Review Article

Effect of ground corn and cassava flour on the flotation of iron ore tailings

Geriane Macedo Rocha *, Nayara Rilla de Souza Machado, Carlos Alberto Pereira

Universidade Federal de Ouro Preto, Campus Morro do Cruzeiro, 35400-000 Ouro Preto, MG, Brazil

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ABSTRACT

Iron ore tailings with particle sizes smaller than 297 μm were used in this experiment. These tailings were obtained from Mineração Usiminas, Brazil. The objective of this study was to evaluate the performance of the reverse cationic flotation of these iron ore tailings, which in turn would allow us to deepen the understanding of the depressant action of ground corn and cassava flour. Bench flotation tests were carried out varying dosages of depressants and pH values of the conditioning processes of the same in 8, 9 and 10. The zeta potential measurements were performed on hematite in the presence of these different depressants. Cassava flour was found to more significantly reduce the zeta potential than ground corn, and it also altered the isoelectric point of hematite. Nevertheless, the results of the bench flotation tests did not result in a clear distinction between the effect of ground corn and cassava flour. The iron recoveries increased with reduction of pH conditioning from 10 to 9 and 8, but these also led to a slight increase in the silica content of the iron concentrate.

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Geriane Macedo Rocha holds a bachelor’s degree in Mining Engineering (2011) and master’s degree in Mineral Engineering (2017), both from the Federal University of Ouro Preto. He served as process engineer in the field of mineral processing in Mineração Usiminas/Minas Gerais/Brazil in the period from 2011 to 2017. She is currently a doctoral student in Mineral Engineering in the Federal University of Ouro Preto.

Nayara Rilla de Souza Machado is currently undergraduate student in mining engineering at the Federal University of Ouro Preto.

* Corresponding author.
E-mail: geriane.ufop@hotmail.com (G.M. Rocha).
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Carlos Alberto Pereira is currently associate Professor in the Federal University of Ouro Preto and fellow researcher of CNPq 2. He served as engineer 12 years at the mine of Paranaapanema in Rondônia/Brazil. He develops projects in the areas of research on mineral processing, teaching and extension. He mentored numerous undergraduate and 20 graduate students. He has 53 articles published in periodicals and 163 articles in congresses.

1. Introduction

The selection of the most adequate concentration technique for each ore includes as mainly criteria the mineralogy, particle size distribution and the liberability [1]. Flotation is a worldwide consolidated method for the concentration of iron ore with size range – 150 μm.

In reverse cationic iron ore flotation, the amine is typically used as the quartz collector, and gelatinized starch is used as an iron mineral depressant. Starch consists of two major components: an insoluble and linear chain of glucose molecules called amylose, and a soluble and a highly branched structure called amyllopectin. The amylose/amyllopectin ratio is different in different vegetables or even in different varieties of the same vegetable, and it determines some of the properties of the starch [2]. For application of the starch as a flotation reagent it is necessary to subject it to a process of irreversible transformation of its structural organization, called gelatinization, which occurs as verified by Souza and Magalhães [3], through the chemical reaction energy with the use of sodium hydroxide, and the mechanical energy provided by the stirring.

Starch macromolecules are highly hydrophilic due to the large number of hydroxyl groups in the monomer unit, D-glucose, and they are able to extend in a solution and form a bridge between mineral particles due to their large molecular size; this allows them to act as flocculants [4]. Weissenborn [5] has shown that amyllopectin is responsible for the flocculation ability of starch, while amylose does not exhibit any sort of flocculating action. Amylopectin was also found to behave like a bulk flocculant, and the combination of amyllopectin and amylose was found to produce the best selective flocculation results for iron minerals. The significant flocculation ability and the affinity for hematite of amyllopectin has been attributed to its higher molecular weight and branched structure. The ability of amylose to suppress the bulk flocculation by amyllopectin and increase selective flocculation may be due to the association between the two molecules and co-adsorption.

Using adsorption isotherms, Pavlovic and Brandão [6] verified that starch, amylose, and amyllopectin were all adsorbed on hematite in a similar manner. But on quartz, amylose was adsorbed more than starch, and amyllopectin was not adsorbed. Despite its adsorption on quartz, amylose showed the worst performance to depression of this mineral. This result may be because amylose is not a flocculant, indicating that flocculation effect is necessary for quartz depression. Based on these analyses, for quartz it is not possible to correlate the depressant action with the amount of polysaccharides adsorbed. Another conclusion that can be made is that hematite is depressed even without the occurrence of flocculation, although this probably is positive to flotation.

Starch adsorption studies at the solid–solution interface presented by Bulatovic [2] indicated that the adsorption of starch on hematite and quartz is pH-dependent and that this adsorption decreased as the pH increased. He also determined that starch was more readily adsorbed on the surface of hematite than on the surface of quartz.

According to Araújo et al. [7] corn starch is by far the most widely species employed in the mineral industry due to its availability in large amounts, being the EUA the largest producer in the world. Cassava flour is also an interesting starch source because grows widely in warm weather countries, with no need of fertilizers or soil correction. In comparison to other forms of starch, Breuninger et al. [8] found that cassava starch produces only a few residual materials (i.e., oil, protein, and ash), has lower amylose content, and has higher molecular weights of both amylose and amyllopectin. Furthermore, because of its low amylose content, cassava starch produces a viscous paste that has a low tendency to retrograde.

Matos et al. [9] observed that for an iron ore pulp with a small amount of slurry, the state of the aggregation of its particles does not change significantly either as a function of pH or when corn and cassava starches were added. For iron ores in which the amount of particles smaller than 10 μm was 14% and 22%, the degree of dispersion increased at pH above 10, and reduced when the starch dosage was increased. Cassava starch showed higher aggregation effect than corn starch.

In this study, bench flotation tests and zeta potential measurements on hematite were carried out to evaluate the depressant action of ground corn and cassava flour, with the dosages and pH of the depressants conditioning being varied.

2. Materials and methods

Samples containing iron ore tailings were sourced from a dam located in Mineração Usiminas, which is in Quadrilátero Ferrífero (the Iron Quarter), Minas Gerais, Brazil. Chemical analyses of the samples were conducted using X-ray fluorescence (WDXRF PANalytical). The particle size analyses were made by screening and laser granulometer (CILAS 1064). To mineralogical identification was used X-ray diffraction (PANalytical Empyrean).

The particle size of the tailing was adjusted by screening in 300 μm and disliming until fractions +150 μm = 5.3% and −10 μm = 9.5% were obtained to flotation tests. Chemical analysis of the feed flotation found that the feed consisted of 43.6% Fe, 34.6% SiO₂, 0.027% P, 0.017% Mn and 1.16% Al₂O₃. The ignition loss was 1.58%. Using the X-ray diffraction, the main mineral phases identified were hematite and quartz.

2.1. Flotation tests

Flotation tests were performed in a 1.5 L CDC laboratory machine, model CFB-1000-EFPNBA. Reagents used in the
Table 1 - Characteristics of the depressants, as reported by their suppliers.

<table>
<thead>
<tr>
<th>Depressants</th>
<th>&gt;1.0 mm (%)</th>
<th>&gt;0.59 mm (%)</th>
<th>Oil (%)</th>
<th>Starch (%)</th>
<th>Protein (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ground Corn – Flotam75</td>
<td>1.0 (max)</td>
<td>12.0 (max)</td>
<td>1.8 (max)</td>
<td>75.0–80.0</td>
<td>–</td>
</tr>
<tr>
<td>Ground Corn – Flokit415</td>
<td>–</td>
<td>4.0 (max)</td>
<td>1.5 (max)</td>
<td>83.0 (min)</td>
<td>7.0 (max)</td>
</tr>
<tr>
<td>Cassava Flour – FF01</td>
<td>2.49</td>
<td>–</td>
<td>0.45</td>
<td>75.0</td>
<td>–</td>
</tr>
<tr>
<td>Cassava Flour – FF73</td>
<td>2.72</td>
<td>–</td>
<td>0.45</td>
<td>82.57</td>
<td>–</td>
</tr>
</tbody>
</table>

Table 2 - Experimental conditions of the bench flotation tests.

<table>
<thead>
<tr>
<th>Depressants</th>
<th>Variables</th>
<th>Minimum</th>
<th>Moderate</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ground Corn – Flotam75</td>
<td>pH conditioning</td>
<td>8</td>
<td>9</td>
<td>10</td>
</tr>
<tr>
<td>Ground Corn – Flokit415</td>
<td>Dosage (g/t)</td>
<td>400</td>
<td>–</td>
<td>600</td>
</tr>
<tr>
<td>Cassava Flour – FF01</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cassava Flour – FF73</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

flotation experiments were the collector alkyl ether mono-amine (Clariant's Flotigam EDA), and the depressants corn starch (Caramuru's Flotam75 and Kowalski's Flokit415) and cassava flour (Tecknoamido's FF01 and FF73). Table 1 shows the main characteristics of the depressants, as reported by their suppliers. Collector and depressants were used as 1% (w/v).

Depressants, gelatinized at a depressant:NaOH weight ratio of 8:1, were conditioned for 5 min and the amine for 1 min. The conditioning of the reagents and flotations were carried out at 45% solids content by weight. The dosage of amine was 100 g/t. The agitation rate was 1100 rpm. The flotation time was 5 min. The pH flotation was 10. Sodium hydroxide (NaOH) and CO₂ (carbon dioxide) were used to control the pH. The reaction of CO₂ gaseous with H₂O forms the carbonic acid (Eqs. (1) and (2)), leading to a reduction in the pH of the pulp.

H₂O + CO₂ ↔ H₂CO₃  
H₂CO₃(aq) ↔ H⁺(aq) + HCO₃⁻(aq)

The variables used in the flotation tests are presented in Table 2; and generated, in duplicate, 48 tests.

2.2. Zeta potential measurements

The zeta potential measurements were conducted in a Zeta Meter 4.0 with video direct images, using electrophoretic mobility. The hematite sample from Quadrilátero Ferrífero area presented level of purity of 97.4% identified by X-ray diffraction analysis. The hematite sample was comminuted to the size range <38 μm. A NaCl (10⁻³ M) solution was used as the supporting electrolyte. The suspension with mineral was allowed to stand for approximately 60 min to gravity sedimentation of the 10 μm particles. The pH was adjusted to the desired value using NaOH or HCl. The depressants used in the bench flotation tests were conditioned for 5 min at concentration of 1.5 mg/L. The final zeta potential value for each condition was determined using the arithmetic average of the minimum of 10 measures.

3. Experimental results and discussion

3.1. Flotation tests

Figs. 1 and 2 show the iron recovery for each depressant as a function of its pH depressing for dosages of 400 and 600 g/t, respectively. It can be seen that in general the reducing of the pH conditioning of the depressant from 10 to 9 and 8 resulted in higher iron recovery percentages (Table 3). When used pH
of 10 the average of SiO$_2$, considering all tests, was 71.7%, pH 9 was 72.7% and pH 8 was 73.8%. This result is consistent with the adsorption study presented by Bulatovic [2], which showed that a reduction in the pH level led to an increase in the starch adsorbed onto hematite. Kar et al. [10] studying four different starches found that the maximum adsorption on hematite occurred at pH between 5 and 9 and found to be less at more alkaline pH values. In the hematite flotation experiments, considering the pH range 6.5–9.5, it was noted that the depressing action of hematite decreased with the increase in pH values. Martins et al. [11], who also found that more metal was recovered when lower pH conditionings were performed, correlated this to the fact that at a pH value of approximately 8, starch more readily interacts with the surface of an iron mineral. At around a pH value of 8, the iron mineral surface becomes highly hydroxylated and the maximum adsorption of dextrin occurs [4].

The iron recovery was found to increase as the dosage increased for all depressants and conditions availed. The ground corn Flokit415 achieved highest iron recovery when the pH conditioning was 8 and Flotamill75 achieved the lowest iron recovery in the same pH. The cassava flour FF73 led to good results in all pH conditioning, mainly pH 8.

The effects of variable tested to SiO$_2$ content in iron concentrate for dosages of depressants of 400 g/t and 600 g/t are presented in Figs. 3 and 4, respectively. The results indicate, in general, that alongside the increase in the iron recovery, the reduction in pH conditioning of depressants led to a slight increase in the SiO$_2$ content. When used pH of 10 the average of SiO$_2$, considering all tests, was 2.4%, pH 9 was 2.6% and pH 8 was 2.8%. According to Bulatovic [2], in spite of the preferential adsorption of starch onto the surface of hematite, the reduction in pH also increases the adsorption of this reagent onto a quartz surface, which may contribute to the lower flotation of this mineral. With regards to the flotation of a pure mineral, Kar et al. [10] found that reagents that increase the hematite depression rates also increase the quartz depression rates.

The silica content in the iron concentrates increased as the dosages of depressants were increased, irrespective of the pH conditioning. Flotamill75 was found to result in a higher SiO$_2$ content in the iron concentrate in all pH conditioning, despite the smaller iron recovery, indicating low selectivity. The FF01 was found to result in similar SiO$_2$ and iron recovery, regardless of the pH conditioning. For FF73, the silica content was higher at pH 8 and 9. Flokit415 was found to have the highest silica content at a pH of 8 in both dosages, which coincided with it having the highest metal recovery percentage. Using pH conditioning of 9 and 10 its behavior was similar.

In the flotation tests, no clear distinction was observed between ground corn and cassava flour; this supports the theory put forward by Breuning et al. [6], which states that in addition to botanical sources, other factors, such as cultivation practices, growing seasons, processing conditions, and granulometry, affect the properties of a reagent and, consequently, interfere in the behavior of the same.

### 3.2. Zeta potential measurements

The curves of the zeta potential for hematite in both the absence and presence of ground corn and cassava flour are shown in Fig. 5. The isoelectric point (IEP) of hematite was determined in pH 6.7.
It is possible to observe that at acidic pH values, the positive zeta potentials of hematite approach a neutral potential in the presence of starches, which indicates that there is an electrostatic interaction between starches and the surface of hematite. After the IEP, which is in the region of more alkaline pH values, the continuous reduction of the zeta potential can be due to the chemisorption between the reagent and the surface of hematite. According to Raju et al. [4] the adsorption of dextrin to the surface of magnetite could occur irrespective of the surface charge, provided that the metal sites of its surface are hydroxylated, being the maximum hydroxylation in the alkaline pH region, characterizing a chemical adsorption.

At more alkaline pH, between pH values of 8 and 10, the reagents Flokit415 and FF73 were found to more significantly affect the zeta potential, can be associate to higher density of adsorption on hematite. This is consistent with results of flotation tests, in which the depressants were conditioned in pH’s 8, 9 and 10, and the highest iron recovery, in general, were obtained using FF73 and Flokit415.

A much more intense reduction of the zeta potential was observed for cassava flour than for ground corn at acidic pH values. The presence of FF73 shifted the IEP from a pH of 6.7–5.0, while with FF01 shifted to 5.5. The value of the IEP not changed when ground corn (i.e., Flokit415 and Flotami75) was added. The lower values of the zeta potential in the presence of cassava flour may indicate that there was a higher degree of aggregation in these systems and that the density of the adsorption was greater. In dispersion tests, Matos et al. [9] observed that for iron ores containing slurry, cassava starch resulted in a greater amount of aggregation occurring than corn starch did. According to Breuninger et al. [8], the amyllopectin content in cassava starch is greater than in other starches, which is the component that is responsible for the flocculation ability of starch, as demonstrated by Weissenborn [5].

4. Conclusions

The reduction of the pH values of the depressant conditioning from 10 to 9 and 8 resulted in higher iron recovery, but it also led to a slight increase in the silica content in the iron concentrate.

The depressant cassava flour FF73 presented the highest iron recovery and intermediates SiO2 content in the iron concentrate, being the recommended. The results of FF01 showed no significant variation to iron recovery and SiO2 content, regardless of the pH conditioning. Flokit415 was found to have the highest iron recovery and SiO2 content at pH conditioning of 8. Flotami75 was found to result in a higher SiO2 content in the iron concentrate, despite the smaller iron recovery, indicating low selectivity.

The reagents FF73 and Flokit415 affected more significantly the zeta potential around pH of depressant conditioning (8–10) and these reagents achieved, in general, the highest iron recovery.

A much more intense reduction of the zeta potential in the acidic pH range was observed for cassava flour than for ground corn, which indicates that there was a higher degree of aggregation in these systems as well as a greater density of adsorption. But in the flotation tests, no clear distinction could be made between ground corn and cassava flour.

Conflicts of interest

The authors declare no conflicts of interest.

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