Copper–molybdenum ores flotation in sea water: Floatability and frothability

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A B S T R A C T

Laboratory rougher flotation tests were conducted with two samples of Cu–Mo ores in fresh water and in sea water as a function of pH. In both cases Cu recoveries were slightly lower in sea water than in fresh water for a wide range of pH (pH 7–12). Flotation of molybdenite was however strongly depressed in sea water at pH higher than 9.5. Frothers were characterized by measuring froth thickness in a modified laboratory flotation cell as a function of pH, salinity, frother type, and solids content (%). It was found that for all tested frothers, foamability in two-phase systems was better in sea water than in fresh water. However, froth layer thickness measurement showed that frothability also depends on solids content and increases with increasing pulp density. At high solids content (35%) the frothability depended strongly on pH. At pH of 9 it was similar for fresh water and sea water, however, once the pH is raised further frothability increases sharply when the tests are carried out in fresh water, but this was not observed in sea water. The froth in sea water is drier than in fresh water, and this probably also depends on solids content.

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1. Introduction

Cu and Mo recoveries are lower when Cu–Mo sulfide ores are floated in sea water (Castro et al., 2012b). The high salinity of sea water seems to be the main responsible factor. Also frothability of flotation pulps is affected by the presence of inorganic electrolytes and this raises the question whether sea water requires different flotation conditions, or whether new criteria for selection of frothing agents are needed (Castro et al., 2012a). In this paper relationships between Cu and Mo recovery and pulp frothability in rougher flotation both in fresh water and sea water are considered.

Mineral flotation requires formation of a froth layer that is to some extent stable. Frothing agents prevent bubble coalescence and reduce bubble size. It is known that foams are stabilized not only by surface-active compounds (e.g. frothers) but also by surface-inactive compounds (e.g. inorganic ions) (Quinn et al., 2007; Castro et al., 2010). Foamability of frothing agents in distilled water does not necessarily predict froth stability under flotation conditions. Lekki and Laskowski (1975) have shown that frothers do not have to be strongly surface active agents. For example, they reported that di-acetone alcohol, a commercial flotation frother which was used by the copper industry in Poland, was 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 froamability was tested with pine oil, both in fresh water and in sea water, the presence of hydrophobic particles was found to strongly stabilize the pine oil froth (Castro et al., 2012a).

The reverse criterion is also valid, i.e., strong foaming agents do not necessarily produce the most stable froths. Melo and Laskowski (2007) reported for DF-1012 that while the froths generated with the use of this frother were the most stable and carried most water, the froth studied in the presence of hydrophobic bituminous coal particles was remarkably less voluminous 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 froth. Froth stability depends on the frother type and concentration, but also is a function of other variables, such as particle size, hydrophobicity, solids per cent, pH, and airflow rate. 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 –100 mesh size fraction (−150 μm) destabilized froth at lower concentrations but stabilized it at higher concentrations, while micronized coal particles showed froth-breaking power. In
this work the variables affecting froth stability are extended to electrolyte concentration, particularly to sea water.

Dynamic froth stability – which has been further explored in this paper – has been the subject of several investigations. Barbian et al. (2003) reported that the equilibrium height and the dynamic stability factor\(^1\) increase when airflow rate and frother concentration increase. Aktas et al. (2008) reported that the dynamic froth stability strongly depends on particle size, showing that finer particles increased froth height.

To study the effect of frothing agents, solids content, pH and type of water (sea water or fresh water) particle size, hydrophobicity (type and dosage of collectors), airflow rate, impeller speed, etc., were maintained constant. While the primary objectives were to study frothing phenomena with different frothing agents, pH and pulp densities, the relationship between frothing and Cu and Mo recovery has also been looked into.

2. Experimental material and methods

In this work rougher flotation tests were conducted with two copper ores at laboratory flotation scale under standard industrial conditions, and Cu and Mo recoveries were calculated as a function of pH with sea water and tap water. Subsequently, frothing experiments were conducted with the same copper ores and flotation conditions, modifying the flotation cell and applying a digital photographic method coupled to image analysis. Froth layer thickness and mass of water transferred to the froth volume were measured as a function of pH and solids content, with sea water and fresh water.

2.1. Materials

2.1.1. Samples tested

Two chalcopyritic Cu–Mo ore samples were tested, which were obtained from two different Chilean copper mines. The chemical assay for both samples is given in Table 1.

2.1.2. Flotation reagents

Sample A: The following flotation reagents were used. Collectors: Matcol TC-123 (22 g/ton) (isopropyl ethyl thionocarbamate) (Mathiesen); Sascol-95 (11 g/ton) (n-butanol and pentanol isomers) (Hitech Chemicals); Diesel (10 g/ton). Frother: Matfroth-355 (10 g/ton) (blend of polyglycols-alkyl alcohols). Sample B: The following flotation reagents were used. Cytec’s collectors: Aero MX-7017 (26 g/ton) and Aero MX-945 (21 g/ton) (modified thionocarbamates). Frother: MIBC (21 g/ton).

2.1.3. Frothing gents

Methyl isobutyl carbinol (MIBC), DF-250, and Matfroth-355 were commercial products provided by Cytec-Chile, Moly-Cop Chile S.A., and Mathiesen S.A.C., respectively.

A local sample of sea water (with a salinity of 3.35%) from near Concepción City was employed. Fresh water was local tap water, and pH in flotation and frothing tests was adjusted with the use of lime.

1 The dynamic stability factor represents the lifetime of a bubble in the froth, and is defined as the ratio of the total volume of froth at equilibrium to the volumetric gas rate introduced into the system (Bikerman, 1973). The dynamic stability factor \((\Sigma)\) is expressed as \(\Sigma = \frac{V_f}{Q} = \frac{V_{max}}{Q}\) where \(V_f\) is the foam volume, \(Q\) is the gas volumetric flowrate and \(V_{max}\) and \(A\) are the total foam height and the cross-sectional area of the vessel.

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### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu (%)</th>
<th>Mo (%)</th>
<th>Fe (%)</th>
<th>Moisture (%)</th>
<th>Specific gravity (g/cm(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.56</td>
<td>0.017</td>
<td>5.76</td>
<td>2.60</td>
<td>2.60</td>
</tr>
<tr>
<td>B</td>
<td>0.43</td>
<td>0.008</td>
<td>6.26</td>
<td>1.31</td>
<td>2.60</td>
</tr>
</tbody>
</table>

2.2. Methods

2.2.1. Flotation tests

These tests were carried out in a 3 L Agitair LA-500 laboratory mechanically agitated flotation cell, at 900 rpm and airflow rate of 10 L/min.

2.2.2. Experimental conditions

- **Sample A**: feed particle size \(P_{50} = 210 \mu m\) (29% +100 Tyler mesh); conditioning time = 5 min, and rougher flotation time = 7 min.
- **Sample B**: feed particle size \(P_{50} = 150 \mu m\) (20% +100 Tyler mesh); conditioning time = 5 min, and rougher flotation of time = 10 min.

2.2.3. Froth layer thickness measurements

These measurements were carried out in the same but modified flotation cell without discharge of concentrate, as was described elsewhere (Castro et al., 2012a).

3. Results

3.1. Rougher flotation tests

Figs. 1 and 2 show flotation results obtained with two different chalcopyritic Cu–Mo ore samples floated in fresh water and sea water. Molybdenite flotation in sea water was depressed in alkaline solutions when pH was higher than 9.0–9.5. At the same time, Cu recovery was only slightly reduced and was not significantly affected by pH. As was previously discussed (Castro et al., 2012a; Laskowski and Castro, 2012) in sea water, that is, in around 0.6 solution of NaCl containing around 1,300 ppm Mg\(^{2+}\) ions, magnesium hydroxy-complexes (\(\text{Mg(OH)}_2^{2+}\)) and colloidal magnesium hydroxide precipitate (\(\text{Mg(OH)}_2(s)\)). The molybdenite depression seems to result from the adsorption of such Mg species on the surface of molybdenite particles.

3.2. Frothing measurements

As Figs. 3 and 5 demonstrate (Sample A and B), at pH > 9 the froth layer thickness measurements under rougher flotation conditions, modifying the flotation cell and applying a digital photographic method coupled to image analysis. Froth layer thickness and mass of water transferred to the froth volume were measured as a function of pH and solids content, with sea water and fresh water.

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![Fig. 1. Cu and Mo rougher flotation recovery at laboratory scale in fresh water and sea water as a function of pH (35% solids content, Sample A).](image-url)
conditions, are clearly lower when measured in sea water than in fresh water. Also the amount of water transferred to the froth is lower in sea water (Figs. 4 and 6). All these measurements were carried out at 34–35% pulp densities. At pH < 9 frothability is low, but the frothability in sea water is similar to that in fresh water. In fresh water a strong effect of pH is observed and the froth layer thickness increases up to a maximum at around pH of 10.5.
If profiles of Cu and Mo recovery (Figs. 1 and 2) are compared with the froth layer thickness (Figs. 3 and 5) as a function of pH no relationship is observed. It is likely that pH 10.5, usually employed in rougher flotation circuits operating with process water, is selected because of the higher frothability at this pH.

Figs. 7–9 show the effect of solids content (ore Sample A) on the froth layer thickness in rougher flotation experiments. These tests were carried out with three frothers: Matfroth-355, DF-250 and MIBC. Similar tests but with the ore Sample B are shown in Fig. 10 (with DF-250) and Fig. 11 (with MIBC).

Results for Sample A, in absence of solid particles, show that the foamability in sea water is higher than in fresh water, particularly for polyglycol frothers. If pulp density is slightly increased, the foam collapse is observed with DF-250 and Matfroth-355. This phenomenon characterizes the foam-to-froth transition in sea water. However, at higher pulp densities froth is stabilized as solids content increases. The froth layer thickness profile shown in Figs. 3 and 5 corresponds to 34% and 35% solids content, where the frothability of pulps in sea water is lower than in fresh water. However, at more diluted pulp densities (below 25–30%) this behavior reverses and the frothability in sea water is similar or higher than in fresh water, particularly with DF-250 and Matfroth-355 (polyglycol type frothers). This behavior is of great interest and it extends our results to the frothing phenomena in cleaner and scavenger circuits, which are usually operated at lower solids content. A similar trend was observed with Sample B, as shown in Figs. 10 and 11.

4. Discussion

As Figs. 1 and 2 demonstrate flotation of molybdenite is clearly depressed in sea water when pH is higher than 9.5. In the first stage of processing Cu–Mo ores, in which Cu–Mo bulk concentrate is produced, commonly lime is used to depress pyrite, and it has been well established that any excess of calcium depresses flotation of molybdenite. In this system hydrolyzing ions play a very important role. When flotation is carried out in sea water the use of lime results in precipitation of magnesium hydroxide which is much less soluble than calcium hydroxide. This has been shown to be the main reason for poor flotation of molybdenite in sea water in alkaline environment (Castro et al., 2012b). NaCl concentration in sea water is about 0.6 M but it is not the high ionic strength of sea water but the presence of secondary ions (such as Mg²⁺ and Ca²⁺) that depresses flotation when pH is raised above 9.5 (Laskowski and Castro, 2012).

Other important factor to be considered is the charge of bubbles, particularly when cationic hydroxy-complexes are formed in the system. Chin and Somasundaran (1991) have shown that magnesium hydroxy-complexes and magnesium hydroxide are characterized by a very high affinity towards the liquid/gas inter-
face. Their adsorption makes bubbles positively charged. This has been entirely confirmed by Han et al. (2004). Eigeles and Volova (1968) results leave no doubt that any precipitates accumulating on the surface of bubbles affect very strongly the flotation process. As Figs. 4 and 6 shows when pH of sea water is raised above 9.5 both frothability in the rougher flotation and the mass of water carried out by the froth are affected. These indices are higher in fresh water in which there is no precipitating colloidal magnesium hydroxide and the ionic strength is lower.

Frothability is different from foamability as it is also affected by the presence of solid particles. In this paper we did not investigate pure minerals, two samples of Cu–Mo ores were used in our tests. Such samples contain only limited amounts of valuable components (Cu sulfides and molybdenite), some other hydrophobic particles (e.g. pyrite), but the majority of the particles are hydrophilic gangues. These tests then show how mostly hydrophilic particles affect frothability. As Figs. 7–11 indicate, in general, frothability increases with increasing solids content. Such gangue particles are present in the froth mainly by an entrainment mechanism. When magnesium hydroxy-complexes and colloidal magnesium hydroxide are present in bulk solution, bubbles are positively charged by adsorption of these magnesium species. This system is then likely to be very different from other flotation systems. Tao et al. (2000) reported that (hydrophobic) coal particles are positively charged by adsorption of these magnesium species. These tests then show how mostly hydrophilic particles affect frothability. As Figs. 7–11 indicate, in general, frothability increases with increasing solids content. Such gangue particles are present in the froth mainly by an entrainment mechanism. When magnesium hydroxy-complexes and colloidal magnesium hydroxide are present in bulk solution, bubbles are positively charged by adsorption of these magnesium species. This system is then likely to be very different from other flotation systems. Tao et al. (2000) reported that (hydrophobic) coal particles are positively charged by adsorption of these magnesium species.

5. Conclusions

Several conclusions are evident from the discussed data:

- The most important variable in the flotation of Cu–Mo ores in sea water is pH.
- For chalcopyritic ores Cu recovery is slightly lower in sea water than in fresh water under similar conditions over the pH range from 7 to 12.
- Mo recovery in sea water is strongly depressed at pH higher than 9.5, the conditions under which magnesium hydroxide start precipitating in sea water.
- Foamability of flotation frothers is higher in sea water than in fresh water, but it changes in the presence of solid particles. However the frothability increase with solids content is negligible over the solids concentration range up to 20%.
- At higher solids per cent (>30%) more voluminous froth is generated in fresh water than in sea water.
- At high solids content (30–35%), frothability in fresh water is a strong function of pH; frothability in sea water under these conditions is clearly depressed when compared with frothability in fresh water and does not depend on pH much.

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