Effect of EDTA on quartz and hematite flotation with starch/amine in an aqueous solution containing Mn\(^{2+}\) ions

Abstract

In this paper, a detailed study of the influence of Mn\(^{2+}\) ions on quartz and hematite flotation (at pH 10.5 with starch/amine as depressor/collector) in the absence and presence of ethylenediaminetetraacetic acid (EDTA) is presented. By using zeta potential measurement and a careful analysis of manganese species present in water for dosages in which manganese hydroxide precipitated, we confirmed that the depression of both minerals by Mn\(^{2+}\) ions is due to the following: (i) the adsorption of Mn hydroxy complexes (Mn\(_3\)(OH)\(_4\))\(^{2+}\) and Mn(OH)\(^{2+}\)); (ii) Mn\(^{2+}\) and mainly (iii) the precipitation of Mn(OH)\(_2\) on mineral surfaces. These effects hindered the adsorption of amine species on the surfaces of the minerals (quartz and hematite). EDTA was used to complex Mn\(^{2+}\) to restore the recoveries of both minerals. This was confirmed by the species distribution diagrams of Mn and EDTA-Mn in water. Conditioning with starch followed by amine at pH 10.5 enabled a selective separation of these minerals.

Keywords: Iron ore, cationic flotation, amine, corn starch, ethylenediaminetetraacetic acid complexing agent, EDTA, manganese species.

1. Introduction

Reverse cationic flotation is commonly used to concentrate the pellet feed fraction (~150 µm) of low-grade iron ores (25% to 45% Fe). Currently, ether amine acetate with a neutralization degree of 30%–50% is used as the silicate gangue (quartz) collector and starch is used as the depressant of iron oxide minerals (hematite, magnetite or goethite) at pH 10–10.5 (Araujo et al., 2005, Filippov et al. 2014). Reductions in the performance of the cationic flotation of iron ores of high grade Mn (MnO > 1%) has been observed in some mines of the Quadrilátero Ferrífero/Brazil.

通常，多元金属离子（如Ca\(^{2+}\), Al\(^{3+}\) and Mg\(^{2+}\)）在水中被电荷中和的矿物表面吸引，导致絮凝。此外，Mn\(^{2+}\)等金属离子也可能与这些表面的氢氧根（OH\(^-\)）反应形成氢氧化物，这可能导致絮凝。此外，Mn\(^{2+}\)还可能与与之反应的金属氢氧化物形成复合物，从而增加絮凝效果。因此，通过调整絮凝条件，如pH值、温度和EDTA浓度，可以优化絮凝效果。
concentration. However, this reaction is very slow, with an equilibrium time of 4 days (Chang et al., 1983).

Cruz and Lima (2015) studied the influence of Mn$^{2+}$ ions in water on reverse cationic flotation of an iron ore sample (44.7% Fe and 31.8% SiO$_2$). They verified the minor influence of Mn$^{2+}$ ions on all response variables evaluated: mass recovery, Fe metallurgical recovery and the grade of Fe and SiO$_2$ in the obtained concentrates for MnCl$_2$ concentrations from 600 g/ton. The conditioning of a pulp with EDTA (720 g/ton) in the presence of MnCl$_2$ (600 g/ton) at natural pH before addition and conditioning with corn starch (400 g/ton) and amine (50 g/ton) at pH 10.5 produced a concentrate with 63% Fe and 5.1% SiO$_2$.

This study presents the influence of Mn$^{2+}$ ions on the floatability and zeta potential values of quartz and hematite, which are the main minerals present in the iron ore previously studied by Cruz and Lima (2015), at pH 10.5 with: i) ether amine, ii) starch/ether amine and iii) chelating EDTA/starch/ether amine. The effects of manganese ions on both minerals’ surface properties have not been deeply investigated.

2. Materials and methods

2.1 Mineral samples and reagents

Table 1 presents the chemical compositions of the mineral samples from the Quadrilátero Ferrífero, Brazil, used in the micro flotation (size fraction of −295 +147 μm) tests and zeta potential determinations (size fraction of −37 μm) (Lelis, 2014).

<table>
<thead>
<tr>
<th>Size (μm)</th>
<th>Quartz</th>
<th>Hematite</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>ppm (x10$^{-3}$)</td>
<td>%</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>LOI</td>
<td>Fe</td>
</tr>
<tr>
<td>−295+147</td>
<td>99.54</td>
<td>0.19</td>
</tr>
<tr>
<td>−37</td>
<td>98.88</td>
<td>0.25</td>
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</table>

LOI - loss of ignition

The reagents used in the micro-flotation tests and zeta potential measurements were as follows: i) commercial ether amine acetate with a 50% neutralization degree (Clariant A.S.) as the collector; ii) commercial corn starch (Unilever A.S.) as the depressant; iii) manganese chloride tetrahydrate (MnCl$_2$·4H$_2$O) (LabSynth Ltd.); iv) EDTA (C$_{10}$H$_{14}$N$_2$O$_7$·4H$_2$O) (LabSynth Ltd.) as the complexing agent; v) sodium chloride (NaCl) (Santa Helena Ltd.) as the ionic medium; vi) thymolphthalein (LabSynth Ltd.) to buffer the pH at 10.5 and vii) sodium hydroxide (NaOH) and HCl (Vetec Ltd.) for pH control. Distilled water was used in all tests and reagent preparation, except for thymolphthalein solutions, which were prepared using hydrated ethyl alcohol.

2.2 Micro flotation tests

The micro flotation tests (two replicates for each condition) were performed in a Hallimond modified cell at pH 10.5 at maximum recovery (−100%) for both minerals, which was achieved with dosages of ether amine acetate of 50 mg/L (13.5 mg/g) for hematite and 2.5 mg/L (0.675 mg/g) for quartz (Lelis, 2014). The weight of each mineral sample was 1 g, and the solution in the Hallimond cell was of 270 mL. The recoveries of both minerals were determined as a function of the following conditions: i) corn starch dosage (0 to 1000 mg/L (0 to 270 mg/g)); ii) MnCl$_2$ dosage (0 to 200 mg/L (0 to 54 mg/g)); iii) corn starch dosage (0 to 10 mg/L (0 to 2.7 mg/g)) at 10 mg/L (2.7 mg/g) and 200 mg/L (54 mg/g) dosages of MnCl$_2$; iv) EDTA dosage to 200 mg/L (54 mg/g) MnCl$_2$; and v) EDTA at 600 mg/L (162 mg/g), 200 mg/L (54 mg/g) MnCl$_2$, with and without corn starch.

The conditioning times of the reagents were respectively: 3 min for the amine, 6 min for the MnCl$_2$, and 5 min for the starch and EDTA. In the complexation tests of Mn$^{2+}$ by EDTA (iv), initially the mineral samples were conditioned with MnCl$_2$ (5 min) at approximately pH 7 and were followed by EDTA conditioning (5 min). Subsequently, the pH was adjusted to 10.5 by the addition of thymolphthalein and NaOH, and the samples were conditioned for 3 min more after amine was added. After the conditioning time in each condition as described before in (i) to (v) at the appropriate dosage of reagents, the mineral samples were floated for 1 min using commercial nitrogen (flow rate of 60 mL·min$^{-1}$).

2.3 Zeta potential measurements

The zeta potentials of the mineral samples were determined using a zetameter (Malvern Zetasizer Nano Z–ZEN 2600), which automatically determines the electrophoretic mobility of the particles and transforms it to the zeta potential ($\zeta$) using the Smoluchowski equation. All zeta potential measurements were performed at a constant ionic strength (10$^{-4}$ M NaCl) and pH (10.5).

Considering the size distribution of the −37 μm size fraction, performed by a laser size analyser (Cilas 1064) as presented in Table 2, it was observed that approximately 15.3% and 16.7% of the quartz and hematite particles, respectively, were smaller than 10 μm. Mineral suspensions (0.01% w/w) were
prepared by the addition of 0.164 g (for quartz) and 0.150 g (for hematite) of the −37 µm size fraction in 250 mL of the 10−4 M NaCl solution. The suspensions were homogenized by inversion and settled for 20 min for hematite (density of 5.31 g cm−3) and 40 min for quartz (density of 2.65 g cm−3) in such a manner that supernatant particles had a size below 10 µm, in accordance with Stokes’ law. The suspensions were then transferred to 50 mL beakers, and the pH was adjusted with NaOH, followed by the addition of the reagents (as described in the previous paragraph) under constant agitation in a magnetic shaker. The suspension pH was measured, and an aliquot removed by a syringe from the top of suspension was slowly poured into the folded capillary cell and introduced to the zetameter.

3. Results and discussion

3.1. Manganese species in water

Figure 1 shows the diagram of Mn species that are present at 25 °C in water and were determined on the basis of the solubility and equilibrium constants of the following reactions (Martel and Smith, 2003):

\[
\begin{align*}
\text{Mn}^{2+} + \text{OH}^- & \rightleftharpoons \text{Mn(OH)}^+ & \log K = 3.4 \\
\text{Mn}^{2+} + 4\text{OH}^- & \rightleftharpoons \text{Mn(OH)}_4^{2-} & \log K = 7.7 \\
2\text{Mn}^{2+} + \text{OH}^- & \rightleftharpoons \text{Mn}_2(\text{OH})^{3+} & \log K = 3.4 \\
2\text{Mn}^{2+} + 3\text{OH}^- & \rightleftharpoons \text{Mn}_2(\text{OH})_3^+ & \log K = 18.1 \\
\text{Mn(OH)}_{2(S)} & \rightleftharpoons \text{Mn}^{2+} + 2\text{OH}^- & \log K_{SO} = -12.8
\end{align*}
\]

Based on Figure 1, at pH 10.5, the significant Mn species in the water solution are Mn2(\text{OH})^{3+} (10−4 M), Mn2+ (10−5.8 M) and MnOH+ (10−5.9 M). This means that for the addition of 200 mg/L of MnCl2 (−1.6 × 10−3 M), almost 87 mg of Mn(OH)2 is deposited.

The equations for Mn complexation by EDTA, and the respective equilibrium constants are presented below (Martel and Smith, 2003):

\[
\begin{align*}
\text{Mn}^{2+} + \text{EDTA}^{−4} & \rightleftharpoons \text{MnEDTA}^{2−} & \log K = 13.9 \\
\text{MnEDTA}^{2−} + \text{H}^+ & \rightleftharpoons \text{MnHEDTA}^{−1} & \log K = 3.1
\end{align*}
\]

By combining Equations (6) and (7), we obtain

\[
\text{Mn}^{2+} + \text{EDTA}^{−4} + \text{H}^+ \rightleftharpoons \text{MnHEDTA}^{−1} \quad \log K = 17
\]

From the equilibrium constant of Equation (8), at pH 10.5, we get

\[
[MnEDTA^{−1}] = 10^{6.5} [\text{Mn}^{2+}] [\text{EDTA}^{−4}]
\]

The mass balance of the Mn species in the solution can be written as

\[
[Mn] = [\text{Mn}^{2+}] + 2 \times 10^{11} [\text{Mn}^{2+}][\text{OH}]^3 + 10^{13} [\text{Mn}^{2+}][\text{EDTA}^{−2}]
\]
Effect of EDTA on quartz and hematite flotation with starch/amine in an aqueous solution containing Mn$^{2+}$ ions

3.2 Microflotation tests

Figures 2a and 2b depict the recoveries of quartz and hematite, respectively, as a function of the corn starch and MnCl$_2$ concentrations under the conditions of the maximum recoveries of both minerals: pH 10.5, amine concentrations of 2.5 mg/L (0.675 mg/g) for quartz and 50 mg/L (13.5 mg/g) for hematite.

As observed in Figure 2a, the quartz recoveries have almost the same values (up to 10 mg/L or 2.7 mg/g) for both starch and MnCl$_2$. At concentrations above 10 mg/L (2.7 mg/g), MnCl$_2$ is more efficient than starch at depressing quartz. In addition, flotation results show that a decrease in quartz recovery could be due to a competitive adsorption of Mn(OH)$_{2+}$ deposited on the quartz surface; the adsorption of Mn$_3$(OH)$_4^{2+}$, Mn$_2^+$, Mn(OH)$^+$ and aminium ions and/or the precipitation of Mn(OH)$_{2+}$ on the mineral surfaces (see Figure 1) (Fuerstenau et al., 1985).

MnCl$_2$ is a powerful depressant for hematite (Figure 2b) compared to quartz (Figure 2a). According to previous studies (Carlson and Kawatra, 2013, Rao, 2004), the Cl$^-$ ion reacts with the uncharged hydrated iron oxide surface of hematite to form a positively charged chlorocomplex. Therefore, the electrostatic attraction of other aminium ions by hematite decreases, which causes the depression. The flotation of both minerals pretreated with MnCl$_2$ (Figures 3a and 3b) is severely affected by Mn and corn starch together, showing a synergetic effect (i.e. greater than the depression effects of both reagents separately), as presented in Figure 2. The addition of starch had a reduced effect on the flotation of hematite pretreated with MnCl$_2$ compared to quartz, which can be ascribed to the previous adsorption of Cl$^-$ on the hematite surface (Cromières et al., 2002, Carlson and Kawatra, 2013, Rao, 2004) (see Figure 3b).

Figure 2 presents the influence of EDTA on hematite and quartz recoveries. The mineral recoveries are restored after conditioning with EDTA. However, the reagent concentration is approximately three times that of Mn species in aqueous solution. The EDTA concentration required to restore quartz recovery is 100 mg/L less than that required for hematite recovery, probably because of the higher amine affinity with quartz compared to hematite. The addition of corn starch after conditioning the minerals with EDTA (500 mg/L (135 mg/g) for quartz and 600 mg/L (162 mg/g) for hematite) results in high quartz recovery (90%) and very low hematite recovery because of the higher affinity of starch for hematite than for quartz. Based on these results, it is possible to restore the selectivity between quartz and hematite by reverse cationic flotation in an aqueous solution containing Mn$^{2+}$ after complexing it with EDTA, which is in accordance with the results of bench flotation tests of Cruz and Lima (2015) mentioned previously.

Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2</td>
</tr>
<tr>
<td>Quartz</td>
<td>2.59</td>
</tr>
<tr>
<td>Hematite</td>
<td>3.56</td>
</tr>
</tbody>
</table>

Corn starch is much more efficient in depressing hematite (Figure 2b) than quartz (Figure 2a), which is in accordance with the adsorption mechanisms of starch on hematite proposed by several researchers:

i) hydrogen bonding (Kar et al., 2013) and

ii) the chemical character, such as the formation of a surface complex with iron ions (Kar et al., 2013, Pavlovic and Brandão, 2003).

Figure 3

Recovery of quartz (a) and hematite (b) as a function of corn starch and MnCl$_2$ concentration at pH 10.5 and amine (2.5 mg/L (0.675 mg/g) - quartz and 50 mg/L (13.5 mg/g) - hematite). Standard deviation of 0.79% for quartz and 0.04% for hematite.

Figure 4

Recovery of quartz (a) and hematite (b) as a function of corn starch and MnCl$_2$ concentration at pH 10.5 and amine (2.5 mg/L (0.675 mg/g) - quartz and 50 mg/L (13.5 mg/g) - hematite). Standard deviation of 0.86% for MnCl$_2$ (10 mg/L (2.7 mg/g)) and 0.29% for MnCl$_2$ (200 mg/L (54 mg/g)).
3.3 Zeta potential measurements

The influence of the studied reagents (ether amine acetate, corn starch, MnCl₂, and EDTA) at pH 10.5 on the zeta potentials of quartz and hematite is presented in Figure 5.

The zeta potential of quartz varies from −51.8 to −40.94 mV (Figure 5a I and II) and from −44.4 to −31.4 mV for hematite (Figure 5b I and II) after conditioning with only MnCl₂ and 200 mg/L EDTA at pH 10.5. I - without reagent; II - ether amine (50 mg/L); III - corn starch (100 mg/L); IV - MnCl₂ (200 mg/L); V - MnCl₂ (200 mg/L)/ether amine (50 mg/L); VI - MnCl₂ (200 mg/L)/EDTA (600 mg/L); VII - MnCl₂ (200 mg/L)/EDTA (600 mg/L)/starch (100 mg/L) and VIII - MnCl₂ (200 mg/L)/EDTA (600 mg/L)/starch (100 mg/L)/amine (50 mg/L). Standard deviation of 2.56 mV for quartz and 2.01 mV for hematite.

The negative zeta potential moduli of both minerals (quartz and hematite) compared to the values without reagents (Figures 5a I and 5b I) drop after conditioning with corn starch (Figures 5a III and 5b III). This is probably related to a partial concealment of the hematite and quartz surface charges by very large adsorbed starch molecules. Based on microflotation tests, isotherm adsorption, zeta potential measurements and infrared spectroscopy, several researchers concluded that starch adsorption on the hematite surface occurs through hydrogen bonding (Kar et al., 2013) and surface reactions involving iron ions (Kar et al., 2013, Pavlovic and Brandao, 2003). Montes-Sotomayor et al. (1998) reported that starch adsorbed on quartz will desorb in an alkaline medium in the presence of alkylammonium salt according to the collector concentration and pH (competing adsorption), which can explain the stronger depression of hematite compared to quartz (Figures 2a and 2b).

The zeta potential reversion from negative to positive for quartz and hematite in the presence of MnCl₂ (concentration of 200 mg/L = 1.6 × 10⁻³ M) (Figures 5a IV and 5b IV) is probably related to the adsorption of Mn species (Mn₃(OH)₆⁺ (10⁻⁴ M), Mn₂⁺ (10⁻⁵.8 M) and MnOH⁻ (10⁻⁵.9 M)) in an aqueous solution at pH 10.5 (Marcel and Smith, 2003, Fuerstenau et al., 1985). After conditioning the minerals with amine (Figures 5a V and 5b V), the zeta potentials return to negative values. However, the absolute values are smaller than the values determined in conditions 1, II and III. Vidyadhar et al. (2002) proved by infrared spectroscopy that beyond the ether amonium ions and molecular ether amine, the acetate anions adsorb on the quartz surface, which explains the negative zeta potential of quartz conditioned with MnCl₂/amine. Probably the same behaviour occurred with hematite. The large difference in magnitude between the negative zeta potentials of hematite and quartz could be related to the adsorption of Cl⁻ ions in the solution (1.6 × 10⁻³ M) on the hematite surfaces, which drops IEP of hematite (Carlson and Kawatra, 2013, Hesleiter et al., 1987). However, the adsorption of Mn hydroxyl complex and the precipitation of Mn(OH)₂ sufficiently prevent hydrophobicity by ether amine adsorption (Figures 2a and 2b).

EDTA can leach the Fe³⁺ ions from hematite (Chang and Matijevic, 1983) and from β-FeOOH (Rubio and Matijevic, 1979) in the range pH 7.5-12. But, the equilibrium time for this reaction is high and its zeta potential did not have a pronounced variation as in pH < 7 (specific adsorption of anionic EDTA species on mineral surface). However, as shown in Figures 5a VI and 5b VI, the zeta potentials of quartz and hematite conditioned with MnCl₂/EDTA are more negative than those of the minerals conditioned with only MnCl₂ (IV) or MnCl₂/amine.
(V), suggesting the complexation of Mn by EDTA. By considering the mass balance of Mn species (Equation 10), from the addition of 600 mg (−1.8 × 10⁻³ M) of EDTA in the solution, where [Mn²⁺] = 1.6 × 10⁻³ M, the Mn species concentrations in water are [MnEDTA²⁻] = 2.3 × 10⁻² M and [Mn₂(OH)₆]⁺ = 2.04 × 10⁻¹⁹ M. These results demonstrate that almost all Mn species were complexed by EDTA.

The negative zeta potentials of both minerals conditioned with MnCl₂/EDTA/starch (Figures 5a VII and 5b VII) and Mn(OH)₂ on the mineral surfaces. The addition of EDTA restored the mineral recoveries through Mn²⁺ complexation; after conditioning the minerals with starch followed by amine at pH 10.5, only the recovery of quartz was restored. This means that the selectivity in the reverse cationic flotation of iron ores in pulps containing Mn²⁺ species is possible when the iron ores are first conditioned with EDTA at a pH ~7 before additional conditioning with starch and amine at pH 10.5.

4. Conclusions

Based on the results obtained in this study, we conclude that the depression of both quartz and hematite by Mn²⁺ specimens is due to: (i) the adsorption of Mn hydroxy complexes (Mn₃(OH)₁⁴ and Mn(OH)₉), (ii) Mn²⁺, and mainly (iii) the precipitation of Mn(OH)₂, on the mineral surfaces. The addition of EDTA restored the mineral recoveries through Mn²⁺ complexation; after conditioning the minerals with starch followed by amine at pH 10.5, only the recovery of quartz was restored. This means that the selectivity in the reverse cationic flotation of iron ores in pulps containing Mn²⁺ species is possible when the iron ores are first conditioned with EDTA at a pH ~7 before additional conditioning with starch and amine at pH 10.5.

5. Acknowledgments

The authors gratefully acknowledges the financial support provided by the FAPEMIG, CAPES, PROPP/UFOP and CNPq scholarships.

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Received: 22 January 2016 - Accepted: 07 June 2016.