Original Article

Sorghum starch as depressant in mineral flotation: part 2 – flotation tests

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In order to find a feasible replacement for cornstarch, the flour and starch of a graniferous variety of sorghum was tested as a depressant of hematite and quartz in a cationic microflotation in a modified Hallimond tube, using an ether amine as collector. Hematite and quartz samples from the Brazilian Iron Quadrangle were used in the flotation tests. The mineral samples were characterized by XRF, and SEM/EDS. Zeta potential measurements were performed in the pH range from 3.5 to 12.5. A commercial cornstarch was used as the depressant benchmark. Four depressants dosages and pH values were tested. A statistical test was used to verify the pH, dosage, and starch type influence on the minerals recoveries. At pH 10.5, the lowest average hematite recovery using sorghum starch was 7.27 ± 1.22% for a dosage of 40 mg/L, 13.24% lower than the value achieved for cornstarch. The results indicated that sorghum starch has a stronger depressant action on hematite than cornstarch. Quartz recovery was deeply influenced by the presence of cornstarch. Dosages below 40 mg/L of sorghum starch recovered more quartz than cornstarch in all tested pH values. At pH 9 and dosage of 5 mg/L, sorghum starch recovered 387% more quartz than cornstarch. The ANOVA test showed that pH, dosage, and starch type had significant impact on hematite and quartz recovery. The results suggest that sorghum has a great potential to replace corn as default depressant in iron ore flotation.

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1. Introduction

According to Tuck [1], Brazil is the second largest producer of iron ore in the world. In 2017 the estimated mine production was 280 million metric tons of iron content. Brazilian iron ores have high grades of total Fe and low contents of impurities, especially the deposits located in the state of Pará, with average total Fe of 64.8%, accounting for 10.7% of the Brazilian deposits. One of the most important Brazilian iron ore mining sites is the Iron Quadrangle (locally called as “Quadrilátero Ferrífero”). Situated in the state of Minas Gerais, this deposit accounts for 72.5% of the Brazilian deposits with average total Fe of 46.3%. According to Rosière & Chemale [2], the banded iron formations (BIFs) are metamorphic jaspilites named itabirites that occur in the Paleoproterozoic platformal sequence of the Minas Supergroup (2.6–2.12 Ga).

The steel making industry usually requires iron ores with total Fe higher than 60%. Therefore, ores with lower grade must undergo mineral processing in order to remove the impurities and enhance the iron content. Beneficiation of iron ores by flotation is an important part of the concentration process, where the quartz and other silicates are removed by reverse cationic flotation using ether amine as collector. The iron oxide is depressed with the aid of depressants, such as starch, dextrin, or carboxymethyl cellulose (CMC) [3]. According to Laskowski et al. [4], the depressant acts as an inhibitor of flotation in a mineral, and this happens by adsorption of reagent onto mineral surface, preventing the collector adsorption or inducing strong hydrophilic properties on the mineral surface. Starch is not soluble in cold water and needs to be gelatinized before its use as depressant. This process could be done by heating the suspension of starch in water or adding an alkaline solution, such as sodium hydroxide [5]. Nowadays the alkaline gelatinization is adopted in Brazilian mineral industry as the standard procedure. Since most industrial flotation operations are performed in alkaline pH, this gelatinization method also aids the pulp pH control. The reverse iron ore flotation is usually performed at pH around 10.5 [6–8].

According to Araujo et al. [5], starches are the universal depressant of iron oxides and may be extracted from several vegetable species, such as corn, cassava, potato, wheat, rice, arrowroot, etc. In Brazil, more than 300 million tons of iron ore concentrate production per annum is achieved using a starch depressant and an amine collector [8]. Cornstarch is the most widely used depressant in the reverse flotation of iron ore due mainly to its availability, cost, and low impact on the environment [5]. Brazil is the third largest producer of corn, being responsible for around 8% of the world production. However, a big slice of the corn production is reserved for the food industry and for exportation. This scenario has raised the corn price above the limit that the mineral industry could afford, pushing the corn industry to offer a finer product, locally known as fubá. Fubá is the ground product obtained after the removal of the pericarp (or hull) and degeneration of the corn kernels [5].

Other starch sources have been studied in the last decades, and some have been industrially adopted. Cassava starch is used as iron ore depressant in some mineral processing plants in Brazil. Cassava starch can enhance the flotation selectivity. On the other hand, its price fluctuations render the substitution of cornstarch a risk. Potato flour has been used industrially in Europe for many years, but there are no records of its use in the Brazilian mining industry so far, mainly due to the fact that potato degrades much faster than corn [10].

Sorghum (Sorghum bicolor (L.) Moench) is a crop that is widely grown over the world for production of food and animal feed. Quantitatively, it is the world’s fifth most important cereal grain, after wheat, maize, rice, and barley. It is mostly cultivated across the world in the warmer weather areas. Sorghum is the main staple food for the world’s poorest people. Starch is the major storage form of carbohydrate in sorghum, making up about 60–80% of normal (non-waxy) kernels. Nowadays sorghum is cultivated in Brazil only for animal food despite the fact of its possible usefulness in different food products [10]. Sorghum culture is fully mechanized and the same equipment used with other cultures, such as corn, rice, wheat, or soy, can be used. Sorghum is marketed with prices 70–80% smaller than those of corn, which can be a major feature considering the necessity of cost reduction in mining companies, driven by the economic crisis that Brazil has been facing in the last years.

The aim of this work was to study the recovery of hematite and quartz using sorghum (starch and flour) as depressant in microflotation tests. A commercial cornstarch was used as the depressant benchmark. Since corn is used in Brazil in both forms, starch and fubá, with different granules sizes and relative success in the mineral industry, the sorghum flour was tested mainly focusing on cost reduction. Four depressant dosages (5, 10, 20, and 40 mg/L) and four pH values (9, 9.5, 10, and 10.5) were tested. The sorghum starch extraction and characterization was presented in the article “Sorghum starch as depressant in mineral flotation: Part 1 – Extraction and characterization”.

2. Materials and methods

2.1. Mineral sample preparation and characterization

Hematite and quartz mineral samples from the Iron Quadrangle region in Minas Gerais state, Brazil, were comminuted in a jaw crusher followed by a ball mill, and the size fractions were separated through wet sieving using a Tyler sieving series during 15 min. The samples were then dried in an oven at 60 °C during 24 h. A ferrite magnet with field of 2 kG was used in the quartz samples to remove any possible contamination from the previous stages. The chemical composition was determined at Copebras S/A laboratory using an X-ray Fluorescence spectrometer AXIOS MAX series DY 5001 from PANalytical. Sample images were acquired with a SEM JSM-6610 from Jeol coupled with energy dispersive X-ray spectrometer (EDS) probe from Thermo Scientific NSS Spectral Imaging at Labmic/UFMG. The wet particle size analyses were performed with addition of Na2P2O7 (1 g/L) as dispersant agent and tap water at IFAC/TUC using a HELOS laser diffraction particle size analyser from Sympatec. The zeta potential measurements were performed at IFAC/TUC using a ZS90 Zetasizer Nano from Malvern with pH ranging from 3.5 to 12.5, using sodium hydroxide and sulfuric acid solutions 1.0 M as pH modifiers. Mineral suspensions (0.1% w/w) were prepared with particle size below 20 μm in 100 mL of the 10−3 M KCl solution (indifferent electrolyte).
2.2. Flotation tests

Microflotation tests were performed in a modified Hallimond tube (addition of an extender between the bottom and upper parts of the tube in order to reduce the effects of hydraulic entrainment) with 320 mL of internal volume, at room temperature (around 25 °C). The airflow was kept at 40 cm³/min and pressure at 10 psi in order to minimize the hydraulic entrainment. The mineral mass used in each test was 1.0 g with particle size between −149 + 105 µm (−100 + 150#). Flotigam EDA (ether amine) from Clariant was used as collector (20 mg/L for hematite and 5 mg/L for quartz) and its preparation consisted of adding 1.0 g of the collector to distilled water to a total volume of 100 mL (1% w/v) under magnetic stirring, as recommended by the manufacturer. Three different depressants (cornstarch, sorghum flour and starch) and four dosages of the depressants (5, 10, 20, and 40 mg/L), as proposed by Pinto et al. [12], were tested. A graniferous variety of sorghum, farmed on Ipameri, Goiás, Brazil and kindly provided by Agroceres was used. The depressant gelatinization was performed by adding 2.7 mL of sodium hydroxide at 10% to a solution of 20.0 mL of distilled water and 1.0 g of starch. The solution was kept under magnetic stirring until complete gelatinization. Collector and depressant solutions were used fresh daily in order to avoid any degradation of the collector or retrogradation of the depressant. Hydrochloric acid and sodium hydroxide, both at 1%, were used as pH modifiers. Four pH values (9.0, 9.5, 10.0, and 10.5) were tested. These pH values were adopted firstly because the industrial pH adopted in Brazil for hematite flotation is 10.5 [8]. Second, Santos & Oliveira [13] showed that the recovery for both minerals is insignificant outside the pH range from 9.5 to pH 11.5. Finally, because at an alkaline pH the starch adsorption onto the quartz surface is prevented due to a preferred adsorption of the amine collector [9]. The conditioning time was 5 min for the depressant and 1 min for the collector. The flotation time was 1 min. Distilled water was used throughout the experiments. A Two Factor ANOVA with Replication statistical test was used to verify the pH, dosage, and starch type influence on the hematite and quartz recoveries. The level of significance (α) adopted in the ANOVA tests was 0.05. Only the starches (corn and sorghum) were compared since the flour results were statistically different from those of starches.

3. Results and discussion

3.1. Mineral sample characterization

Table 1 shows the results of X-ray fluorescence for hematite and quartz samples. Regarding the chemical composition, it is possible to assume that quartz samples had around 94% of purity and hematite samples around 96% purity, with total Fe around 67.6%.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe₂O₃</th>
<th>SiO₂</th>
<th>K₂O</th>
<th>CaO</th>
<th>P₂O₅</th>
<th>CaO₂O₄</th>
<th>Ta₂O₅</th>
<th>BaO</th>
<th>I</th>
<th>TiO₂</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hematite</td>
<td>96.68</td>
<td>2.59</td>
<td>0.16</td>
<td>0.15</td>
<td>0.19</td>
<td>0.23</td>
<td>0.05</td>
<td>0.58</td>
<td>0.05</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>Quartz</td>
<td>0.16</td>
<td>94.68</td>
<td>4.31</td>
<td>0.12</td>
<td>0.04</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.01</td>
</tr>
</tbody>
</table>

Table 1 – XRF results for hematite and quartz samples (in percentage).

Fig. 1 – SEM images for hematite samples (a) BEC and (b) SEI images at 750× magnification. EDS results for points (c) 1 and (d) 2 marked on figure (a).
Fig. 1 shows scanning electron microscope images for hematite samples using backscattered and secondary electron imaging. It is possible to notice in Fig. 1a and b an association of hematite (major phase) with a secondary mineral phase (marked as point 2 in Fig. 1a). Fig. 1c and d show the EDS results for the two mineral phases. As expected the main mineral phase was composed of Fe and O, compatible with hematite (Fig. 1c). The secondary mineral phase could not be correctly identified based only on the EDS result. Fig. 2 shows the SEM/EDS results for the quartz samples. Two mineral phases were detected. The main phase was identified as quartz and composed mainly by Si and O (Fig. 2c). The secondary mineral phase could not be correctly identified based only on the EDS result (Fig. 2d).

Regarding the zeta potential measurements (Fig. 3a), the isoelectric point (IEP) for hematite was determined at pH 6.95. Similar result (IEP at pH 6.2) was found by Kar et al. [3] working with hematite samples from mines of Odisha, India. No IEP was determined in the tested pH range (3.5 to 12.5) for the quartz samples, being their superficial charge always negative. Fig. 3b presents the particle size distribution of the hematite and quartz samples used in the flotation tests. It is noticeable that around 80% of the hematite and 50% of the quartz samples were below 100 μm and around 11% of the hematite and 7% of the quartz samples were below 20 μm.

3.2. Flotation results

Fig. 4 presents the results of microflotation tests for hematite. In the absence of the depressant, the hematite recovery increased with the increase of the pH, ranging from 82.92 ± 2.53% at pH 9 to 89.06 ± 1.02% at pH 10.5. In the presence of depressant, however, the hematite recovery drastically decreased. The same behavior was observed for all tested depressants, dosages and pH, indicating that all starches were able to depress hematite. Pinto et al. [12] obtained similar results using dodecylamine hydrochloride (5 × 10⁻⁵ mol/L) as collector and starch (tapioca and potato), amyllose, and amylopectin at pH 10.

In general, an increase in the cornstarch dosage decreased the hematite recovery. Kar et al. [3] described similar behavior for different depressants with dosages up to 800 g/t. The lowest average hematite recovery was 8.38 ± 1.46%, at pH 10.5 and dosage of 40 mg/L. The only exception was found at pH 9, where the hematite recovery increased for dosages above 10 mg/L. Sorghum starch showed similar behavior at pH 9.5 and 10. The lowest average hematite recovery using sorghum starch was 6.07 ± 0.66%, at pH 9 and dosage of 20 mg/L. At the industrially adopted pH (10.5) for iron ore flotation, sorghum starch showed a behavior similar to that of cornstarch (an increase in the depressant dosage promoted a decrease in the hematite recovery). At this pH, the lowest average hematite recovery using sorghum starch was 7.27 ± 1.22% for a dosage of 40 mg/L (13.24% lower than cornstarch). The results indicate that sorghum starch has a higher depressant action on hematite than cornstarch. The only exception happened at pH 9.5 and dosage 40 mg/L. The hematite recovery using sorghum flour was higher than corn and sorghum starches for all tested conditions. The lowest average hematite recovery for this depressant was 39.20 ± 2.09%, at pH 10 and dosage of 5 mg/L.

The ANOVA results for hematite recovery are presented in Table 2. In all statistical tests, the obtained P-value was
Fig. 3 – (a) Zeta potential and (b) particle size distribution for hematite and quartz samples.

Fig. 4 – Hematite flotation results in (a) pH = 9.0, (b) pH = 9.5, (c) pH = 10.0, and (d) pH = 10.5.

Table 2 – ANOVA results for hematite recovery using cornstarch and sorghum starch as depressants.

<table>
<thead>
<tr>
<th>pH</th>
<th>Dosage (mg/L)</th>
<th>P-value</th>
<th>F</th>
<th>F-critical</th>
<th>Starches</th>
<th>P-value</th>
<th>F</th>
<th>F-critical</th>
</tr>
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<tbody>
<tr>
<td>9</td>
<td></td>
<td>6.57E–07</td>
<td>31.09</td>
<td>3.24</td>
<td></td>
<td>1.16E–15</td>
<td>946.35</td>
<td>4.49</td>
</tr>
<tr>
<td>9.5</td>
<td></td>
<td>5.5E–09</td>
<td>61.17</td>
<td>3.24</td>
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<td>244.77</td>
<td>4.49</td>
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<td>10</td>
<td></td>
<td>3.59E–10</td>
<td>88.36</td>
<td>3.24</td>
<td></td>
<td>7.42E–09</td>
<td>120.45</td>
<td>4.49</td>
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<tr>
<td>10.5</td>
<td></td>
<td>3.49E–08</td>
<td>47.39</td>
<td>3.24</td>
<td></td>
<td>5.04E–10</td>
<td>174.58</td>
<td>4.49</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>3.03E–06</td>
<td>24.70</td>
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<td>698.37</td>
<td>4.49</td>
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<tr>
<td></td>
<td>10</td>
<td>8.00E–11</td>
<td>107.74</td>
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<td>7.22E–15</td>
<td>749.49</td>
<td>4.49</td>
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<tr>
<td></td>
<td>20</td>
<td>4.58E–07</td>
<td>32.79</td>
<td>3.24</td>
<td></td>
<td>5.67E–12</td>
<td>317.27</td>
<td>4.49</td>
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<tr>
<td></td>
<td>40</td>
<td>1.03E–15</td>
<td>457.45</td>
<td>3.24</td>
<td></td>
<td>8.00E–03</td>
<td>9.17</td>
<td>4.49</td>
</tr>
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</table>
lower than adopted significance level (0.05). Therefore, the differences between some of the means tested are statistically significant. This result can be confirmed by the F-test, also presented in the same table, since the F-value was higher than the F-critical for all tests. It is possible to notice that tested parameters had significant impact over the hematite recovery, being the starch type the most important parameter, followed by the depressant dosage.

The quartz flotation results are shown in Fig. 5.

As expected, all tested depressants were more effective on hematite than on quartz. According to Shrimali & Miller [9], the adsorption of starch occurs onto both, quartz and iron oxide mineral surfaces, but at an alkaline pH, the interaction between quartz and the amine collector is stronger, preventing the starch adsorption. In general, an increase in the depressant dosage promoted a decrease in quartz recovery. Somasundaran & Cleverdon [14] obtained similar results when testing the effect of the PAMA polymer addition on quartz flotation using amine at two different amine levels. According to the authors, the quartz recovery decreased with the increase of the PAMA concentration, with quartz complete depression achieved at 1 mg/kg. The presence of amine had a significant effect on the quartz zeta potential with charge reversal in a narrow pH range (between 9 and 11) in which the highest quartz flotation is usually obtained. This phenomenon has been explained by the authors as being due to the formation of the highly surface-active amine-aminium complex in this pH range. At pH values higher than 10.63, most of the amine is in the neutral form, which does not lend itself to adsorption. According to Shrimali et al. [8], monoether amine quickly forms a monolayer on the quartz surface at pH 10.5 and there is no interaction between quartz and a cornstarch-only solution at pH 10.5. Though starch has no affinity for quartz, and hence, no adsorption when added with mono ether amine, it may change the surface property of the quartz surface at higher concentrations, suggesting an interaction between cornstarch and mono ether amine forming a clathrate. The authors suggest that the clathrate interaction takes place in such a way that the starch masks the hydrophobic tail of the mono ether amine, decreasing the contact angle at the quartz surface from 62° to 43° in the presence of excess starch. The results for sorghum starch suggest a possible similar interaction with amine, leading to clathrate formations.

In the absence of depressant, the quartz recovery showed statistically relevant changes in the tested pH range, with a slight decrease with the pH increase and average recovery of 96.91 ± 1.45%. However, the quartz recovery was deeply influenced by the presence of cornstarch, with the lowest quartz recovery (19.89 ± 2.40%) at pH 9 and dosage of 5 mg/L. On the other hand, the use of sorghum flour did not produce major impacts on the quartz recovery. For this depressant, the lowest quartz recovery was 91.49 ± 4.94%, obtained at pH 9.5 and dosage of 5 mg/L. Dosages below 40 mg/L of sorghum starch recovered more quartz than cornstarch in all tested pH values. The lowest quartz recovery using sorghum starch was 34.49 ± 2.60% at pH 10.5 and dosage of 40 mg/L. At pH 9 and dosage of 5 mg/L, sorghum starch recovered 4.87 times as many quartz as cornstarch. Pavlovic & Brandão [7] found similar results for hematite and quartz recovery using cornstarch.
and Flotigam EDA-B (decyletheramine acetate) from Clariant at pH 10.5, with the presence of valleys in the recovery curves for both minerals.

As expected, the ANOVA test showed that the pH, dosage, and starch type had significant statistical influence on the quartz recovery (see Table 3). However, for pH 10.5 or for dosage of 20 mg/L no significant statistical difference was found between corn and sorghum starches results (P-value < 0.05 but F-value < F-critical).

A simultaneous comparison of the flotation results for both minerals, at the same flotation conditions, was performed for each tested pH for cornstarch and sorghum starch (Fig. 6). Two theoretical limits were established regarding the minerals recovery. The lower acceptable quartz recovery was fixed at 90% and the highest acceptable hematite recovery was 20%.

<table>
<thead>
<tr>
<th>pH</th>
<th>Dosage (mg/L)</th>
<th>F-value</th>
<th>F</th>
<th>F-critical</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>5</td>
<td>3.04E-10</td>
<td>90.33</td>
<td>3.24</td>
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<tr>
<td>9.5</td>
<td>10</td>
<td>1.74E-12</td>
<td>177.30</td>
<td>3.24</td>
</tr>
<tr>
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<td>20</td>
<td>5.93E-09</td>
<td>60.55</td>
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<tr>
<td>10.5</td>
<td>40</td>
<td>1.31E-12</td>
<td>184.02</td>
<td>3.24</td>
</tr>
</tbody>
</table>

Cornstarch was able to achieve the established limit only at pH 10 and dosage of 10 mg/L, recovering 90.90±1.77% of quartz and 13.18±0.79% of hematite (see Fig. 6c). For the same conditions, sorghum starch was able to recover 97.56±1.36% of quartz (an increase of 7.33%) and 6.31±0.44% of hematite (a decrease of 47.87%). Neither corn nor sorghum starches were able to achieve the established limit for quartz recovery at pH 10.5 (Fig. 6d). This result agrees with industrial data, which show that normally the SiO₂ grade tends to increase with the increase of the Fe₂O₃ recovery.

For dosages below 20 mg/L and pH below 10.5, sorghum starch was able to achieve the established recovery limits. The best results obtained for sorghum starch were for dosage of 10 mg/L and pH values 9 (Fig. 6a) and 10 (Fig. 6c), with recoveries of 94.46±1.89% for quartz and 6.72±0.17% for hematite.

Fig. 6 – Flotation results for hematite and quartz using cornstarch and sorghum starch at pH (a) 9.0, (b) 9.5, (c) 10.0, and 10.5.
4. Conclusions

The role of three different depressants was investigated in the cationic reverse flotation of hematite using ether amine as collector. High purity samples of hematite and quartz from Brazil were used in the flotation tests. Corn and sorghum starches are effective depressants of hematite in the alkaline pH (9–10.5). Sorghum flour required higher dosages to reach similar performance. Quartz floatability was deeply reduced by the presence of corn or sorghum starches, but was barely affected by the presence of sorghum flour. High dosages of the depressants lead to poor floatability results, confirming the data available in literature. As expected, the statistical analysis showed that pH, depressant dosage, and starch type had significant impact on hematite and quartz recovery. No significant statistical difference was found between corn and sorghum starches results for quartz floatability at pH 10.5 or for dosage of 20 mg/L. When comparing simultaneously hematite and quartz floatability, good results were obtained at pH values different from 10.5. The best floatability results were obtained using sorghum starch, especially at low dosages and at pH 9 and 10. Flotation tests on bench scale (cell or column) using iron ore samples are required to validate the results on Hallimond tube, especially nowadays where itabirites have risen as the predominant iron ore typologies within Brazil. However, the results indicate that sorghum starch could be a feasible depressant of hematite.

Conflicts of interest

The authors declare no conflicts of interest.

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