Effect of inorganic and organic depressants on the cationic flotation and surface charge of rhodonite-rhodochrosite

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Abstract

Silicates (rhodonite, tephroite, spessartine) and the carbonate (rhodochrosite) of manganese are of economic interest in silicate-carbonated manganese ores. The recovery of both mineral classes by flotation constitutes a challenge; rhodochrosite is a slightly soluble mineral that can release Mn^{2+} ions in pulp. In this work, the effects of inorganic and organic depressants on the cationic flotation at pH 10 with ether amine acetate and the surface charges of rhodonite and rhodochrosite have been investigated. For rhodonite, the influence of Mn^{2+} species on its recovery and surface charge at the conditions of maximum yield with amine has also been investigated. The organic depressants, especially the corn starch, were more effective depressants for both minerals. The poor recovery of rhodonite conditioned with $MnCl_2$ is probably related to the colloidal $Mn(OH)_2$ deposition on mineral surface. The increase in the rhodochrosite recovery with increasing water glass content is probably related to its negative value of species adsorbed on the mineral surface, since the rhodochrosite zeta potential, conditioned with this reagent, becomes more negative compared with the mineral without reagent, which attracts the ether ammonium.

keywords: Rhodonite, rhodochrosite, cationic flotation, inorganic and organic depressants, manganese ions.

1. Introduction

The beneficiation flowsheets of high grade oxidized manganese ores normally consist of crushing followed by screening. The screening oversize constitutes the lump ore products, and the undersize of the last screen is classified by hydraulic classifiers. Based on the Mn content and size distribution, in some industrial plants, the underflow from the classifier step (fraction size +0.15 mm-sinter feed) is a final product or can be concentrated by gravimetric methods, high intensity magnetic separation, and flotation (Sampaio and Penna, 2001, Aplan, 1985).

The flotation of oxide and carbonate manganese ores is carried out by fatty acid soap at alkaline pH (Lima *et al*., 2008, Acevedo, 1977, Aplan, 1985). Oxide ores with silicate gangue can be successfully concentrated by reverse flotation with amine and the depression of manganese oxides at alkaline pH. Silicate manganese ore can be floated by cationic collectors (e.g. amines) at acidic pH or by anionic collectors (e.g. oleate or hydroxamate) after manganese silicate activation with polyvalent ions. Hydrolyzed metals are formed and precipitated at pH values above the isoelectric point (IEP) of manganese minerals (Andrade, 1978; Ciminelli, 1980, Fuerstenau and Palmer, 1976).

In the flotation of manganese ores, which contain silicate manganese, carbonate manganese, dolomite and other carbonates (slightly soluble minerals), the recovery and selectivity can be very difficult due to the presence of polyvalent ions, hydroxyl complexes and hydroxide species in pulp, especially when recycled water is used in the flotation circuit. This paper presents the results of micro-flotation tests and zeta potential determination for rhodonite and rhodochrosite using a cationic collector, which is usually applied in iron ore flotation, with inorganic and organic depressants. The influence of Mn species on rhodonite recovery and surface charge at pH 10 were also investigated.

2. Materials and Methods

2.1 Mineral samples and reagents

Table 1 depicts the chemical compositions of the mineral samples (natural and synthetic). In the micro-

flotation tests and zeta potential measurements were used: Ether amine acetate with 50% of neutralization degree (Clariant A. S.) as collector; water glass (Na_2SiO_2), Na-fluorisilicate, and $MnCl_2.2H_2O$ of analytical purity (VETEC A.S.), commercial corn starch (Unilever A.S) and quebracho (Unitan A.S.) as depressants; NaOH and HCl of analytical purity (VETEC A.S.) as pH control, NaCl analytical purity (VETEC A.S.) as ionic strength control.

Mineral	Compound (wt%)										
	MnO	SiO_2	FeO	CaO	MgO	Al_2O_3	BaO	TiO_2	K_2O	Na_2O	S
Rhodonite	42.83	50.56	3.08	2.11	0.93	0.095	0.05	0.003	-	-	-
Manganese Carbonate*	61.23	0.11	-	0.21	-	-		-	0.06	0.13	0.02

*Synthetic rhodochrosite (manufactured by VETEC)

Table 1
Chemical composition of rhodonite and synthetic rhodochrosite (Andrade *et al.*, 2011, Andrade *et al.*, 2012).

Fig. 1 shows the diagram of mononuclear manganese species at 25°C in water, which was calculated based on the solubility and equilibrium constants of the following reactions (Snoeyki and Jenkins, 1980):
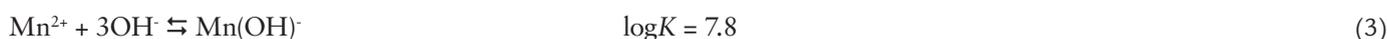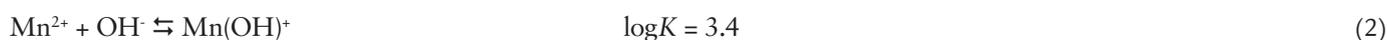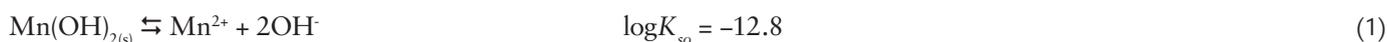
$$Mn(OH)_{2(s)} \leftrightarrows Mn^{2+} + 2OH^- \qquad \log K_{so} = -12.8 \qquad (1)$$

$$Mn^{2+} + OH^- \leftrightarrows Mn(OH)^+ \qquad \log K = 3.4 \qquad (2)$$

$$Mn^{2+} + 3OH^- \leftrightarrows Mn(OH)^- \qquad \log K = 7.8 \qquad (3)$$

2.3–Experimental methods

The micro-flotation tests (three replicates) were performed using a modified Hallimond cell equipped with a magnetic stirrer. In all tests, 1 g of rhodonite with a fraction size of –74+37 μm and not classified for manganese carbonate (synthetic rhodochrosite) was used. The rhodonite tests were first performed using 5 mg/L of amine (conditioning time of 5 min) at pH values ranging from 2–12 in order to verify the optimal flotation conditions (5 mg/L and pH 10) determined previously for this mineral (Alcântara *et al.*, 2013). These values were fixed in the tests performed with rhodochrosite. Furthermore, depression studies were performed for each mineral after conditioning with different depressant concentrations for six minutes followed by five minutes of conditioning with the previously determined optimal amine concentration. After conditioning, the mineral sample was floated for one minute using commercial nitrogen (flow rate of 75 mL/min.).
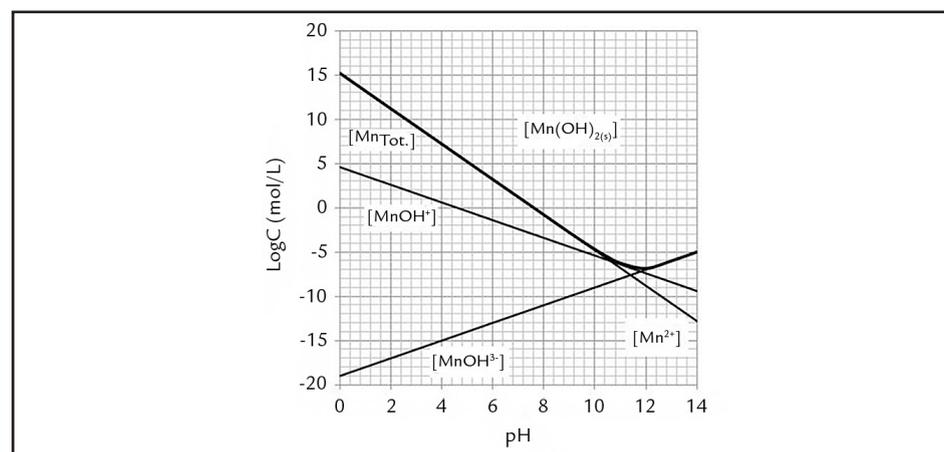
Figure 1
Diagram of manganese species in solution vs. pH; activity coefficient = 1 and T = 25 °C.

A zeta-meter (Malvern Zetasizer Nano Z–ZEN 2600) was used to determine the zeta potentials of the mineral samples. This equipment automatically determines the electrophoretic mobility of the particles and transforms it into a zeta potential (ζ) using Smoluchowiski's equation. Firstly, the zeta potential of rhodonite was determined in the pH range of 4 to 12 without reagent and conditioning with 5 mg/L of amine. For rhodochrosite and for both minerals conditioned with depressants, zeta potential was determined only at pH 10.

The experimental procedure for the zeta potential measurements was based on Nascimento *et al.* (2013). Briefly, a 0.01% w/w suspension was prepared by the addition of 0.025 g of the mineral (d_{90} of 10 μm) into a 250 mL solution of $NaCl_2$ 10^{-3} M. The suspension was transferred to a 50 mL beaker, and the pH was adjusted with hydrochloric acid (HCl) and sodium hydroxide (NaOH) under constant agitation in a magnetic shaker. The suspension pH was measured, and an aliquot was slowly poured into the folded capillary cell to measure the zeta potential using the zeta-meter. For each pH value, the zeta potential was determined as the average of the values obtained in four replicate measurements. The pH value of the suspension under constant stirring was measured after each zeta potential measurement was finished. Thus, the pH for each measurement was the value obtained at the end of each zeta potential test.

3. Results and Discussion

3.1 Micro-flotation tests

As can be observed in Fig. 2, the maximum recovery of rhodonite with 5 mg/L of amine was obtained at pH 10, confirming the value determined by Alcântara *et al.* (2013). Thus, the amine concentration and pH were fixed at 5 mg/L and 10, respectively, for all micro-flotation tests.

Figs. 3 and 4 depict the effects of different depressants on the recover-

ies of rhodonite and rhodochrosite, respectively. In general, rhodonite recovery decreased with increasing depressant dosage (Fig. 3). The organic depressants were more efficient to depress this mineral than the inorganic ones.

The recoveries of rhodonite conditioned with $MnCl_2$ were smaller than those for all tested depressants (Fig. 3).

In accordance with the Log[Mn] vs. pH diagram (Fig. 1), the Mn species present in solution at pH 10 are Mn^{2+} ($10^{-5.8}$ M = 0.0870 mg/L) and $MnOH^+$ ($10^{-5.9}$ M = 0.0692 mg/L). Table 2 shows that $Mn(OH)_2$ precipitates at all tested $MnCl_2$ dosages. The depression of rhodonite is mainly ascribed to the deposition of this colloidal species on the mineral surface.

Figure 2
Rhodonite recovery
vs. pH for 5 mg/L of ether amine acetate.
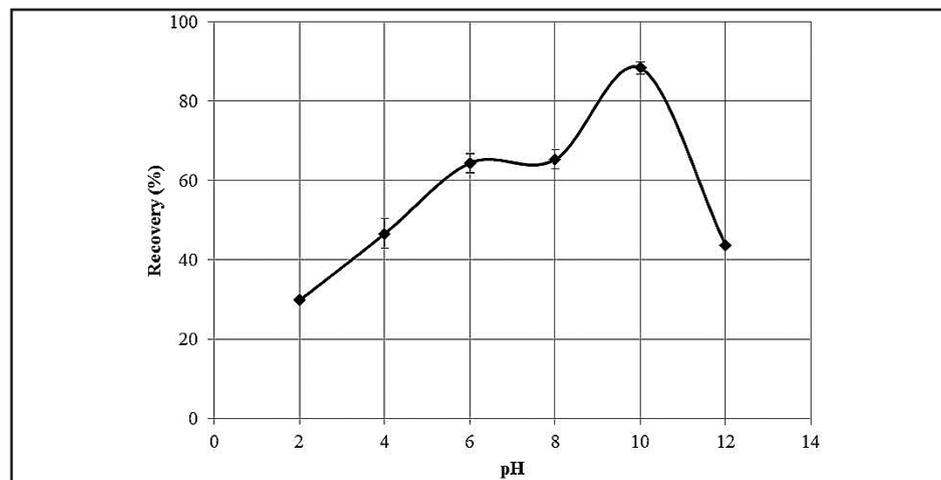
Figure 3
Recovery of rhodonite
vs. depressant dosage at pH 10
and 5 mg/L of ether amine acetate.
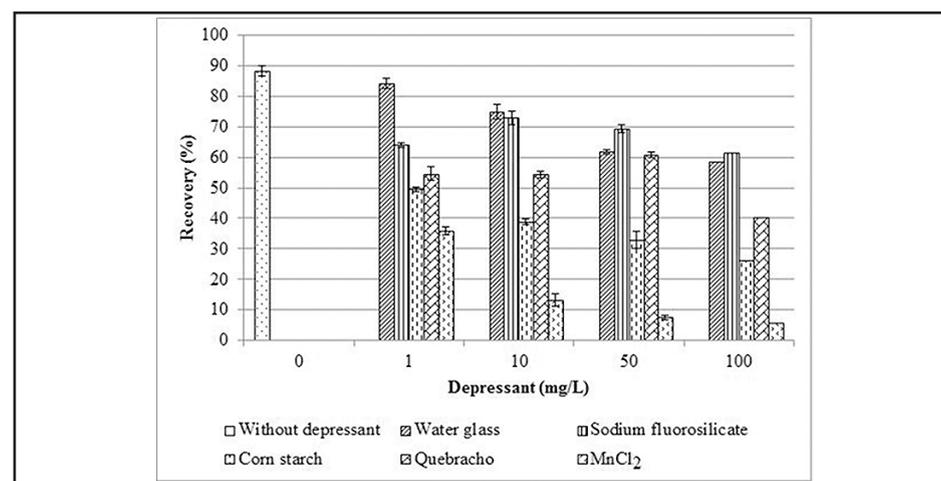
Figure 4
Recovery of rhodochrosite
vs. depressant dosage at pH 10
and 5 mg/L of ether amine acetate.
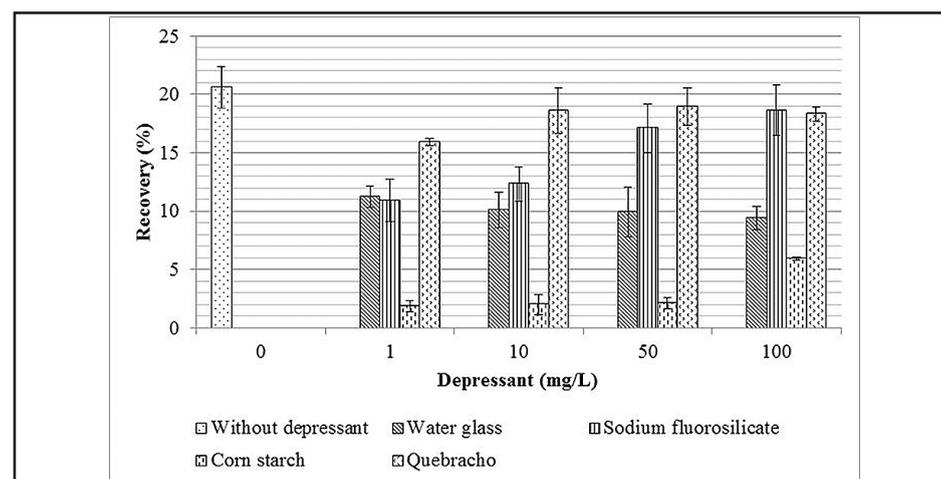
MnCl$_2$ (mg/L)	Mn^{2+}		Mn(OH)$_2$ (mg)
	M	(mg/L)	
1	7.95 x 10^{-3}	0.4366	0.2804
10	79.5 x 10^{-3}	4.366	4.2098
50	397.4 x 10^{-3}	21.83	21.6738
100	794.7 x 10^{-3}	43.66	43.5038

Table 2
Mn(OH)$_2$ precipitated as a function of MnCl$_2$ added to the solution at pH 10.

Due to the solubility of MnCO$_3$ and the complexion of MnCO$_3$, the species present in water are as follows: Mn^{2+}, HCO$_3$-, CO$_3$$^{-2}$, MnOH$^+$, OH$^-$, H$^+$, MnHCO$_3$$^+$, MnCO$_3$^{0} (Snoeyki and Jenkins, 1980). The low recovery (21%) of rhodochrosite with 5 mg/L of ether amine acetate (Fig. 4) is ascribed to these ionic species in solution.

Duarte (2012) performed bench flotation tests at pH 10 with a manganese ore sample constituted by manganese silicates (rhodonite, tephroite and spessartine) and manganese carbonate (rhodochrosite). The collector used was ether amine acetate, inorganic (water glass, fluorosilicate) and organic (corn starch, quebracho) depressants. The author verified only the mechanical drag of the fines particles (mass recovery of 9%) present in pulp and there was no selectivity in the separation of manganese minerals from gangue minerals (dolomite, magnesite, huntite, muscovite, biotite, phlogopite, quartz, feldspar, magnetite, rutile, ilmenite, pyrite and others). Filtration of the separation products was not possible due the blinding of filter medium. As can be seen in Fig. 3, the recoveries of rhodonite dropped drastically with the increase of MnCl$_2$ dosages, which is related to the precipitation of the colloidal dominant specie (Mn(OH)$_2$)(s) at pH 10 (Fig. 1 and Table 2) on the mineral surface. The same effect could have occurred with all mineral particles present in manganese ore. Furthermore, the presence of several ionic species and hydroxides in pulp come from the dissolution of the carbonates and oxidized sulfides.

3.2 Zeta potential measurements

The rhodonite zeta potential without reagent was negative at all tested pH values (4 to 12; Fig. 5). This result is consistent with the results in literature, as the isoelectric point of this mineral is pH 2.8 (Fuerstenau and Palmer, 1976; Andrade *et al.*, 2011). After conditioning with ether amine acetate, the zeta potential values became positive, with the exception of at pH 12. This behavior is in accordance with the increased recovery of rhodonite from pH 2 to pH 10 (Fig. 3), which can be ascribed to the electrostatic attraction between positive ether ammonium ions and the negative mineral surface. The maximum recovery at pH 10 (Fig. 2) is ascribed to the adsorption of ether ammonium ion-molecular species in solution, which decreases the electrostatic repulsion between the polar heads of positive ions adsorbed on the mineral surface. The smaller recovery observed at pH 12 (Fig. 2) is related to the low concentration of ether amine positive species in solution (Fuerstenaul *et al.*, 1985). This was confirmed by the negative zeta potential at this pH before (higher negative value) and after conditioning with ether amine (smaller negative value; Fig. 5).

The zeta potential of rhodonite became more negative in the presence of water glass and quebracho compared to the measurement carried out without reagent. The opposite occurred for the measurement performed with sodium fluorosilicate, corn starch, and MnCl$_2$ (Fig. 6). The zeta potential of rhodochrosite at pH 10 was ~−29 mV (Fig. 7I). This value is consistent with the point of zero charge values (5.5 to 6.85) reported by Charlet *et al*. (1990). With the exception of MnCl$_2$, the tested reagents had the same effects on the zeta potential of rhodochrosite as they did on the zeta potential of rhodonite.

In accordance with Marinakis and Shergold (1985), for 10^{-3} M of water glass at pH 10, the concentrations of the present species decrease in the following order: [SiO(OH)$_3$-] (~10^{-3} M), [Si(OH)$_4$] (~10$^{-3.5}$ M), [SiO$_2$(OH)$_2$$^{2-}$] (~10$^{-4.3}$ M) and [Si$_4$O$_6$(OH)$_6$$^{2-}$] (~10^{-6} M). The increased negative zeta potentials of rhodonite and rhodochrosite conditioned with water glass (Figs. 6II and 7II) compared to the minerals without reagent at pH 10 (Figs. 6I and 7I) is likley related to the adsorption of anionic species, particularly [SiO(OH)$_3$-], which is the dominant species at this pH.

Figure 5
Zeta potential of rhodonite without reagent and conditioned with 10^{-3} M of ether amine acetate.
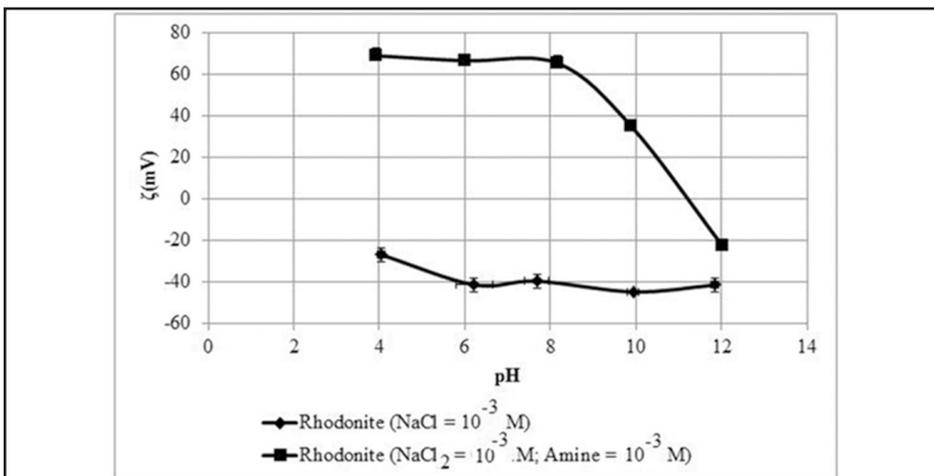
Figure 6
Zeta potential of rhodonite at pH 10 and constant ionic strength (10^{-3} M NaCl) in the following conditions: (I) without reagent; (II) water glass (10^{-3} M); (III) sodium fluorosilicate (10^{-3} M); (IV) Mn (10^{-3} M); (V) corn starch (10 mg/L); and (VI) quebracho (10 mg/L).
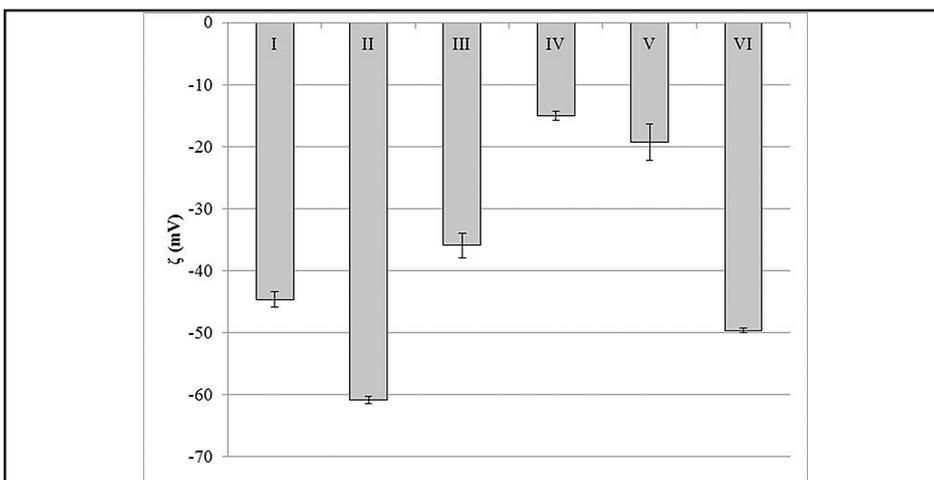
Figure 7
Zeta potential of rhodochrosite at pH 10 and constant ionic strength (10^{-3} M NaCl) in the following conditions: (I) without reagent; (II) water glass (10^{-3} M); (III) sodium fluorosilicate (10^{-3} M); (IV) corn starch (10 mg/L); and (V) quebracho.
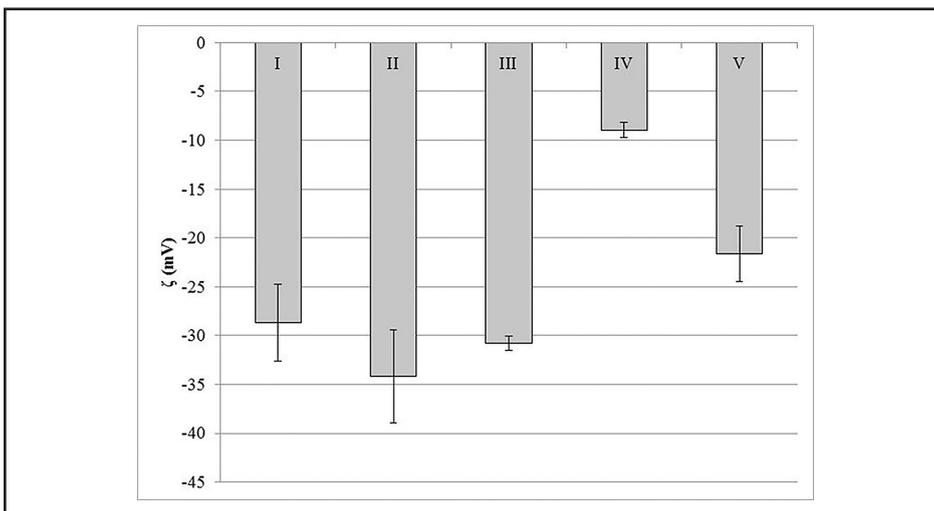
The zeta potential of rhodonite without reagent (Fig. 6I) was more negative compared to that mineral conditioned with sodium fluorosilicate (Fig. 6III), which is likely related to the adsorption of Si(OH)$_4$ on the mineral surface. In accordance with Song *et al.* (2002), Si(OH)$_4$ species are dominant at pH values ranging from 9 to 11.

The lower efficiency of water glass for the depression of rhodonite compared to corn starch (Fig. 3) can be attributed to the more negative charge of the mineral after conditioning with water glass (Fig. 6II) compared to corn starch (Fig. 6V); the adsorption of amine on the quartz surface occurs by physical processes (Fuerstenau *et al.*,1985; Lima (1997) and Vidyadhar *et al.*, 2002), primarily electrostatic attraction (Fuerstenau *et al.*,1985).

Although the concentrations of Mn^{2+} and MnOH$^+$ at pH 10 are $10^{-5.8}$ and $10^{-5.9}$ M, respectively (Fig. 1), the smaller negative zeta potential modulus of rhodonite conditioned with Mn^{2+} (10^{-3} M; Fig. 6IV) compared to the mineral without reagent (Fig. 6I) is likely ascribed to the adsorption of Mn^{2+} and MnOH$^+$ on the mineral surface by electrostatic attraction.

The recovery of rhodochrosite increases with increasing sodium fluorosilicate and quebracho concentrations (Fig. 4). This is likely related to the adsorption of negatively-charged SiF$_6^{2-}$ (fluorosilicate) and negative quebracho, which attract the positive ether ammonium positive ions.

4. Conclusions

Based on the results of microflotation tests and zeta potential measurements carried out with manganese minerals (rhodonite and rhodochrosite) with amine and different depressants (inorganic and organic), the recovery of rhodochrosite with amine was very low, likely due to the several ionic species present in solution. The organic depressants were more effective for the depression of rhodonite at pH 10. The strong depression of rhodonite with $MnCl_2$ is mainly related to the deposition of colloidal $Mn(OH)_2$ on the mineral surface. The increased rhodochrosite recovery with increasing water glass and quebracho concentrations can be ascribed to the anionic species of these reagents adsorbed on the mineral surfaces, which attracted the positive ether ammonium ions.

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