

# Influence of $Mn^{2+}$ ions on depression of quartz and spessartine in gondite ore

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## Abstract

Low-grade manganese ores that are composed of manganese oxides, wad, quartz, iron oxides, gibbsite, and especially of spessartine ( $Mn_3Al_2(SiO_4)_3$ ) are known as gondite. Spessartine is a mineral with a high content of silica ( $SiO_2$ ) and alumina ( $Al_2O_3$ ) that causes a decrease of the enrichment in manganese oxide concentrates by flotation, giving this ore more complexity for processing. Thus, by ensuring a higher selectivity between manganese oxides minerals and silicates, the use of gondite reserves becomes viable, and the correct reagent type can be useful for this objective. Moreover, there are few publications devoted to the study of spessartine in flotation. So, this study investigated the effects of  $Mn^{2+}$  ions on quartz and spessartine depression and showed positive results with the reduction of quartz floatability from 7.06% to 1.23% and the spessartine from 27.30% to 17.12% respectively when the  $Mn^{2+}$  (1000 mg/L) was added previously to the depressant. Zeta potential determinations showed that  $Mn^{2+}$  can act as a silicate activator, possibly by facilitating the  $SiO(OH)_3^-$  adsorption. Infrared spectroscopy analysis revealed absorption bands at 3,450  $cm^{-1}$  and 3,400  $cm^{-1}$  frequency for quartz and spessartine and the adsorption of  $Mn(OH)_2$  was responsible for this result.

**Keywords:** depressant reagents,  $Mn^{2+}$  ions, spessartine, quartz, gondite ore.

## 1. Introduction

The exploitation of manganese ores has become important for several industrial sectors; the metal is intensively used in steel productions, non-ferrous alloys, fertilizers, batteries, and other products (Sahoo *et al.*, 2001). From the data made available by Mineral Commodity Summaries (USGS, 2019), the Brazil production of manganese in 2018 increased 3.45%, compared with the previous year. In the Brazilian crust, pyrolusite ( $\alpha$ - $MnO_2$ ), the main manganese mineral can be found in association with other minerals at ore deposits known as gondite, a type of protore. Protore is a mineral matrix with low metal content; that becomes an ore through secondary enrichment. Gondite (an example of protore) is a metasedimentary rock, com-

posed of spessartine ( $Mn_3Al_2(SiO_4)_3$ ), a manganese-aluminosilicate (Souza, 1979), that decomposes into manganese oxide, silica, and alumina by weathering. This manganese oxide crystallizes and becomes pyrolusite in the rock (Faria, 2008), and the high silica content, due to the presence of quartz and spessartine, makes this ore more complex for processing (Andrade, 1978). Nevertheless, considering the probable decline of rich ores deposits, the gondite could be an important source of manganese and thus, more studies that explore the way to process this complex ore are essential for its future application.

Depressing reagents are essential for flotation selectivity since they accentuate the existing hydrophilic feature or

prevent the hydrophobization of gangue minerals (Bulatovic, 2007). Sodium silicate, sodium hexametaphosphate, and sodium fluorosilicate are among the reagents with depressant action for silicates; all are intensively used in mineral processing plants. Sodium silicate is intensively used in flotation, consisting of metasilicate ( $Na_2SiO_3$ ), dimetasilicate ( $Na_2Si_2O_5$ ), and orthosilicate ( $Na_4SiO_4$ ) in its composition. Fundamental studies have already been carried out to investigate ion effects on mineral flotation, whereby these ions can help reagents to improve their performance, acting as activators, for example, and widening the selectivity gap between different mineral species. For example, Lelis (2014) concluded that additions of  $Mn^{2+}$  ions were

able to influence the quartz flotation in microflotation tests, in the presence of the collector Flotigam EDA (2.5 mg/L) and at pH 10.5. The values were reduced from approximately 100% of floatability to less than 5% with the use of 200 mg/L of Mn<sup>2+</sup>.

In this study, the evaluation of reagent schemes can offer greater selectivi-

ty in the direct flotation of oxidized manganese minerals, based on the depressant action for quartz and spessartine, as gangue minerals in gondite, representing more than 80% (De São José, 2019) of the ore mass. The spessartine is the mineral responsible for the low manganese content, high silica and alumina contents in the oxidized manganese concentrate

by flotation (Abreu, 1973). Therefore, it is extremely important to reduce the amounts of silica to increase the product quality and to lower the costs for gondite processing. Thus, this study investigated the influence of Mn<sup>2+</sup> ions (intentionally added) on some depressants for quartz and spessartine as an attempt to improve the beneficiation of gondite.

## 2. Material and methods

The minerals used at experiments were spessartine (a mineral that is difficult to find with purity greater than 95% w/w) and quartz. Spessartine was purchased from a mineral hoarder in Natal - RN and quartz pebbles were obtained in *Ribeirão do Carmo* located in the Mariana - MG. The samples were ground in a ceramic mortar and pestle, and after comminution, were classified between -106 +38 µm by wet screening (sieves of Tyler's series). The representative aliquots were subjected to semi-quantitative analysis using X-Ray Diffractometer (XRD), performed at PANalytical Empyrean diffractometer

using radiation CuKα ( $\lambda = 1,54056 \text{ \AA}$ ) and a graphite crystal monochromator to confirm the samples mineralogy and data analyzed by the Rietveld method. The chemical composition was determined by X-Ray Fluorescence (PANalytical, MagiX - PW 2540/2.4 kW).

Microflotation tests were carried out in duplicate in a modified Hallimond tube (volume = 310 cm<sup>3</sup>) to evaluate the performance of depressants (sodium silicate, sodium hexametaphosphate, and sodium fluorosilicate) added after the Mn<sup>2+</sup> ions. For each test, 1 gram of minerals was used and

the gas N<sub>2</sub> was injected at a flow rate of 75 mL/min to produce the bubbles. The depressant performance was evaluated at three concentrations: 20; 40; and 80 mg/L and the conditioning time of 5 minutes. These experiments were performed at pH values close to 6, 8, and 10. The Mn<sup>2+</sup> concentrations were: 1, 10, 100, and 1000 mg/L and the conditioning time of 5 minutes. The all solutions and the microflotation tests used distilled water. In this phase of the studies, no collector was used. Table 1 shows the conditions of the microflotation tests in a more accessible way.

Table 1 - Conditions for researching the best quartz/spessartine depressant.

Depressant	Depressant concentration (mg/L)	pH
-	-	Natural ≈ 7.07
-	-	6; 8; 10
Sodium silicate	20; 40; 80	6; 8; 10
Sodium hexametaphosphate		6; 8; 10
Sodium fluorosilicate		6; 8; 10

An electrophoresis cell (Zeta Meter 4.0) determined the mineral zeta potentials for the reagent evaluation. Sodium silicate and manganese (II) chloride dehydrate (MnCl<sub>2</sub>·2H<sub>2</sub>O), Mn<sup>2+</sup> ion source, with analytical purity (SYNTH) were used for zeta potential measurements. Using Smoluchowski's equation, the Zeta determines the electrophoretic mobility and transforms into zeta potential ( $\zeta$ ). Moreover, the

zeta potential for spessartine and quartz was determined in the pH range of 1 to 12. A 0.01% w/v suspension was prepared by the adding 1 g of the mineral (-38 µm) into a 1000 mL solution of KNO<sub>3</sub> (10<sup>-3</sup> mol/L), as an indifferent electrolyte. After 24 hours (an arbitrarily chosen period), the suspension was transferred to a 500 mL beaker, the reagents were added according to each test, and the pH was adjusted with HCl

and NaOH under constant agitation. For each pH value, the zeta potential was determined as the average obtained from the duplicate values.

Infrared Fourier Transform Spectroscopy of MnCl<sub>2</sub> salt dissolution species adsorbed on the surface of the spessartine and quartz was also performed. Thermo Nicolet model 6700 infrared spectrometer and FTIR-OMNIC software were used.

## 3. Results

### 3.1 Samples characterization

Semi-quantitative analysis refined XRD data by the Rietveld method showed the sample mineral proportions (Table 2): the spessartine sample was comprised of 94.70% of spessartine, considered a rare mineral, so the proportion was satisfactory for the

proposed study. Quartz represented less than 5.0% of the spessartine proportion, and it was an acceptable impurity. The purification of spessartine sample by leaching was discarded, since such a procedure would not be controlled unidirectionally for the iron element and

due to the great difficulties of finding pure spessartine, the use of the available sample was decided. The quartz sample was pure, free of others crystalline phases. Table 2 shows the chemical compositions of each mineral sample, useful for confirming its quality.

Table 2 - Contents and crystalline phases identified in the spessartine and quartz samples.

Sample name	Crystalline phases (%wt)			Contents (%)				
	spessartine	quartz	enstatite	Mn	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	P
spessartine	94.7	4.6	0.7	31.74	36.44	19.80	9.14	0.10
quartz	0.0	100.0	0.0	0.00	99.20	0.46	0.04	0.03

### 3.2 Microflotation tests

Fig. 1 summarizes the results of recovery for quartz and spessartine by flotation. Quartz showed 20% recovery at natural pH (~7.07) for the three depressants tested. The pH adjustment to 6 and the using of sodium silicate, for example, reduced the quartz and spessartine floatability at more than 12% and 15% respec-

tively. Despite some oscillation, increased pH further reduced quartz and spessartine recoveries, but the exception was observed with sodium hexametaphosphate, which acted as a dispersant for quartz at pH 10. As such, the elevation in the dispersion role favored the quartz recovery by drag. As pH was increased, the reagents depres-

sant role was intensified (except sodium hexametaphosphate), and with pH 10 the best result was reached (Fig. 1). At pH 10, the sodium silicate and sodium fluorosilicate provide the SiO(OH)<sub>3</sub><sup>-</sup> species, which could be acting as a depressant for the minerals. However, the assumption needs to be confirmed through future research.

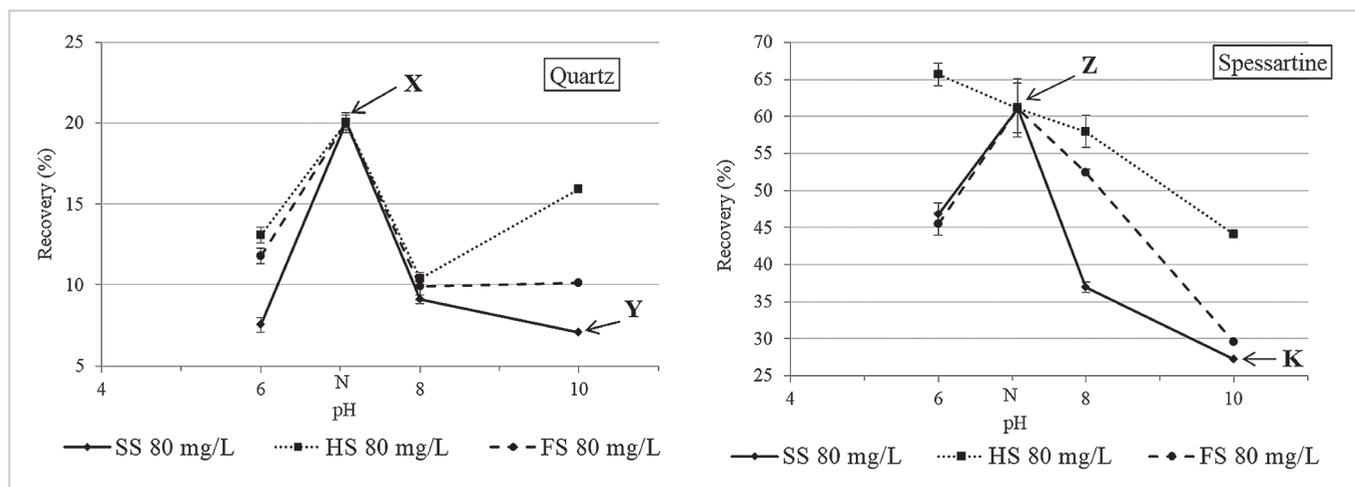


Figure 1 - Minerals recovery effect of sodium silicate (SS), sodium hexametaphosphate (SH), sodium fluorosilicate (SF) as a function of pH values. N = pH natural and without depressant (point X and Z for quartz and spessartine, respectively).

Initially, the microflotation tests were carried out using three depressants reagents and Mn<sup>2+</sup> dosages to investigate the depression for quartz and spessartine. The result pointed out that sodium silicate was the best depressant for quartz. The depressant concentration and pH value were found

to be 80 mg/L at a pH of 10.00 ± 0.15. In these conditions, the sodium silicate reduces the quartz floatability by 13.24% (X-Y, Fig. 1). For spessartine, the reduction was more expressive and equal to 33.85% (Z-K, Fig. 1). When analyzing Fig. 3, it can show that Mn<sup>2+</sup> additions can assist the depression of

both quartz and spessartine. The effects of Mn<sup>2+</sup> ions on quartz and spessartine depression showed positive results, such as reduction of quartz floatability from 7.06% (point A, Fig. 2) to 1.23% (point C, Fig. 3) and spessartine floatability of 27.30% (point B, Fig. 2) to 17.12% (point D, Fig. 3).

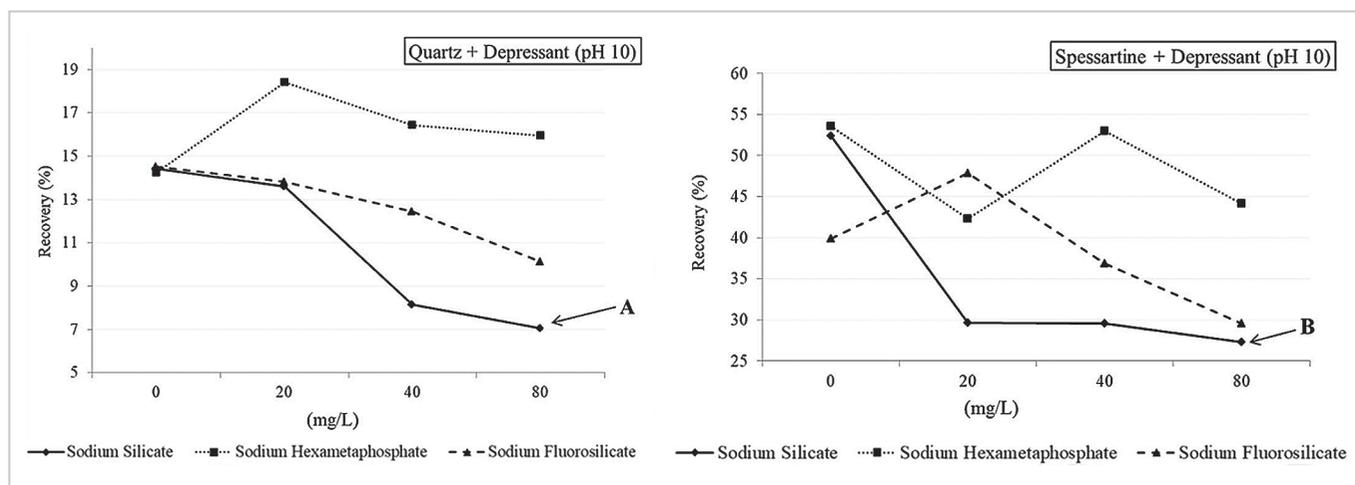


Figure 2 - Flotation recovery of minerals vs. depressant concentration. pH = 10.00 ± 0.15.

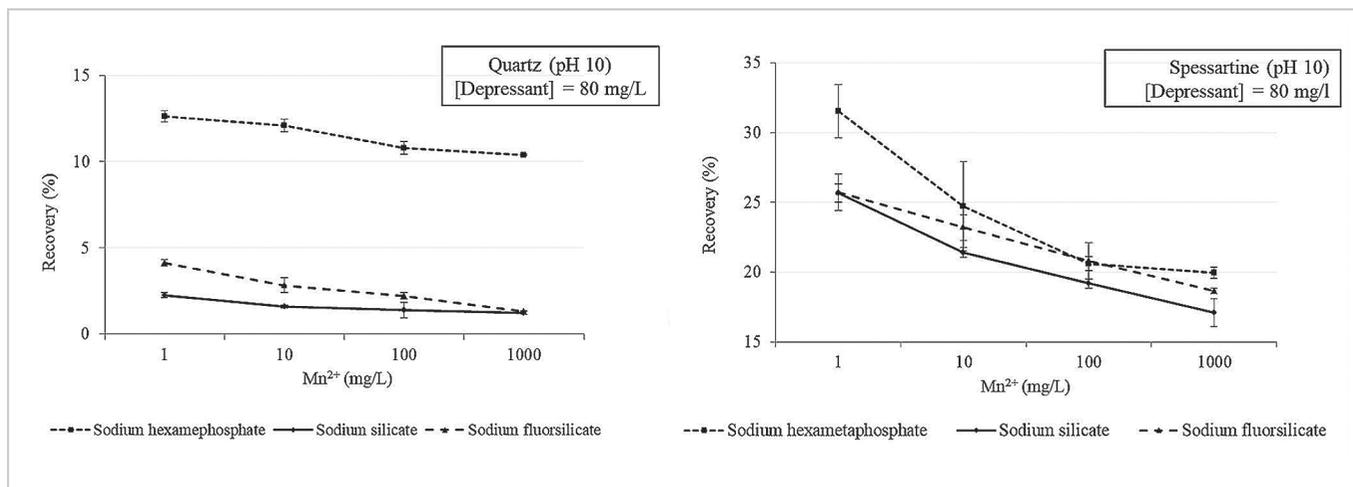


Figure 3 - Minerals flotation submitted to depressant after the  $Mn^{2+}$  conditioning. pH = 10.00 ± 0.15.

### 3.3. Zeta potential

As shown in Fig. 4, the quartz sample presented an isoelectric point close to 1.8, using only  $KNO_3$  ( $10^{-3}$

mol/L) and sodium silicate (80 mg/L) because it produced a satisfactory depression). Similar to quartz, the spess-

sartine zeta potential was negative in a wide range of pH values (Fig. 5).

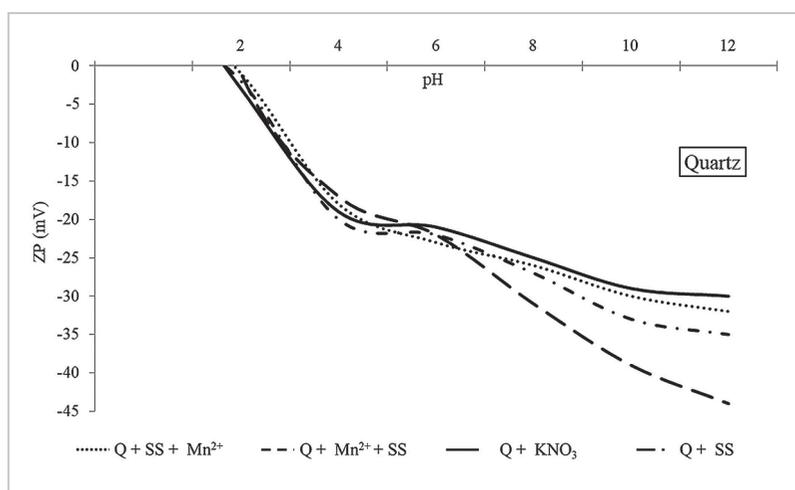


Figure 4 - Quartz zeta potential. Q + SS +  $Mn^{2+}$ : (1st sodium silicate; 2nd  $MnCl_2$ ); Q +  $Mn^{2+}$  + SS: (1st  $MnCl_2$ ; 2nd sodium silicate); Q +  $KNO_3$ : quartz conditioned with  $KNO_3$  ( $10^{-3}$  mol/L); Q + SS: quartz; conditioned with sodium silicate.

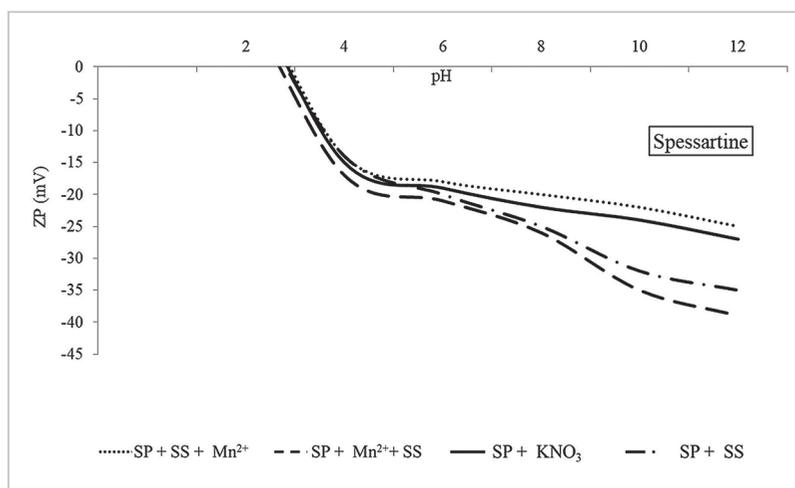


Figure 5 - Spessartine zeta potential. SP: spessartine conditioned with  $KNO_3$  ( $10^{-3}$  mol/L); SP+SS: spessartine conditioned with sodium silicate (80 mg/L); SP+SS+ $Mn^{2+}$ : (1st sodium silicate; 2nd  $MnCl_2$ ); SP+ $Mn^{2+}$ +SS: (1st  $MnCl_2$ ; 2nd sodium silicate).

### 3.4. Infrared spectroscopy

Fig. 6 and 7 show the results of infrared spectroscopy analysis to the spessartine

and quartz samples conditioned with  $MnCl_2$ . In Fig. 6, the letter A refers to the

test in which the quartz was conditioned with  $Mn^{2+}$  and the letter B without this ion.

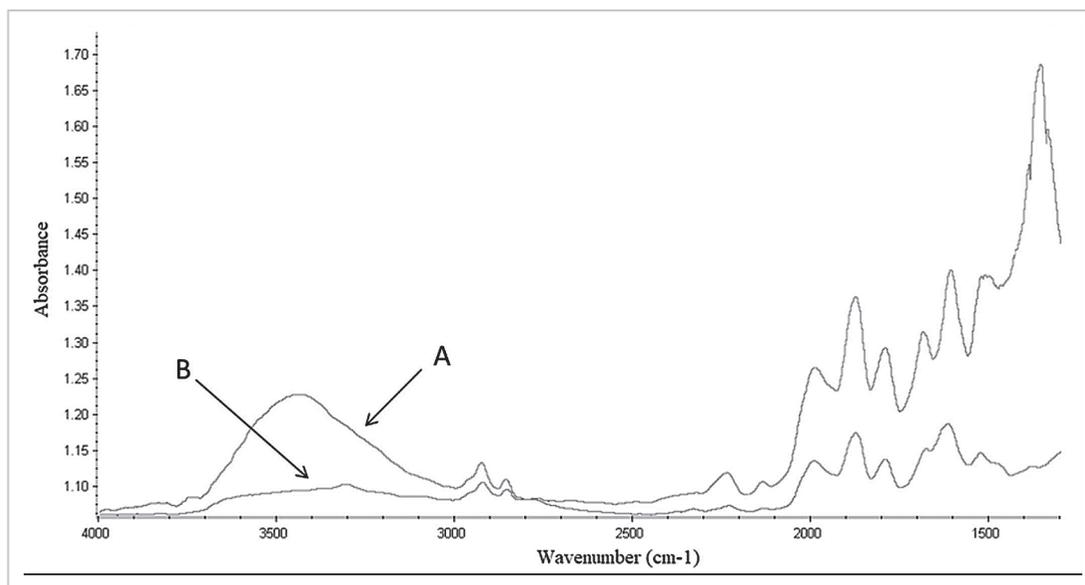


Figure 6 - Infrared spectra and manganese species adsorbed on the quartz (pH 10.00 ± 0.15).

In Fig. 7, the letter A refers to the test in which the spessartine was conditioned with  $Mn^{2+}$  and the letter B without this ion.

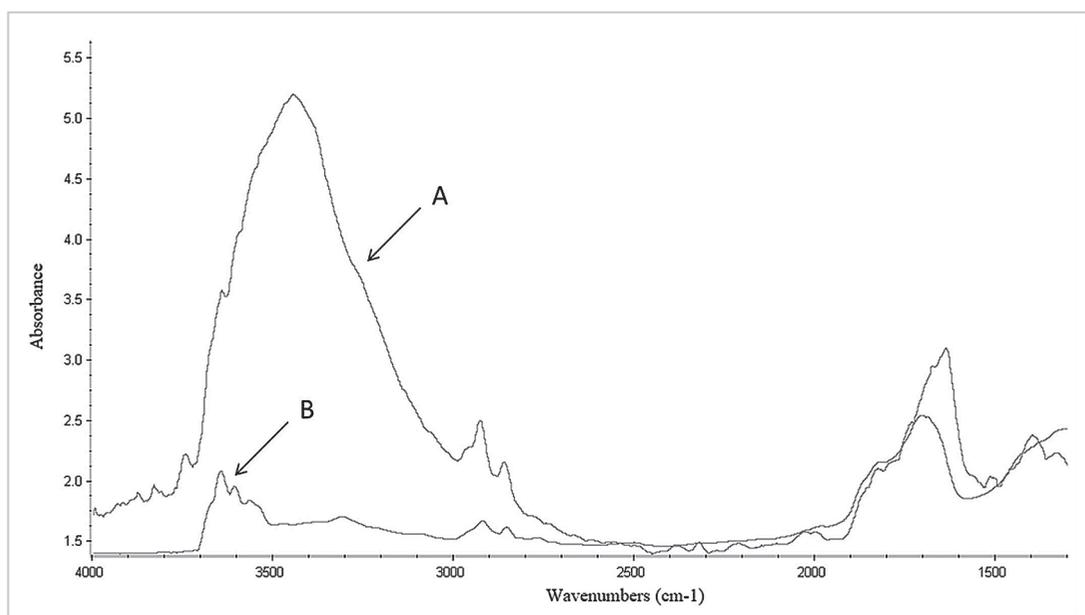


Figure 7 - Infrared spectra and manganese species adsorbed on the spessartine (pH 10.00 ± 0.15).

## 4. Discussion

### 4.1 Microflotation tests

It can be noted that when the  $Mn^{2+}$  ion was previously added to the depressant reagents, it assisted in the depressant action of quartz and spessartine minerals. A suggested mechanism to explain the sodium hexametaphosphate undesirable effect, as dispersant, was based on the stable hydrophilic complex owing to the complexation between sodium hexametaphosphate and metal ions present in a mineral surface (Yang *et al.*, 2014). The sodium silicate can act in the same way and interact with the metal ions solution, forming nearly insoluble

silicates precipitates on the mineral surface (Radley, 1968). The sodium silicate is hydrophilic hydroxyl and increasing the mineral's depression. Mishra (1982) concluded that sodium silicate molecules can adsorb on apatite and form a hydrophilized layer on their surface, thereby promoting mineral depression.

Yang *et al.*, (2014) show by Fourier Transform Infrared Spectroscopy and Scanning Electron Microscopy-Energy Dispersive Spectroscopy analysis that the  $Mn^{2+}$  ion can form precipitates and adsorb on the quartz surface negatively

charged. This induces the quartz recovery drops in alkaline pH systems. Duarte *et al.*, (2015) used a manganese calcium silicate mineral and provided results about the  $MnCl_2$  depression effects on it. In agreement with the Mn speciation diagram, the manganese species in solution (at pH 10) are  $Mn^{2+}$  (0.0870 mg/L) and  $MnOH^+$  (0.0692 mg/L), and such species in solution enable the formation of precipitates like  $Mn(OH)_2$  that adsorb on the mineral surface, causing depression. The speciation diagram highlighted in Figure 8 reinforces that

pH 10 can favor the existence of  $Mn^{2+}$  as the ionic species predominant at this pH. However, due to possible slow dis-

solution kinetics of manganese oxide minerals, which implies insufficient ions useful for the activation process, it

is necessary to study mechanisms that can intensify the dissolution of minerals containing manganese.

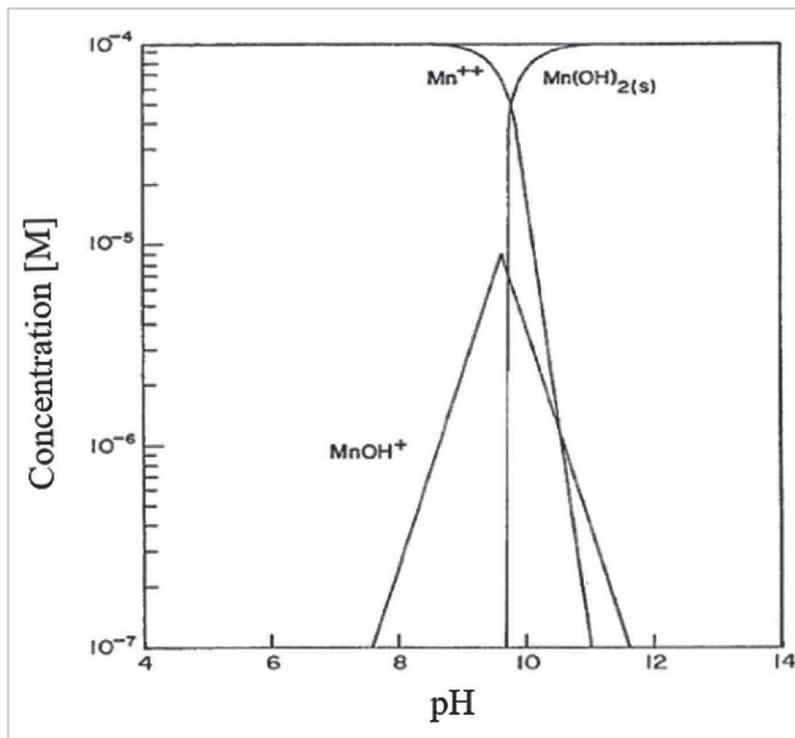


Figure 8 - Diagram of the log concentration of the  $Mn^{2+}$  cation with a concentration of  $10^{-4}$  M. (Fuerstenau *et al.*, 1985).

## 4.2 Zeta potential

The isoelectric point (IEP) value for quartz conditioned with  $KNO_3$  is consistent with other previous studies, such as Parks (1967) and Ney (1973) apud Rao (2004) who registered the quartz IEP equal to 1.9. Using the sodium silicate, the zeta potential was lowered to negative levels during the determinations and this behavior was intensified from pH 8.00. The sodium silicate dissociation results in species, such as  $Si(OH)_4$  and  $Si_2O(OH)_6$ , give rise to the anionic species  $SiO(OH)_3^-$  and  $SiO_2(OH)_2^{2-}$  in alkaline systems. The quartz surface has a negative charge net balance for all pH ranges below its IEP, showing that it has the same charge signal of the products dissociated from sodium silicate. Thus, chemical adsorption is responsible for reducing the zeta potential of the mineral in this case. Araújo and Lima (2017) showed similar results for smithsonite depression with sodium silicate and in the pH alkaline range, and the authors assumed that the  $SiO(OH)_3^-$  and  $SiO_2(OH)_2^{2-}$  species should adsorb and be responsible for intensifying the negative charge on the mineral surface (-20 mV to -50 mV). In the microflotation tests involving  $Mn^{2+}$  additions, there was observed a decline in quartz recovery until reaching the lowest value of 2.03% (point C, Fig. 3) at pH 10.

And this result is in accordance with zeta potential determinations when the  $Mn^{2+}$  additions previous to the sodium silicate intensified the displacement of the quartz zeta potential to more negative values. The  $Mn^{2+}$  added previously to sodium silicate ( $Q + Mn^{2+} + SS$  curve, Fig. 4), can activate the adsorption of silicate species and therefore lead to this more negative potential on the quartz surface.

About spessartine, few studies have investigated the electrokinetic behavior of this mineral because it is a grenade and its industrial applications in the comminuted form have not been reported. Cases (1968) and Andrade (1978) showed a spessartine's IEP equal to 4.45, more than the value found for the available spessartine. Variation in composition and the presence of contaminants can change the minerals electrokinetic parameters, as revealed in this study.

It should be emphasized that spessartine is a manganese aluminosilicate mineral, consisting of aluminum, manganese, and contaminant elements, with the power to raise the surface energy of the mineral and to reflect its electrokinetic behavior on flotation. The inclusion of the sodium silicate at the system not changed the spessartine's IEP. However, the sodium silicate showed

to increase the density of charge at the mineral's double electric layer. At pH 10 (point of the greatest depression in microflotation), it was possible to generate a potential difference of 8 mV in the module. Regarding the species from the sodium silicate dissociation at pH 10, i.e.,  $SiO(OH)_3^-$  and  $SiO_2(OH)_2^{2-}$ , these are responsible for the intensification of the negative charge at the electrical interface of the spessartine, for driving a negative charge balance.

Comparing the zeta potential for quartz and spessartine after conditioning with sodium silicate, higher effect on spessartine than the quartz is observed. The superficial  $Al^{3+}$  and  $Mn^{2+}$  cations present on spessartine act as preferential anchoring points to negative species and intensify the superficial negative net charge. For example, the adsorption of  $SiO(OH)_3^-$  on the kaolinite ( $Al_4(Si_4O_{10})(OH)_8$ ) surface occurs on the surfaces terminated in planes (001) with exposed aluminum atoms. As a result of  $SiO(OH)_3^-$  adsorption, the kaolinite surface becomes more hydrophilic and more negative (Jia *et al.*, 2017).

The order of addition  $Mn^{2+}$  (first) and sodium silicate (second) showed an equal phenomenon for quartz and spessartine when the zeta potential changed to more negative values.

### 4.3 Infrared spectroscopy

For quartz (Fig. 6), a more marked absorption band was observed at the  $3,450\text{ cm}^{-1}$  frequency band. The result is correlated with Lelis (2014) determinations. The compound  $\text{Mn}(\text{OH})_2$  exhibits absorption in the band near this

frequency, which induces its presence as a precipitate on the surface of the quartz. For the spessartine (Fig. 7), absorption peak was identified at approximately  $3,400\text{ cm}^{-1}$ . The adsorption of  $\text{Mn}(\text{OH})_2$  was responsible for the result. Duarte

(2012) registered a reduction in the quartz recovery due to  $\text{Mn}^{2+}$  ions action because at pH 10, the  $\text{Mn}(\text{OH})^+$  hydroxyl complex was formed, which adsorbed on the mineral surface and decreased the mineral floatability.

## 5. Conclusions

As a low-grade manganese ore, gondite can be a viable source of metal manganese after adequate industrial beneficiation. The demand for manganese is growing, rich manganese ores are being overexploited (Liu *et al.*, 2014), and the poorer ones being set aside. Microflotation studies and zeta potential determinations show that  $\text{Mn}^{2+}$  acts as an activator and favors

the adsorption of the depressants. The activation mechanisms are responsible for increasing the hydrophilization of sodium silicate capacity, related to the creation of anchorage points for species such as  $\text{SiO}(\text{OH})_3^-$ . Moreover, the precipitation of manganese  $\text{Mn}(\text{OH})^+$ , favored by pH 10, had a depressant role for quartz and spessartine minerals. Zeta potential studies proved that the

order of addition of  $\text{Mn}^{2+}$  and sodium silicate plays a key role in increasing mineral depression. The microflotation tests showed that pH 10 was crucial to the silicates' depression process because at this pH, the depressant reagents were hydrolyzed to negative species, with a stronger power of hydrophilization, and the precipitation phenomenon also helped mineral hydrophilization.

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