Polymeric Depressants in Purification by Flotation of Molybdenite

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ABSTRACT

In Brazil, there are no official reserves of molybdenum, and the unofficial reserves are modest. Therefore, the molybdenum ore (molybdenite) produced as a co-product or by-product of emerald mining in the region of Campo Formoso, BA, has arisen as the only economic option.

The flotation process is commonly used in Brazil for the recovery of molybdenite from emerald mining tailings, but it produces low-content molybdenite concentrates, thereby resulting in a product with low economic value. The molybdenite concentrate produced in Campo Formoso contains 83.5% MoS\(_2\) (50% Mo), which is less than the international standard product that contains > 90% MoS\(_2\) (54% Mo). This low value is due to the presence of talc, which is a naturally hydrophobic mineral that is also floated with the molybdenite during the flotation process. Separability studies were done in a Partridge-Smith cell using dextrin and quebracho as a molybdenite depressor in solution at different concentrations and pH values to produce a technical-grade concentrate (i.e., 90% MoS\(_2\)). These basic studies were accompanied by measurements of the zeta potential and contact angle, which was determined by the capillary rise method. The results of these floatability studies were used in bench flotation tests, which were performed in a Denver laboratory flotation cell. A molybdenite concentrate of 93.4% MoS\(_2\) was obtained when dextrin was used at a concentration of 100 g/t.
INTRODUCTION
In Brazil, there are no official reserves of molybdenum and non official reserves are modest. An option for supply and economic use emerges from Mo ore (molybdenite) generated as a co-product or by-product of emerald mining in the region of Campo Formoso, BA (Braga et al., 2014).

In 2012, the Brazilian trade balance of the molybdenum chain (primary, semi-manufactured, manufactured and chemical compounds) was characterized by a deficit of approximately US$ 162 million, of which 50% corresponds to the import of concentrate (Alice-Web System, 2012).

To recover molybdenite in mining waste, low-content concentrates are produced by the process of flotation, which results in a product with low economic value. The produced molybdenite concentrate contains 83.5% MoS$_2$ (50% Mo), which is less than the internationally traded product, which contains more than 90% MoS$_2$ (54% Mo). The chemical analysis of the molybdenite concentrate showed high concentrations of magnesium oxide (MgO) and silicon dioxide (SiO$_2$), which indicates the presence of talc, phlogopite, chlorite and clinochlore (Braga, 2013).

Studies on depression and dispersion mechanisms for separating molybdenite from insoluble, highly hydrophobic minerals, such as talc, have been performed (Vicent & Shirley, 1985).

Molybdenite exhibits a laminar crystalline structure that is based on two types of chemical bonds: covalent bonds between sulfur (S) and Mo, whose rupture generates high energy sites that are referred to as “edges” on its surfaces and van der Waals interactions between the S-Mo-S layers, which generate low energy sites that are referred to as “faces” when broken. These different sites cause molybdenite to exhibit heterogeneity at its intrinsic surface due to the proportion between the faces and edges (Castro & Correa, 1995). A strong covalent bond, which generates hydrophilic sites with high superficial free energy when broken, exists inside the layers (Jara & Castro, 2006).

Influenced by the study of Chander & Fuerstenau (1972), López-Valdivieso et al. (2012) extended the study of the surface properties of molybdenite on a nanometric scale through atomic force microscopy (AFM). The effects of pH and the presence of calcium (Ca$^{2+}$) on the floatability and electrokinetic properties of molybdenite were investigated via the evaluation of the texture of the mineral surface. They concluded that the molybdenite faces are naturally heterogeneous and composed of MoS$_2$ micro crystals with nano-faces and nano-edges. The authors confirmed that the faces are not completely hydrophobic due to the presence of nano-edges, which generate hydrophilic sites. These nano-edges contain negative electric charges that increase with pH and impede the interaction of air bubbles with the surfaces (faces) of molybdenite crystals, which promote the low floatability of molybdenite.

The purpose of this study is to evaluate the use of polymeric depressants in purification by the flotation of molybdenite and talc minerals, which adds value to the concentrate produced in Brazil.

METHODOLOGY
Materials and reagents
Molybdenite concentrate from Campo Formoso, with 90% MoS$_2$, was employed in this study. Talc with
30.7 % MgO was provided by Paranaense Mining (Mineração Paranaense).

The mineral samples, which exhibited a particle size of -74 +37 μm, were previously treated with diluted nitric acid and diluted potassium hydroxide to remove the superficial oxidation, impurities and residual reagents. The samples were also washed with distilled water and dried under vacuum. Prior to the tests, the molybdenite and talc samples underwent an ultrasound treatment for better dispersion.

Anionic polymers, such as humic acid (Sigma-Aldrich), and nonionic polymers, such as dextrin (Vetec), guar gum (Sigma-Aldrich) and quebracho (Unitan Saica), were employed as depressants. Methyl isobutyl carbinol (MIBC), which was employed as a frother, was added to a 100 ppm aqueous solution. Potassium hydroxide and hydrochloric acid were used as pH regulators. Potassium chloride was added to a 10⁻³ mols/L aqueous solution to maintain ionic strength during the flotation tests (Braga et al., 2014).

Methods

The flotation tests were performed in a 250 mL Partridge-Smith cell according to the procedures of Ozkan & Yekeler (2003) and Jara & Castro (2006).

The pH of the mineral suspension, which was prepared with 3g of the sample, was adjusted in a beaker under magnetic agitation. The suspension was conditioned with the depressant polymer for 5 min and with the frother (MIBC) for more than 5 min.

After conditioning, the suspension was floated in the Partridge-Smith cell for 3 min. Pressurized filtered air, which was introduced in the cell by a porous plate at 1 L/min adjusted by a flowmeter, was used to generate bubbles. The agitation of the mineral suspension was maintained with a magnetic bar.

The flotation tests were performed at pH 2, 4, 6, 8, 10 and 12, and a depressant concentration of 100 ppm was maintained. Complementary tests were performed to verify the influence of the depressant concentration on the floatabilities of talc and molybdenite.

At the end of the flotation tests, the concentrate and the tailings were separately filtered, dried and weighed to evaluate the flotation recovery. A difference of more than 50% (separability window) was established as the criterion of separability of molybdenite/talc for the flotation recovery of each mineral.

To verify the influence of pH on the zeta potential of molybdenite and talc in the presence and absence of depressant agents, measurements of the potential were obtained with a Zetasizer Nano-ZS meter.

Based on the results obtained from the investigation of floatability in the Partridge-Smith cell, of which the main objective was to confirm the interaction of molybdenite with dextrin, purification tests of the low-content molybdenite concentrate were performed by bench flotation tests in a Denver laboratory flotation cell Mod. D12 with a cell capacity of 1000 mL. At this stage, the chemical additions were calculated in terms of grams of chemical per ton (metric) of feed to the flotation (molybdenite concentrate). The applied doses in the micro flotation tests were adjusted for adaptation to the bench tests. MIBC was used as a frother in the additions of 150 g/t (routher) and 75 g/t (cleaner). The tests were performed using approximately 300 g of molybdenite concentrate (71.6% MoS₂ and 5.3% MgO) in the feed of the rougher stage (Braga et al., 2014).
RESULTS AND DISCUSSIONS

Flotation recovery and particle size

The influence of particle size on the flotation recovery of talc and molybdenite was investigated using samples of minerals in the following particle size ranges: -150 +74 µm, -74 +37 µm and -37 µm. A reduction of approximately 20% in flotation recovery was verified for both molybdenite and talc for the three granulometric ranges, as shown in Figure 1.

The significant reduction in flotation recovery of the molybdenite and talc minerals is attributed to the reduction in the hydrophobicity of both minerals, which is intrinsic to the face-to-edges ratio. These minerals exhibit anisotropy in relation to their surfaces. Their hydrophobic properties are dependent on the faces and their hydrophilic properties are dependent on the edges.

Table 1 presents the results of the surface area measurements obtained with the Mastersize 2000 equipment, as a function of the particle size of the minerals, which corresponds with the reduction in flotation recovery. As the particle size decreases, the faces-to-edges ratio decreases, which infers a reduction in hydrophobicity and a consequent reduction in its natural floatability.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Surface area (m²/g)</th>
<th>-150 +74 µm</th>
<th>-74 +37 µm</th>
<th>-37 µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molybdenite</td>
<td></td>
<td>0.082</td>
<td>0.449</td>
<td>0.539</td>
</tr>
<tr>
<td>Talc</td>
<td></td>
<td>0.125</td>
<td>0.212</td>
<td>0.461</td>
</tr>
</tbody>
</table>

Castro & Correa (1995) demonstrated that the values of the polar component of the surface tension ($\gamma_p$) of molybdenite samples with finer granulometries exhibit higher polarity (hydrophilic) compared with the coarser fractions. These results confirmed that the decrease in the faces-to-edges ratio promotes the loss of
floatability in finer and polar molybdenite fractions due to the interactions between the edges of the mineral and the water through polar forces.

**Flotation recovery and pH**

Figure 2 displays the results for the flotation tests with the variation in pH, in which different organic polymers were used as depressants for the molybdenite/talc system.

In the test with guar gum, a window with greater than 50% separability was not verified for the molybdenite/talc system. The molybdenite and talc flotation recovery curves exhibited an effective depressant effect of the guar gum for both minerals, without the opening of a separation window. The electrokinetic studies of adsorption and flotation, which were performed by Rath et al. (1999) to verify the interaction between guar gum and the hydrophobic and lamellar minerals, demonstrated that the adsorption density of guar gum, compared with hydrophobic minerals, is independent of pH and the adsorption mechanism is influenced by hydrogen bonds and chemical interactions.

In the flotation tests, in which humic acid (anionic polymer) was used as a depressant, a window with greater than 50% separability was not observed for the molybdenite/talc system. The molybdenite and talc flotation recovery values in the pH range of 2 to 8. For molybdenite, the depressant effect of humic acid at a concentration of 100 ppm is independent of pH for the entire range. For humic acid concentrations of less than 5 ppm, the depressant effect is significant in the alkaline pH range (Lai, Stone & Rimmansch; 1984). The flotation recovery curve of talc displays a reduction in the depressant effect of humic acid at pH levels greater than 8.

The humic acid has two constants of equilibrium (pK): the first constant at pH 4 is caused by the protonation of the carboxylic groups and the second constant at pH 8 is caused by the protonation of the phenolate groups. The dissociation of these functional groups contributes to the formation of anionic charges and the consequent reactivity of humic acids, promoted by the high electronegativity at pH levels greater than 7 (Ghabbour & Davies, 2001; Brum, 2005). At the same pH condition, the talc also exhibit high electronegativity (absolute values), which most likely promote desorption (due to the repulsion) of humic acid at the surface of the talc, decreasing its depressant effect.

In the floatation test, in which dextrin (non-ionic polymer) was used as a depressant, windows with greater than 50% separability were obtained in almost the entire pH range for the molybdenite/talc system. The molybdenite and talc flotation recovery curves did not reveal a dependency on pH. Generally, a considerable separation window exists in the entire pH range, which demonstrates the efficiency of dextrin as a depressant of molybdenite at a solution concentration of 100 ppm. Similar flotation recovery results for talc were obtained by Liu et al. (2006), who employed dextrin, carboxymethyl cellulose (CMC) and carboxymethyl starch (CMS) as depressant agents. Although the adsorption of nonionic polysaccharides, such as dextrin, at the surface of talc is independent of pH, the observed reduction in the talc flotation recovery curve (Figure 2) at high pH values can be explained by the greater repulsion of air bubbles, which are most likely caused by the dissolution of particles. The adsorbed hydrolyzed species contributed to the increase in hydrophilicity, as reported by Fuerstenau & Huang (2003).


For the flotation test in which quebracho (nonionic polymer) is employed as a depressant, a window with greater than 50% separability was obtained between pH 8 and pH 10 for the molybdenite/talc system. Low synergy between the molybdenite floatability and the medium pH is verified. A sufficient depression of molybdenite is evident in the entire pH range, which verifies the efficiency of quebracho as a depressant agent. Although the adsorption of organic polymers, such as quebracho, are independent of pH, the effect of quebracho on talc was less effective in the pH range of 6 to 8, which creates a considerable separability window at pH 8.
Flotation recovery and depressant concentration

The results obtained with dextrin and quebracho motivated the performance of a new series of tests to verify the influence of the depressant solution concentration (dextrin and quebracho) on the floatability of molybdenite and talc. These tests were performed at pH 8, which is close to neutrality and where quebracho exhibits the highest solubility (Pearse, 2005). The curves in Figure 3 display the flotation recovery of the molybdenite and talc minerals at pH 8 for different concentrations of dextrin and quebracho (10, 25, 50, 100 and 200 ppm).

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![Figure 3: Flotation recoveries of molybdenite and talc for different concentrations of depressant at pH 8](image)

A window with 68% separability was obtained using dextrin with a concentration of 10 ppm. The most efficient action of dextrin as a depressant of molybdenite observed in this study can be attributed to the greater adsorption of this polymer through hydrophobic interactions at the surface of the mineral. Beattie et al. (2006) examined the floatability of talc in the presence of dextrin as a depressant agent; the results showed a recovery of talc of 87, 70 and 67% for dextrin concentrations of 25, 50 and 75 ppm, respectively, at pH 8.7, which is natural for the study suspension. Similar results were obtained, as shown in Figure 3. With a concentration of 10 ppm and pH 8, 80% of talc and only 12% of molybdenite were recovered.

A window with 63% separability was obtained using quebracho with a concentration of 50 ppm. The efficient action of quebracho as a depressant of molybdenite, which is also shown in Figure 3, is most likely associated with the enhanced adsorption of this polymer at the mineral surface through hydrophobic interactions and the preferential action mechanism of polysaccharides in naturally hydrophobic minerals. In a study by Ciribeni et al. (2002) on the depressant effect of quebracho on the flotation of sulfides, the adsorption mechanism was attributed to the resultant hydrogen bonds between sulfur and oxygen atoms, the formation of complexes between hydroxyl and phenol groups with di- and trivalent metallic cations, the neutralization of charges in alkaline medium at the positively charged...
surface or the electrostatic attraction between positively charged tannin micelles and the mineral surface.

**Measurement of the zeta potential**

The zeta potential was determined to identify the influence of pH on the electric charges at the molybdenite surface due to the presence and absence of dextrin and quebracho as depressant agents.

The curves of the zeta potential for bare molybdenite surface and molybdenite surface treated with dextrin and quebracho (Figure 4) revealed electronegative surfaces for almost the entire pH range, with isoelectric points located at pH values less than 2. Beginning at pH 6, a sharper increase in the electronegativity of the molybdenite surface is evident, which is most likely due to the oxidation and hydrolysis of MoO₃ to HMoO₄⁻ and MoO₄²⁻, which produces a higher electronegative surface.

![Figure 4 Zeta potential curves for bare molybdenite and molybdenite treated with dextrin and quebracho](image)

Although dextrin and quebracho are nonionic polymers with no possible interactions with the surface of molybdenite, their adsorption at the surface of molybdenite affected the zeta potential and promoted a displacement of the curve to the region of lower electronegativity, as shown in Figure 4. Wie & Fusternau (1974) postulated that this reduction in electronegativity is caused by the potential displacement of the Stern plane during the measurement of the zeta potential. The adsorption of dextrin in molybdenite is caused by hydrophobic bonds, which is also suggested by Laskowski et al. (2007) in a study that investigates the adsorption mechanisms of polysaccharides at the surface of minerals.

Few studies on the uses and effects of quebracho as reagents in the mining industry exist. Because quebracho is a natural product obtained from the core of trees (*schinopsis* quebracho colorado) predominant in South America, it is produced by countries which have limited financial resources for science and technology and are traditional importers of trademark products.
Bench scale test

The flotation bench scale tests for the purification of a molybdenite concentrate with a low concentration (75.10% MoS₂) exhibited the viability of the use of dextrin as a selective depressant for molybdenite in the process of reverse flotation. After adjusting the initial amount of dextrin and increasing the number of cleaner steps, the final molybdenite concentrate was gradually enriched. Using 100 g/t of dextrin and five cleaner steps, molybdenite concentrates with 93.4% of MoS₂ were obtained (Braga et al., 2014). The chemical analysis of the molybdenite concentrate, which was purified by reverse flotation with dextrin as a depressant, is shown in Table 2.

<table>
<thead>
<tr>
<th>MgO</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>K₂O</th>
<th>CaO</th>
<th>Fe₂O₃</th>
<th>MoS₂</th>
<th>Bi₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.93</td>
<td>0.87</td>
<td>2.9</td>
<td>0.54</td>
<td>0.17</td>
<td>0.74</td>
<td>93.4</td>
<td>0.33</td>
</tr>
</tbody>
</table>

CONCLUSIONS

A reduction in flotation recovery of approximately 20% was verified for both the molybdenite and the talc as the mineral particle size decreased. This reduction is intrinsic to the faces-to-edges ratio.

The use of dextrin promotes a window with 68% separability when used in solution with a concentration of 10 ppm and pH 8. The use of quebracho promotes a window with 63% separability when used in solution with 50 ppm and pH of 8.

The action of dextrin and quebracho at the surface of molybdenite displaces the zeta potential to regions with lower electronegativity.

Using 100g/t of dextrin and five cleaner steps, a molybdenite concentrate with 93.4% of MoS₂ was obtained. The final concentrate purified using dextrin with 93.4% of MoS₂ satisfied the requirements of the international market.

This study demonstrates the importance of fundamental studies to identify separability windows between the molybdenite and talc minerals. The experimental conditions determined by microflotation (concentrations and amounts of reagents) can be successfully adjusted for the flotation in bench tests with a mineral enrichment of 1.24 times in terms of MoS₂.

REFERENCES


