The froth thickness was measured during 60 s by using a digital photographic method coupled to image analysis with the ImageJ software. The system was continuously

![Image](image_url)

**Fig. 1.** Measurement of the area occupied by froth with the use of the ImageJ program

![Graph](graph_url)

**Fig. 2.** Kinetics of rougher froth layer thickness growth in fresh water as a function of pH
determining the area occupied by the froth and was converting it to a rectangle; its height was taken as a mean froth layer thickness. The height of the froth in the cell was measured versus time (growth kinetic), and the maximum froth layer thickness was determined at the equilibrium time ($t_\infty$) (Figs. 1 and 2). Examples of the results that can be generated using this technique are shown in Fig. 2.

**Results**

The flotation results in seawater given in Figs. 3 and 4 indicate that molybdenite recovery is sensitive to pH. A strong depression of molybdenite takes place at a pH higher than pH 9.5-10.0, and it was demonstrated that molybdenite is depressed by precipitating colloidal magnesium hydroxide (Castro et al., 2012c).

![Fig. 3. Rougher recovery (Cu, Mo and Fe) as a function of pH in fresh water](image)

Figure 5 shows that the frothability of the flotation pulp in the tests carried out in fresh water is very different from all other tests in other solutions (0.6 M NaCl, 0.6 M NaCl with 1,350 mg/dm$^3$ of Mg$^{2+}$ions, fresh water with 1,350 mg/dm$^3$ of Mg$^{2+}$ions, and seawater). All these cases, different from fresh water, are either concentrated NaCl solutions or contain a divalent cation (Mg$^{2+}$ ions).
Fig. 4. Rougher recovery (Cu, Mo and Fe) as a function of pH in seawater

Fig. 5. Profile of equilibrium froth layer thickness as a function of pH in fresh water, NaCl 0.6M; fresh water-Mg$^{2+}$ 1300 ppm, 0.6M NaCl-Mg$^{2+}$ 1300 ppm, and seawater

As Figure 6 demonstrates, the ionic strength has a strong effect on frothing of the pulp under flotation conditions. Figure 7 shows that the concentration of Mg$^{2+}$ ions in fresh water also strongly affects pulp frothability.
Seawater contains various ions and their effect on frothability is compared in Fig. 8. These tests were carried out in fresh water with addition of some ions that appear in sea water (e.g. $\text{SO}_4^{2-}$, $\text{Mg}^{2+}$, $\text{Ca}^{2+}$) at pH of 10.5.
**Discussion**

**Frothability in seawater**

Inorganic electrolytes and seawater prevent bubble coalescence and decrease bubble size. Figure 9 confirms that without frother (in our tests MIBC) fine bubbles cannot be produced in fresh water. It is totally different in seawater where fine bubbles can be obtained even without the frother (Castro et al., 2010).

![Diagram](image_url)  
**Fig. 8. Froth layer thickness as a function of Ca$^{2+}$, Mg$^{2+}$ and SO$_4^{2-}$ ions concentration in fresh water at pH 10.5**

![Diagram](image_url)  
**Fig. 9. Effect of seawater and MIBC frother on bubble size (Castro et al., 2010)**
While critical coalescence concentration CCC values reported for MIBC frother are in the range of a few ppm (about 11 ppm that is 0.1 mmole/dm\(^3\)) (Laskowski et al., 2003), for NaCl solutions CCC was measured at 0.78 mole/dm\(^3\) (Castro et al., 2012a). That means that when frother concentration is greater than CCC both in frother solutions and in electrolyte solutions bubbles do not coalesce. In seawater, bubbles are quite stable and frother is not needed to stabilize them further. In both cases what is stabilizing bubbles are water molecules bound to the bubbles. In the case of frothers, which molecules adsorb at the gas/liquid interface, some amount of water is bound to the bubbles by hydrogen bonding to the adsorbed frother molecules. In the case of electrolytes, the water layer is formed around bubbles since inorganic ions are surface-inactive, they increase water surface tension because they are expelled from the surface layer. Thus, in both cases different is only the mechanism by which water molecules accumulate around the bubbles.

**The effect of magnesium ions on air bubbles**

The results reported in this paper also indicate that frothability in fresh water is highly influenced by pH and shows a peak around pH 10.5. However this strong effect of pH is not observed in the frothability tests in seawater (or in general, in electrolyte solutions).

In flotation of Cu-Mo sulfide ores, lime is commonly applied to depress pyrite/pyrrhotite. The best pH range for pyrite depression is between 10 and 12, and over this pH range, when the flotation process is carried out in seawater, magnesium hydroxide precipitates. As Figure 10 shows, magnesium hydroxide may start precipitating around pH 9.5 as the process depends not only on pH but also on initial Mg\(^{2+}\) concentration (Li and Somasundaran, 1991). It is not yet possible to clarify whether molybdenite depression is just caused by a precipitating hydroxide (which happened to be magnesium hydroxide), or whether this phenomenon results from the ability of Mg(OH)\(^+\) ions and/or colloidal Mg(OH)\(_2\)(s) to accumulate on the surface of bubbles.

Eigeles and his co-workers (Eigeles and Volvenkova, 1963; Eigeles and Volova, 1964; 1968) studied in the 60’s the effect of colloidal species accumulated on the surface of bubbles on flotation. They pointed out that adsorption on solid particles, which are in general heterogeneous, does not lead to an even distribution of the adsorbed surfactant on the solid surface but creates islands, and this does not necessarily affect flotation. On the other hand, accumulation of such species on the surface of bubbles always affects flotation, and translates into a strong depression when these species are hydrophilic.

The zeta potential measurements on air bubbles indicate that the iso-electric point of bubbles is around pH 2–4 (Li and Somasundaran, 1992; Yang et al., 2001; Oliveira and Rubio, 2011), and, practically, is not affected by the adsorption of flotation frothers (Elmahdy et al., 2008). Bubbles in alkaline pH are negatively charged in
Figure 10. Magnesium species distribution as a function of pH at $1 \times 10^{-2}$ mol/dm$^3$ (1) and $1 \times 10^{-5}$ mol/dm$^3$ (2) MgCl$_2$ solutions (Li and Somasundaran, 1991, with the permission of Elsevier)

water and in NaCl solutions. However, in the presence of hydrolysable divalent cations the zeta-potential may, depending on pH, reverse its sign. Li and Somasundaran (1992) showed that the electrical charge change from negative to positive takes place when Mg$^{2+}$ ions are present in the system in the pH range from 9 to 11. This was explained by coating of the bubbles by precipitating Mg(OH)$_2$(s). Han et al (2004) confirmed a very high affinity of Mg(OH)$^+$ and Mg(OH)$_2$(s) to bubble surface. It is therefore quite likely that the highly depressing effect of precipitating Mg(OH)$_2$ on molybdenite flotation results from the fact that these species tend to accumulate on air bubbles and the fact that such bubbles are positively charged may also play an important role.

The effect of ions present in the pulp

Inorganic electrolytes inhibit bubble coalescence and increase foamability (Castro et al., 2010). However, frothability, that is the stability of a three-phase froth, the system which may contain quite different solid particles, may behave differently. As Figure 8 shows, at pH of 10.5, the froth height decreases in 0.6 M NaCl solutions, and in fresh water containing SO$_4^{2-}$, Mg$^{2+}$ and Ca$^{2+}$ ions up to the concentration similar to those in seawater (400 ppm in the case of Ca$^{2+}$ ions, 1300 ppm for Mg$^{2+}$ ions, and 2700 ppm for SO$_4^{2-}$ ions).

In our study the depressing effect of Ca$^{2+}$ ions in fresh water on frothability was higher than the effect of Mg$^{2+}$ ions. This is completely different to what takes place in molybdenite depression by the same ions, were the effect of Mg$^{2+}$ ions is stronger than
that of Ca$^{2+}$ ions (Castro et al., 2012c; Laskowski and Castro, 2012). The surface precipitation and/or hetero-coagulation of colloidal Mg(OH)$_{2(s)}$ has been suggested as the main depression mechanism. Because magnesium hydroxide is much less soluble than calcium hydroxide, whenever lime is added to seawater (to depress pyrite) and pH exceeds 9.5–10.0 magnesium hydroxide starts precipitating (Castro et al., 2012c).

On the other hand, the depressing effect of Ca$^{2+}$ ions on frothability produced in fresh water at pH 10.5 takes place before the precipitation of Ca(OH)$_{2(s)}$, and when zeta potential of bubbles is negative (Yang et al., 2001; Han et al., 2004). Mg$^{2+}$ ions are able to reduce frothability at pH 9 (Fig. 5), i.e., below the critical pH of precipitation of colloidal Mg(OH)$_{2(s)}$ (around pH 10). Apparently, the adsorption of the hydroxylated species, Ca(OH)$^+$ and Mg(OH)$^+$, on air bubbles, which concentration is predominant before the hydroxide precipitation, may be involved in the loss of frothability.

Of particular note, not only hydrolysing divalent cations showed a deleterious effect on frothability. Electrolytes, such as NaCl also reduce frothability (Figs. 6 and 8). It must be noted that, with the exception of fresh water, in all other cases the frothability was practically independent on pH, contrarily to molybdenite depression which takes place at the critical pH of magnesium hydroxide precipitation. Therefore, the inhibition of frothability (by secondary seawater’s ions and NaCl solution), and molybdenite depression, seem to be quite independent phenomena. Depression of the frothability in NaCl solutions takes place at NaCl concentration of about 0.3 M NaCl (Fig. 6), in the solutions containing Mg$^{2+}$ ions similar effect is observed at a concentration of about 0.05 M, while for Ca$^{2+}$ this was observed at around 0.01 M. The fact that much higher concentrations were needed in case of NaCl than in the case of divalent cations of Mg$^{2+}$ and Ca$^{2+}$ may as well indicate that the phenomena discussed here result from coagulation of solid particles.

In general, it can be concluded that while we were able to demonstrate that poor floatability of molybdenite in seawater can be tracked down to the precipitation of magnesium hydroxide when pH is raised above 10 (to depress pyrite), the situation with frothability in such systems is a much more complicated issue.

Conclusions

In the lab flotation tests with Cu-Mo sulfide ore the froth layer thickness (frothability) was measured and compared with Cu and Mo recoveries. The tested parameters included pH, fresh and seawater, and 0.6 M NaCl solutions with addition of various ions that appear in seawater. Several conclusions are evident from the data:

- Frothability in fresh water was higher than in seawater, and it shows a maximum froth layer thickness around pH 10.5.
- In all cases in which either ionic strength of the pulp was high (0.6 M NaCl solution, sea water) or divalent cations (e.g. Mg$^{2+}$) were present in fresh water, the
frothability was depressed over the 9 to 11.5 pH range, that is over the range over which the frothability in fresh water was very high.

- The loss of frothability was observed whenever the prepared aqueous solutions contained the main components of seawater: NaCl or ions such as Mg$^{2+}$, Ca$^{2+}$ and SO$_4^{2-}$ at concentrations similar to those in seawater.
- The obtained results imply that while the effects detected when studying frothability result from the phenomena driven by coagulation, the molybdenite depression by Mg$^{2+}$ ions takes place only above the critical pH of Mg(OH)$_2(s)$ precipitation.
- The results suggest that in flotation of Cu-Mo sulfide ores, the effect of seawater’s ions on molybdenite depression is very different from the role these ions play in stabilizing the froth.

References


