

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

<http://dx.doi.org/10.1590/0370-44672016690014>

## Deisiane Ferreira Lelis

Mestre pela Universidade Federal de Ouro Preto – UFOP  
Escola de Minas  
Departamento de Engenharia de Minas  
Ouro Preto – Minas Gerais – Brasil  
[deisiane.lelis@gmail.com](mailto:deisiane.lelis@gmail.com)

## Versiane Albis Leão

Professor Adjunto  
Universidade Federal de Ouro Preto - UFOP  
Escola de Minas  
Departamento de Engenharia Metalúrgica  
Ouro Preto – Minas Gerais – Brasil  
[versiane@demet.em.ufop.br](mailto:versiane@demet.em.ufop.br)

## Rosa Malena Fernandes Lima

Professora Titular  
Universidade Federal de Ouro Preto - UFOP  
Escola de Minas  
Departamento de Engenharia de Minas  
Ouro Preto – Minas Gerais – Brasil  
[rosa@demin.ufop.br](mailto:rosa@demin.ufop.br)

## 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 ( $Mn_2(OH)^{3+}$  and  $Mn(OH)^+$ ); (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  $\mu m$ ) 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.

Usually, polyvalent ions such as  $Ca^{2+}$ ,  $Al^{3+}$  and  $Mg^{2+}$  in water are attracted electrostatically by the negatively charged surfaces of the minerals or the

adsorption of hydroxy complexes and the precipitation of hydroxides on the mineral surfaces (Fuerstenau *et al.*, 1985), which can interfere with the selectivity of some flotation processes such as the reverse cationic flotation of iron ore (Pinheiro *et al.*, 2012, Lelis, 2014, Carvalho and Peres, 2004).

EDTA reacts with several metallic ions such as  $Ag^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Fe^{2+}$ ,  $Fe^{3+}$ ,  $Mn^{2+}$  and  $Al^{3+}$  (Rao, 2004). The products of these reactions are very stable (formation constant  $> 10^5$ ) (Martel and Smith, 2003). Therefore, EDTA can be used to complex these ions in aqueous solutions to prevent their deleterious effect on system flotation using amines, as in the case of the reverse cationic flotation of iron ores. However, in the flotation

process, this chelating agent interacts with the minerals in solution (Rubio and Matjevic, 1979; Chang *et al.* 1982; Chang *et al.*, 1983; Orthgiess and Dobiás, 1994; Wang and Forsberg, 1990; Rumball and Richmond, 1996).

Zeta potential measurements of sulphide minerals (pyrite, galena, arsenopyrite) (Wang and Forsberg, 1990), and metal hydrous oxides (hematite,  $\beta$ -FeOOH) (Rubio and Matjevic, 1979, Chang *et al.* 1982 ) show that in presence of EDTA, the IEP of these minerals is shifted to lower pH values, which was ascribed to specific interactions between their surfaces with complexing solute species at pH values  $< \sim 7$ . Leaching of  $Fe^{3+}$  from hematite and  $\beta$ -FeOOH depends on pH (7.5–12), temperature and EDTA

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<sup>2+</sup> ions in water on reverse cationic flotation of an iron ore sample (44.7% Fe and 31.8% SiO<sub>2</sub>). They verified the minor influence of Mn<sup>2+</sup> ions on all response variables evaluated: mass recovery, Fe metallurgical recovery and

the grade of Fe and SiO<sub>2</sub> in the obtained concentrates for MnCl<sub>2</sub> concentrations from 600 g/ton. The conditioning of a pulp with EDTA (720 g/ton) in the presence of MnCl<sub>2</sub> (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<sub>2</sub>.

This study presents the influence

of Mn<sup>2+</sup> 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 microflotation (size fraction of -295 +147

µm) tests and zeta potential determinations (size fraction of -37 µm) (Lelis, 2014).

Size (µm)	Quartz								Hematite						
	%		ppm (x10 <sup>-1</sup> )						%						
	SiO <sub>2</sub>	LOI	Fe	Al	Na	Ca	Mg	Ti	Fe <sub>T</sub>	FeO	Al <sub>2</sub> O <sub>3</sub>	MnO	CaO	MgO	TiO <sub>2</sub>
-295+147	99.54	0.19	4.1	5.3	1.0	1.8	1.3	2.3	69.3	0.39	0.39	0.02	0.01	0.01	0.02
-37	98.88	0.25	1	1.6	-	0.57	-	0.6	69.1	0.39	0.60	0.03	0.07	0.02	0.03

LOI - loss of ignition

Table 1  
Chemical composition of quartz and hematite samples used in the microflotation tests and zeta potential measurements.

The reagents used in the microflotation 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 depres-

sant; iii) manganese chloride tetrahydrate (MnCl<sub>2</sub>·4H<sub>2</sub>O) (LabSynth Ltd.); iv) EDTA (C<sub>10</sub>H<sub>14</sub>N<sub>2</sub>O<sub>8</sub>Na<sub>2</sub>·2H<sub>2</sub>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 Microflotation tests

The microflotation 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<sub>2</sub> 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<sub>2</sub>; iv) EDTA dosage to 200 mg/L (54 mg/g) MnCl<sub>2</sub>; and v) EDTA at 600 mg/L (162 mg/g), 200 mg/L (54 mg/g) MnCl<sub>2</sub>, with and without corn starch.

The conditioning times of the reagents were respectively: 3 min for the amine, 6 min for the MnCl<sub>2</sub>, and 5 min for the starch and EDTA. In the complex-

ation tests of Mn<sup>2+</sup> by EDTA (iv), initially the mineral samples were conditioned with MnCl<sub>2</sub> (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<sup>-1</sup>).

### 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 poten-

tial (ζ) using the Smoluchowski equation. All zeta potential measurements were performed at a constant ionic strength (10<sup>-4</sup> 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  $-37\mu\text{m}$  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  $5.31\text{ g cm}^{-3}$ ) and 40 min for quartz (density of  $2.65\text{ g cm}^{-3}$ ) in such a manner that supernatant particles had a size below  $10\text{ }\mu\text{m}$ , 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.

The pH of the suspension that remained in the beaker under constant stirring was measured after each zeta potential determination was completed. The pH considered for each measurement was the value obtained at the end of each test. This procedure was performed twice for each condition test and each instance was measured three times, which means a total of six determinations.

### 3. Results and discussion

#### 3.1. Manganese species in water

Figure 1 shows the diagram of Mn species that are present at  $25\text{ }^\circ\text{C}$  in wa-

ter and were determined on the basis of the solubility and equilibrium constants

of the following reactions (Martel and Smith, 2003):

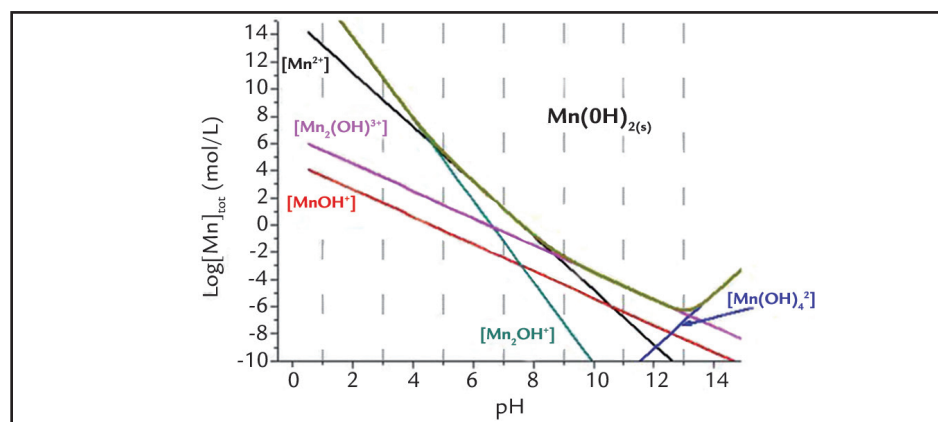
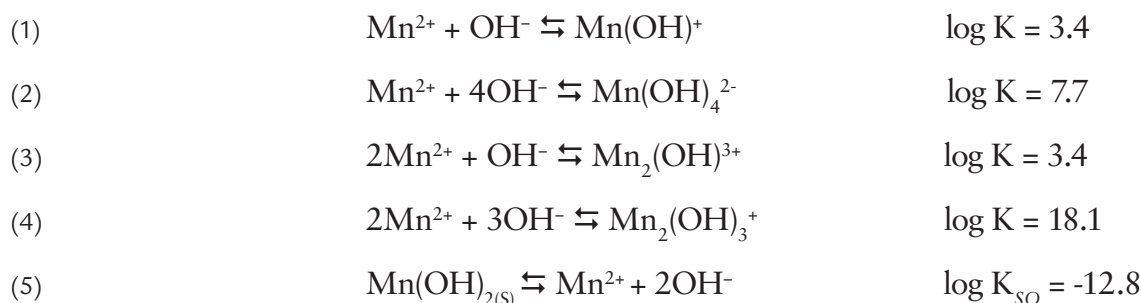


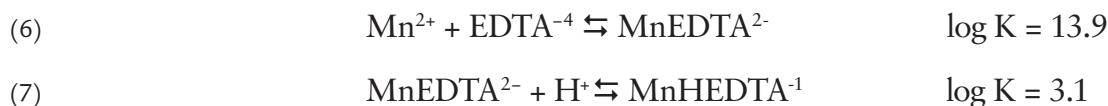
Figure 1

Diagram of Mn species at  $25\text{ }^\circ\text{C}$  in water.

Based on Figure 1, at pH 10.5, the significant Mn species in the water solution are  $\text{Mn}_2(\text{OH})_3^+$  ( $10^{-4}$  M),  $\text{Mn}^{2+}$  ( $10^{-5.8}$  M) and

$\text{MnOH}^+$  ( $10^{-5.9}$  M). This means that for the addition of 200 mg/L of  $\text{MnCl}_2$  ( $\sim 1.6 \times 10^{-3}$  M), almost 87 mg of  $\text{Mn}(\text{OH})_{2(s)}$  is deposited.

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



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



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

$$(9) \quad [\text{MnEDTA}^{-1}] = 10^{6.5} [\text{Mn}^{2+}] [\text{EDTA}^{4-}]$$

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

$$(10) \quad [\text{Mn}]_T = [\text{Mn}^{2+}] + 2 \times 10^{18.1} [\text{Mn}^{2+}]^2 [\text{OH}]^3 + 10^{13.9} [\text{Mn}^{2+}] [\text{EDTA}^{2-}]$$

Sample	Size ( $\mu m$ )										
	2	5	7	10	15	20	25	30	40	60	71
Quartz	2.59	8.01	10.57	15.33	25.73	36.87	48.44	60.10	80.06	97.25	99.40
Hematite	3.56	7.71	10.54	16.74	31.27	46.81	61.71	74.87	91.67	99.70	100.0

Table 2  
Size distribution (% undersize) of samples used in zeta potential measurements.

### 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  $Mn(OH)_{2(s)}$  deposited on the quartz surface; the adsorption of  $Mn_2(OH)_3^+$ ,  $Mn^{2+}$ ,  $Mn(OH)^+$  and aminium ions and/or the precipitation of  $Mn(OH)_{2(s)}$  on the mineral surfaces (see Figure 1) (Fuerstenau *et al.*, 1985).

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).

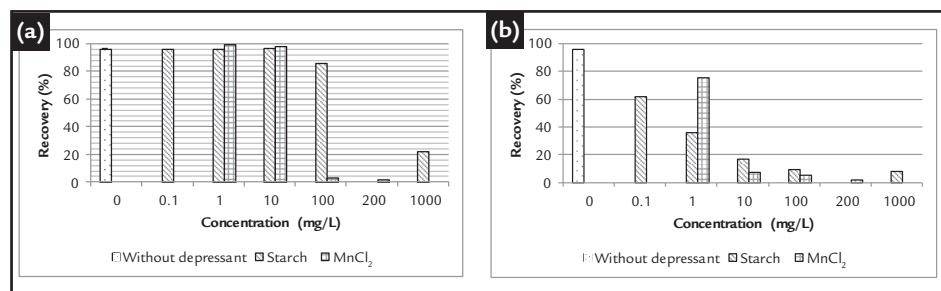


Figure 2  
Recovery of quartz (a) and hematite (b) as a function of corn starch and  $MnCl_2$  concentration at pH 10.5 and amine (2.5 mg/L (0.675 mg/g) - quartz and 50 mg/L (13.5 mg/g) hematite). Standard deviation of 0.79% for quartz and 0.04% for hematite.

$MnCl_2$  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 ether 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 ad-

dition 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 4 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 be-

cause 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.

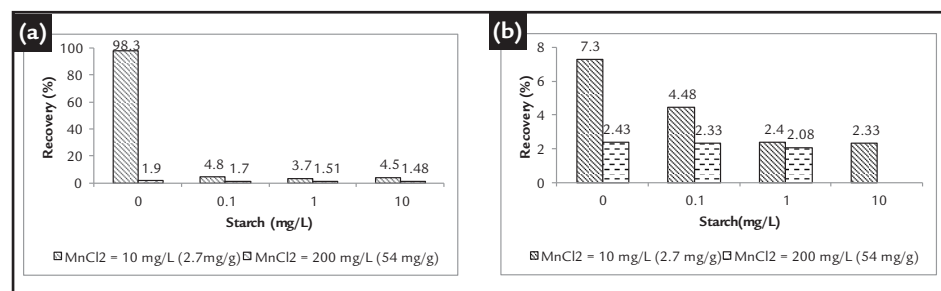
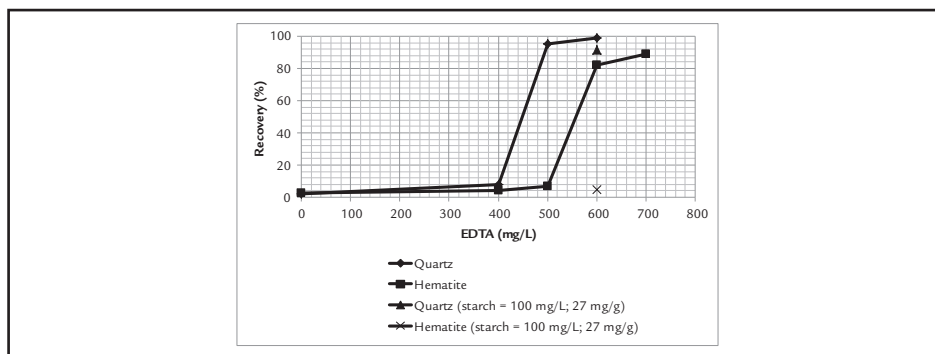


Figure 3  
Recovery of quartz (a) and hematite (b) as a function of corn starch concentration at pH 10.5. Amine concentrations are 2.5 mg/L (0.675 mg/g) for quartz and 50 mg/L (13.5 mg/g) for hematite. Standard deviation of 0.86% for  $MnCl_2$  (10 mg/L (2.7 mg/g)) and 0.29% for  $MnCl_2$  (200 mg/L (54 mg/g)).

Figure 4

Recovery of quartz and hematite as a function of EDTA at pH 10.5 and 200 mg/L (54 mg/g)  $\text{MnCl}_2$ . Amine concentrations are 2.5 mg/L (0.675 mg/g) for quartz and 50 mg/L (13.5 mg/g) for hematite. Standard deviation of 0.87% for quartz and 2.38% for hematite.



### 3.3 Zeta potential measurements

The influence of the studied reagents (ether amine acetate, corn starch,  $\text{MnCl}_2$  and EDTA) at pH 10.5 on the zeta potentials of quartz and hematite is presented in Figure 5.

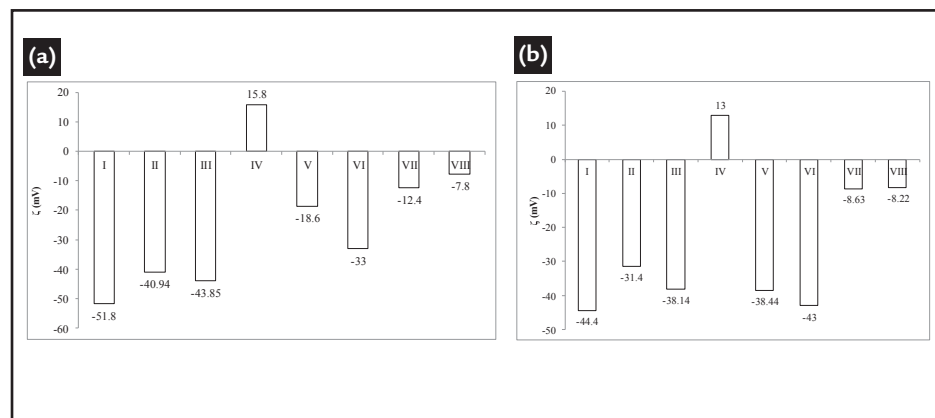
The zeta potential of quartz varies from  $-51.8$  to  $-40.94$  mV (Figure 5a I and II) and from  $-44.4$  to  $-31.4$  mV for hematite (Figure 5b I and II) after conditioning

with ether amine. This is probably due to the electrostatic ether aminium attraction, co-adsorption of molecular amine and molecular amine precipitation on the mineral surfaces at pH 10.5 (Churaev *et al.*, 2000, Kou *et al.*, 2010, Ma, 2008). Because the zeta potential of quartz is more negative than that of hematite (Figure 5) (Fuerstenau *et al.*, 1985), the electrostatic attraction of

quartz by ether aminium is higher owing to hydrogen bonding between silanol groups on the quartz surface and ether aminium ions (Vidyadhar, *et al.*, 2002). This explains the lower collector concentration required for the flotation of quartz (Figure 2a) compared to hematite (Figure 2b), suggesting that ether amine is a more powerful collector for quartz than hematite.

Figure 5

Zeta potential of quartz (a) and hematite (b) at an ionic strength of  $10^{-4}$  M NaCl and pH 10.5. I - without reagent; II - ether amine (50 mg/L); III - corn starch (100 mg/L); IV-  $\text{MnCl}_2$  (200 mg/L); V -  $\text{MnCl}_2$  (200 mg/L)/ether amine (50 mg/L); VI -  $\text{MnCl}_2$  (200 mg/L)/EDTA (600 mg/L); VII -  $\text{MnCl}_2$  (200 mg/L)/EDTA (600 mg/L)/starch (100 mg/L) and VIII -  $\text{MnCl}_2$  (200 mg/L)/EDTA (600 mg/L)/starch (100 mg/L)/amine (50 mg/L). Standard deviation of 2.56 mV for quartz and 2.01mV 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 Brandão, 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  $\text{MnCl}_2$  (concentration of 200 mg/L =  $1.6 \times 10^{-3}$  M) (Figures 5a IV and 5b IV) is probably related to the adsorption of Mn species ( $\text{Mn}_2(\text{OH})_3^+$  ( $10^{-4}$  M),  $\text{Mn}^{2+}$  ( $10^{-5.8}$  M) and  $\text{MnOH}^+$  ( $10^{-5.9}$  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 I, II and III. Vidyadhar *et al.* (2002) proved by infrared spectroscopy that beyond the ether aminium ions and molecular ether amine, the acetate anions adsorb on the quartz surface, which explains the negative zeta potential of quartz conditioned with  $\text{MnCl}_2$ /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  $\text{Cl}^-$  anions in the solution ( $1.6 \times 10^{-3}$  M) on the hematite surfaces, which drops IEP of hematite (Carlson and Kawatra, 2013, Hesleitner *et al.*, 1987). However, the adsorption of Mn hydroxy complex and the precipitation of  $\text{Mn}(\text{OH})_2$  sufficiently prevent hydrophobicity by ether amine adsorption (Figures 2a and 2b).

EDTA can leach the  $\text{Fe}^{3+}$  ions from hematite (Chang and Matijevic, 1983) and from  $\beta\text{-FeOOH}$  (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  $\text{MnCl}_2$ /EDTA are more negative than those of the minerals conditioned with only  $\text{MnCl}_2$  (IV) or  $\text{MnCl}_2$ /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 ( $\sim 1.8 \times 10^{-3}$  M) of EDTA in the solution, where  $[Mn^{2+}] = 1.6 \times 10^{-3}$  M, the Mn species concentrations in water are  $[MnEDTA^{2-}] = 2.3 \times 10^{-8}$  M and  $[Mn_2(OH)_3^+] = 2.04 \times 10^{-19}$  M. These results demonstrate that almost all Mn species were complexed by EDTA.

The negative zeta potentials of both minerals conditioned with  $MnCl_2$ /EDTA/starch (Figures 5a VII and 5b VII) and

with  $MnCl_2$ /EDTA/starch followed by amine (Figures 5a VIII and 5b VIII) are less than those of the minerals conditioned with  $MnCl_2$ /EDTA (Figures 5a VI and 5b VI). When compared with quartz, the magnitude of the decrease of the negative zeta potential of hematite after  $MnCl_2$ /EDTA/starch conditioning is greater. The opposite behaviour is observed for the minerals conditioned with  $MnCl_2$ /EDTA/starch/amine. This is probably related to the high affinity of starch for hematite (hydrogen bonding and iron

ion complexation by starch (Pavlovic and Brandão, 2003) and amine for quartz (electrostatic attraction followed by hydrogen bonding with the silanol group on the mineral surface (Vidyadhar *et al.* 2002). Despite the adsorption of ether aminium ions and ether amine on the hematite surface (Figure 5b VIII), the amount of amine adsorbed on the mineral surface is insufficient to produce surface hydrophobicity, which explains the low recovery of hematite in the microflotation test in this condition, as presented in Figure 4.

#### 4. Conclusions

Based on the results obtained in this study, we conclude that the depression of both quartz and hematite by  $Mn^{2+}$  specimens is due to: (i) the adsorption of Mn hydroxy complexes ( $Mn_2(OH)_3^+$  and  $Mn(OH)^+$ ), (ii)  $Mn^{2+}$ , and mainly (iii) the precipitation of

$Mn(OH)_2$  on the mineral surfaces. The addition of EDTA restored the mineral recoveries through  $Mn^{2+}$  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  $Mn^{2+}$  species is possible when the iron ores are first conditioned with EDTA at a pH  $\sim 7$  before additional conditioning with starch and amine at pH 10.5.

#### 5. Acknowledgments

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

#### 6. References

- ARAUJO, A.C., VIANA, P.R., PERES, A. E. C. Reagents in iron ore flotation. *Minerals Engineering*, n.18, p. 219-224, 2005.
- CARLSON J. J., KAWATRA, S. K. Factors affecting zeta potential of iron oxides. *Mineral Processing and Extractive Metallurgy Review*. n. 34, p.269-303, 2013.
- CARVALHO, M. R., PERES, A. E. C. Interferência de cátions  $Ca^{2+}$  na deslamagem e flotação de minério de ferro. *Revista Escola de Minas*, v. 57, n.2, p. 99-102, 2004.
- CROMIÈRES, L., MOULIN, V., FOUREST, B., GIFFAUT, E. Physico-chemical characterization of the colloidal hematite/water interface: experimentation and modelling. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, v. 202, p. 101-115, 2002.
- CHURAEV, N.V., SERGEEVA, I.P., SOBOLEV, V.D., JACOBASCH, H.-J., WEIDENHAMMER, P., SCHMITT, F.-J. Modification of quartz surfaces using cationic surfactant solutions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, v. 164, p.121-129, 2000.
- CHANG, H-C., HEALY, T. W., MATIJEVIC, E. Interactions of metal hydrous oxides with chelating agents. III. Adsorption on spherical colloidal hematite particles. *Journal of Colloid and Interface Science*, v. 92, n.2, p. 469-478, 1983.
- CHANG, H-C., MATIJEVIC, E. Interactions of metal hydrous oxides with chelating agents. VI. Dissolution of hematite. *Journal of Colloid and Interface Science*, v. 92, n. 2, p. 479-488, 1983.
- CRUZ, D. G., LIMA, R. M. F. Influence of  $Mn^{2+}$  ion in reverse cationic flotation of iron ore. *Revista Escola de Minas*, v. 68, n. 3, p. 319-322, 2015.
- FILIPPOV, L.O., SEVEROV, V.V., FILIPPOVA, I.V. An overview of the beneficiation of iron ores via reverse cationic flotation. *International Journal of Mineral Processing*, v.127, p.62-69, 2014.
- FUERSTENAU, M. C. et alli. Chemistry of flotation. *American Institute of Mining, Metallurgical and Petroleum Engineers, Inc.* 1985. 177p.
- HESLEITNER, P. BABIC, D., KALLAY, N., MATIJEVIC, E. Adsorption of solid/solution interfaces. Surface charge and potential of colloidal hematite. *Langmuir*, v. 3, p.815-820, 1987.
- KAR, B., SAHOO, H., RATH, S. S., DAS, B. Investigations on different starches as

- depressants for iron ore flotation. *Minerals Engineering*, v.49, p. 1–6, 2013.
- KOU, J., TAO, D., XU, G. A study of adsorption of dodecylamine on quartz surface using quartz crystal microbalance with dissipation. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, v. 368, p. 75–83, 2010.
- LELIS, D. F. *Influência dos Cátions  $Ca^{2+}$ ,  $Mg^{2+}$  e  $Mn^{2+}$  na Flotação Catiônica de Minério de Ferro: Estudos Fundamentais*. Ouro Preto: Escola de Minas, Universidade Federal de Ouro Preto, 2014. 88f. (Dissertação de Mestrado em Engenharia Mineral).
- MA, X. Role of solvation energy in starch adsorption on oxide surfaces. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, v. 320, p. 36–42, 2008.
- MARTEL, A.E. SMITH, R. M. NIST critically selected stability constants of metals complexes. In: NIST Standard Reference Database 46, version 7, 2003. CD-ROM.
- MONTES-SOTOMAYOR, S., HOUOT, R., KONGOLO, M. Flotation of silicated gangue iron ores: mechanism and effect of starch (Technical note). *Minerals Engineering*, v. 11, n. I, p. 71-76, 1998.
- ORTHGIESS, E., DOBIÁS, B. Complexing agents as modifiers in mineral flotation - mechanism studies. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, v. 83, p. 129-141, 1994.
- PAVLOVIC, S., BRANDÃO, P. R. G. Adsorption of starch, amylose, amylopectin and glucose monomer and their effect on the flotation of hematite and quartz. *Minerals Engineering*, v. 16, p. 1117–1122, 2003.
- PINHEIRO, V. S., BALTAR, C. A. M., LEITE, J. Y. P. Flotação com amina: a importância da qualidade da água. *Revista Escola de Minas*, v. 65, n. 4, p. 549-552, 2012.
- RAO, S. R. Flotation Surfactants, In: *Surface Chemistry of Froth Flotation* (2. ed.). New York: KA/PP ed., 2004. 744p., cap. 9, p. 454-459.
- RUBIO, J., MATIJEVIC, E. Interactions of metal hydrous oxides with chelating agents. I.  $\beta$ -FeOOH-EDTA. *Journal of Colloid and Interface Science*, v. 68, n. 3, p. 408-421, 1979.
- RUMBALL, J. A., RICHMOND, G. D. Measurement of oxidation in a base metal flotation circuit by selective leaching with EDTA. *International Journal of Mineral Processing*, v. 48, p. 1-20. 1996.
- VIDYADHAR, A., RAO, K. H., CHERNYSHOVA, I. V., PRADIP, FORSSBERG K. S. E. Mechanisms of amine-quartz interaction in the absence and presence of alcohols studied by spectroscopic methods. *Journal of Colloid and Interface Science*, v. 256, p. 59–72, 2002.
- WANG, X., FORSSBERG, E. EDTA-Induced flotation of sulfide minerals. *Journal of Colloid and Interface Science*, v. 140, n.1, p. 217-226, 1990.

---

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