

Influence of cations Ca^{2+} , Mg^{2+} and Zn^{2+} on the flotation and surface charge of smithsonite and dolomite with sodium oleate and sodium silicate



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ABSTRACT

This study aimed to determine the conditions required for selective flotation between smithsonite and dolomite using sodium oleate and sodium silicate. Microflotation test results demonstrated recoveries of 95% and 5% for smithsonite and dolomite, respectively, from 2.5×10^{-5} M sodium oleate and 50 mg/L sodium silicate at pH 9.5. The smithsonite was depressed by the cations Ca^{2+} and Mg^{2+} and, the dolomite was depressed by Zn^{2+} cations, which was probably caused by the reaction of these cations with the oleate anions in the solution, decreasing the concentration of collector available for adsorption onto the minerals. The powerful depression of smithsonite caused by Ca^{2+} cations compared with that caused by Mg^{2+} cations can be considered to have occurred because of the higher concentration of Ca^{2+} in the solution. From the zeta potential measurements at pH 9.5, we concluded that the predominant species of oleate and of sodium silicate were adsorbed onto both minerals, and the silicate species prevented the adsorption of oleate anions onto dolomite. The decrease in the negative zeta potential of both minerals after cation conditioning can be related to the electrostatic attraction between the cations and the negative sites on their surfaces. The negative zeta potential of smithsonite increased at a concentration of 1×10^{-6} M Ca^{2+} and Mg^{2+} , whereas the potential decreases at a concentration of 1×10^{-3} M, which can be related to a lower concentration of oleate anions being available for adsorption.

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1. Introduction

The classification of zinc ore into sulphide and non-sulphide (or oxidised) ores is a function of zinc-bearing minerals present. Non-sulphide deposits are formed by the oxidation of sulphide deposits and the two are generally associated. Carbonate rocks are the main hosts for such deposits, implying the presence of carbonate gangue minerals such as dolomite and calcite in ore (Nuspl, 2009).

The main zinc minerals found in oxide ores are hemimorphite [$\text{Zn}_4\text{SiO}_7(\text{OH})_2(\text{H}_2\text{O})$], willemite (Zn_2SiO_4) and smithsonite (ZnCO_3). In the Paracatu–Vazante region, Minas Gerais, Brazil, Votorantim Metais Zinco is studying a new deposit named Ambrosia, which predominantly contains smithsonite as the zinc mineral. In this deposit the gangue minerals are constituted by dolomite [$\text{Ca,Mg}(\text{CO}_2)_3$], quartz (SiO_2), pyromorphite [$\text{Pb}_5(\text{PO}_4)_3\text{Cl}$], franklinite (ZnFe_2O_4), micas (carriers of Fe, Mg, Si and Al), iron oxide [$\text{FeO} \cdot (\text{OH})$ and Fe_2O_3] and sulphides (Araújo, 2016). On the basis of this vast mineralogical assemblage,

selective flotation routes for smithsonite and gangue minerals need to be investigated.

Separation of smithsonite and carbonate gangue minerals, such as dolomite and calcite, by flotation is particularly challenging as they are semi-soluble in nature. This implies that Zn^{2+} , Ca^{2+} , Mg^{2+} and CO_3^{2-} ions dissolve in aqueous solution, interfering with the selective mineral separation during flotation. Moreover, the presence of carbonate gangue minerals results in a high acid consumption in zinc concentrate leaching process and requires cleaning steps for metal production, performed by precipitating various cations in the leachate liquor. The presence of carbonate gangue minerals also results in high energy consumption and complicates the electrolytic process (Abkhoshk et al., 2014).

Only a few studies have been conducted about the selective flotation of smithsonite and dolomite, but several studies have been conducted on the selective flotation of smithsonite and calcite, involving direct flotation of smithsonite with sodium oleate ($\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COONa}$) over a pH range of 9.0 to 11.0 (Shi et al., 2013b; Ejtemaei et al., 2012, 2011; Irannajad et al., 2009; Hosseini, 2008).

Hosseini (2008) reported that the interaction between oleate ions and zinc cations on the surface of smithsonite occurs via an ion-

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exchange mechanism, thereby forming the insoluble salt zinc oleate, according to Eq. (1) below:



Sodium oleate acts as a collector of both smithsonite and calcite. Their selective separation is possible using sodium silicate ($\text{Na}_2\text{O} \cdot \text{SiO}_2$) as a calcite depressant as it does not have any effect on the smithsonite flotation (Irannajad et al., 2009; Shi et al., 2014). Cations from the dissolution of these minerals are known to interfere with the selectivity flotation process (Shi et al., 2013a).

Generally mineral surfaces are heterogeneous due to defects created by particle size reduction, which expose different crystal faces, impurities in mineral sample and slight surface oxidation, as the case of sulphide minerals. Thus, there are surface sites with different energetic states, which cause random adsorption distribution pattern on mineral surfaces (Nikolaev, 2016; Ali et al., 2013). Taking into account the distribution of surface charge, minerals can be classified in isotropic and anisotropic. Isotropic minerals, such as smithsonite and dolomite, have identical surface charges in different surfaces of crystals. For isotropic minerals the isoelectric point (IEP) (as determined by electrophoretic measurement) and point of zero charge (PZC) (as determined by potentiometric titration method) are identical and occur in the same value. Anisotropic minerals such as talc, kaolinite, muscovite and vermiculite, carry a different surface charge on different crystal facets. For anisotropic minerals the PZC and IEP are different and occur in different values. Due the reasons explained before, zeta potential measurements are extensively used to infer physical or chemical adsorption mechanism of reagents on surfaces of isotropic minerals (Ndlovu et al., 2011; Burdukova et al., 2007).

In the present study, microflotation tests and zeta potential measurements were conducted to study the flotation of smithsonite and dolomite with sodium oleate and using sodium silicate as the dolomite depressant. The influence of the lattice cations of these minerals was also investigated.

2. Materials and methods

2.1. Mineral samples and reactants

Smithsonite and dolomite samples were collected from the Ambrosia zinc ore deposit, Brazil. The samples were first crushed (-2 cm) and dry sieved at $212 \mu\text{m}$. The $+212 \mu\text{m}$ fraction sizes were then ground in a porcelain mill. Each sample was then wet-classified between $75 \mu\text{m}$ and $212 \mu\text{m}$ for use in the microflotation tests. To remove impurities, smithsonite with a fraction size of $-212 + 75 \mu\text{m}$ was purified by a wet high-intensity magnetic separator (Carpco model WHIMS3) with a magnetic field of 11,000 G. The non-magnetic product was purified using a jig to remove the light minerals (dolomite, quartz and mica) from smithsonite. A part of the sorted fraction ($-212 + 75 \mu\text{m}$) of the purified smithsonite and dolomite were ground in an agate mortar ($-38 \mu\text{m}$), then subjected to gravity sedimentation in a $250 \mu\text{m}$ beaker to obtain the fraction size of $-10 \mu\text{m}$, used for zeta potential measurements.

Chemical analysis of the samples was conducted using atomic absorption spectroscopy (Agilent model 240FS AA) and optical emission spectroscopy with inductively coupled plasma (Agilent model 725). The ignition loss was determined using a thermogravimetric analyser

(TA Instruments model TGA Q50). The test conditions were as follows: N_2 atmosphere; 90 mL/min for sample purge and 10 mL/min to cool the micro scale, ramp of $10^\circ\text{C}/\text{min}$ from 20°C to 1000°C and an isotherm of 5 min at 1000°C .

Table 1 shows the chemical composition and ignition loss of the smithsonite and dolomite samples. Using X-ray diffraction analysis, Araújo (2016) identified only traces of quartz in the diffractograms of smithsonite and dolomite. The presence of other cations in the samples suggests an isomorphic substitution of Zn^{2+} cations by Mg^{2+} , Fe^{2+} , Ca^{2+} and Pb^{2+} in the crystalline lattice of smithsonite. For dolomite, Fe^{2+} ions can substitute Mg^{2+} ions (Webbmineral, 2016). The other chemical elements may be from minerals such as quartz, pyromorphite, franklinite, micas (carriers of Fe, Mg, Si and Al), iron oxides and sulphides, all of which are present in the Ambrosia deposit.

The reactants used in the microflotation tests and zeta potential measurements and their functions in this study are listed in Table 2.

2.2. Microflotation tests

The microflotation tests (three replicate tests per condition) were conducted in a modified Hallimond tube with a total volume of 300 mL. A 1 g sample ($-212 + 75 \mu\text{m}$ fraction size) was introduced into the tube, followed by a 50 mL sodium oleate solution at 2.5×10^{-5} M and the pH was adjusted to the desired value in advance. The mineral was then conditioned for 7 min (Araújo, 2016). For tests with a depressant (sodium silicate), 50 mL of depressant solution at the desired concentration and pH 9.5 was added, and the mineral was then conditioned for 3 min, followed by addition of 50 mL sodium oleate (2.5×10^{-5} M) at a previously adjusted pH of 9.5. The mineral was then conditioned for 7 more minutes. For tests performed with the cations (Ca^{2+} and Mg^{2+} for dolomite and Zn^{2+} for smithsonite), a solution of 50 mL, formed using CaCl_2 , MgCl_2 , ZnCl_2 at a desired concentration of each compound, was added separately and then conditioned for 3 min. A 60 mL sodium silicate solution at 10 mg/L was added to this suspension, followed by further conditioning for 3 min. Finally, 15 mL sodium oleate (2.5×10^{-5} M) was added and the resulting dispersion was conditioned for 7 more minutes. After conditioning, the required tube volume (300 mL) was achieved by adding distilled water at the same pH as that used for the solutions and the resulting pulp was conditioned for 2 more minutes. Throughout the test, magnetic stirring at 600 rpm was employed (Fanem model 257). The flotation test was performed for 1 min, under a flow rate of 75 mL/min N_2 gas. The floating and sunken particles were separately removed, filtered, dried and weighted to calculate the mass recovery of the floating product with respect to the total mass (sunk plus floated particles). The final recovery value from each condition was calculated by the arithmetic average of the recoveries of three test replicates.

2.3. Zeta potential measurements

The zeta potential measurements (two replicate tests per condition and three measurements per test) were conducted in a Malvern Zetasizer Nano Z-ZEN 2600 zetameter using electrophoretic mobility. We added 0.01% solids ($<10 \mu\text{m}$) and 250 mL 1.0×10^{-4} M NaCl to a beaker. The beaker was allowed to stand for approximately 15 h. The suspension was then agitated by inversion and allowed to stand for

Table 1
Chemical composition and ignition loss of smithsonite and dolomite samples.

Samples	Chemical composition (%)										LOI (%)
	Zn	Ca	Mg	Fe	Pb	Al	K	P	S	SiO_2	
Smithsonite	44.56	0.55	0.46	0.55	0.34	–	–	–	0.06	2.53	33.33
Dolomite	–	14.68	8.50	0.82	–	0.86	0.86	0.07	0.07	–	37.98

LOI – loss of ignition.

Table 2
Reagents used in microflotation tests and zeta potential measurements.

Reagents	Function	Supplier	Concentrations
Sodium oleate A.P. (C ₁₇ H ₃₃ COOH)	Collector	SYNTH	2.5 × 10 ⁻⁵ M
Sodium silicate (Na ₂ SiO ₃) SiO ₂ /Na ₂ O = 3.33	Depressant	Votorantim supplier	1.0–100.0 mg/L
Calcium Chloride A.P. (CaCl ₂)	Ca ²⁺ ions source	SYNTH	1.0 × 10 ⁻⁶ –1.0 × 10 ⁻³ M
Magnesium Chloride A.P. (MgCl ₂)	Mg ²⁺ ions source	SYNTH	1.0 × 10 ⁻⁶ –1.0 × 10 ⁻³ M
Zinc Chloride A.P. (ZnCl ₂)	Zn ²⁺ ions source	VETEC	1.0 × 10 ⁻⁶ –1.0 × 10 ⁻³ M
Sodium Chloride A.P. (NaCl)	Indifferent electrolyte	ÊXODO	1.0 × 10 ⁻⁴ M
Hydrochloric Acid A.P. (HCl)	pH control	SYNTH	0.1–1.0% v/v
Sodium Hydroxide A.P. (NaOH)	pH control	SYNTH	2.5 × 10 ⁻² –2.5 × 10 ⁻¹ M

approximately 24 min for smithsonite (specific gravity 4.35 g/cm³) and 43 min for dolomite (specific gravity 2.85 g/cm³). The gravity sedimentation of the 10 µm particles was based on Stokes' law. Aliquots of the supernatant were collected and transferred to the beakers. The pH was adjusted to the desired value using NaOH or HCl. The reactants (sodium oleate: 2.5 × 10⁻⁵ M, sodium silicate: 1–150 mg/L, and CaCl₂/MgCl₂/ZnCl₂: 1 × 10⁻⁶–1 × 10⁻³ M) were then added and conditioned for at least the same time as that for the microflotation tests, i.e. sodium oleate, 7 min; sodium silicate, 3 min; and CaCl₂, MgCl₂ and ZnCl₂, 3 min. The final zeta potential value for each condition was determined using the arithmetic average of the replicated sample measurements.

3. Results and discussion

3.1. Microflotation tests

Fig. 1 shows the recoveries of smithsonite and dolomite using 2.5 × 10⁻⁵ M sodium oleate as a function of pH. The maximum smithsonite recovery occurred between pH 9.0 and 10.0. These results agree with those reported by Irannajad et al. (2009), Hosseini and Forssberg (2006a), and Ejtemaei et al. (2011). The recovery curves of smithsonite and dolomite at pH 9.5 (Fig. 1), demonstrate recoveries of 98% and 69%, respectively (with a selectivity window in the flotation of approximately 30%). A pH of 9.5 was thus fixed for our subsequent studies.

On the basis of the species distribution diagram of oleic acid, the sodium oleate species present in a solution at a pH value near 9.5 are ion oleate R-COO⁻ and its dimer (R-COO)₂²⁻ (Somasundaran, 1984 apud Ejtemaei, 2014). Hosseini and Forssberg (2006b) reported that Fourier transform infrared spectroscopy (FTIR) studies conducted on smithsonite conditioned with oleic acid indicated the presence of COO⁻ on the mineral surfaces. The predominant species at a pH value of approximately 10 is RCOO⁻, which interacts with the mineral surfaces, forming insoluble zinc oleate (see Eq. (1)). Xiao and Chen (1992), on the basis of

their analysis of Ca²⁺ and Mg²⁺ species in a supernatant of dolomite conditioned with oleate at pH 9.2, suggested that the oleate anions form calcium and magnesium oleate salts on the mineral surfaces.

Fig. 2 shows that the depression of dolomite was significant even at low concentrations of sodium silicate. At 10.0 mg/L (3000 g/t), its recovery was 6.5%. Smithsonite flotation decreased only at sodium silicate dosages higher than 50.0 mg/L. For microflotation tests performed with pure smithsonite and calcite samples from the Angooran region in Iran, using 2000 g/t sodium silicate and 500 g/t oleate, Irannajad et al. (2009) concluded that calcite recovery was reduced from 90% to 15% and there was no effect on smithsonite recoveries.

According to species distribution diagrams demonstrated in various studies (Sjoberg and Ohman, 1985 apud Rao and Forssberg, 2007), at pH values lower than approximately 9.5, the predominant species is the monosilicic acid Si(OH)₄, and at pH values higher than 9.5, monosilicates and polysilicate ions, such as SiO(OH)₃⁻ are the predominant species. Thus, for the tests conducted in this study, both monosilicic acid and the anion SiO(OH)₃⁻ may be responsible for the depression of dolomite by preventing the oleate species from solution reacting with the surface sites. Matis and Gallios (1989) observed a strong depression of dolomite by sodium silicate and oleate at pH < 9.0. This was attributed to monosilicate ions which are predominant in the solution in the pH range from 4 to 10.

Marinakis and Shergold (1985) observed maximum adsorption of sodium silicate by calcite at pH 9 and 10. On the basis of the species distribution diagram of saturated calcite and silicate solutions, they suggested that the Si(OH)₃⁻ species in the solution was adsorbed on to the Ca²⁺ sites on the mineral surfaces. For dolomite, the dominant species at pH 9.5 are Ca²⁺ and Mg²⁺ (Chen and Tao, 2004), which form positive sites on the mineral surfaces where Si(OH)₃⁻ anions can be adsorbed. For smithsonite at pH 9.5, deprotonation of ZnOH₂⁺_{surf} by adsorption of solution species HCO₃⁻ and CO₃²⁻ produces ZnHCO₃⁰_{surf} and ZnCO₃⁻_{surf}, respectively (Shi et al., 2012). The reason that sodium

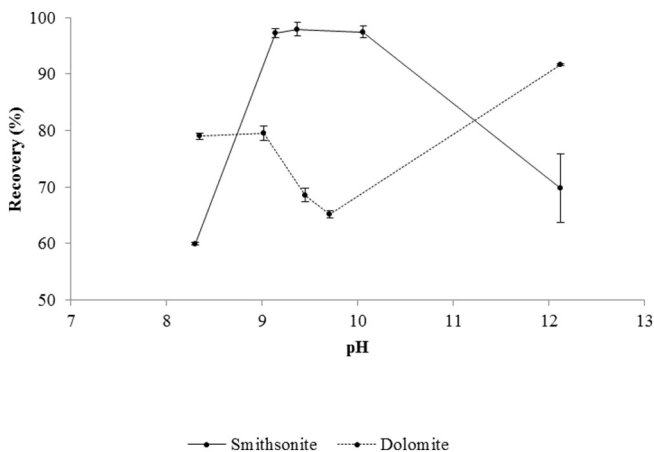


Fig. 1. Smithsonite and dolomite recoveries with 2.5 × 10⁻⁵ M sodium oleate versus pH. Error bars represent the 95% confidence interval of the average values.

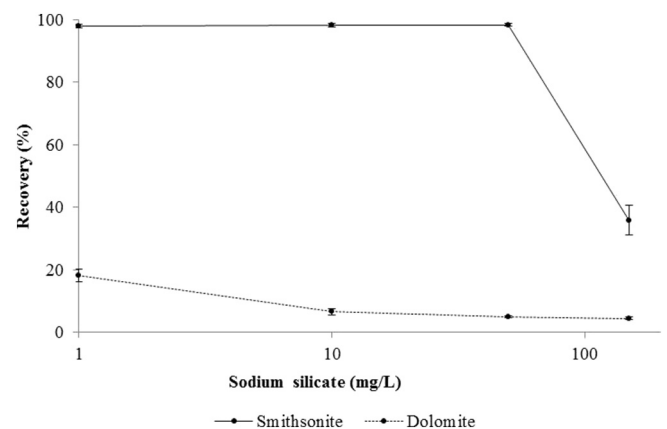


Fig. 2. Smithsonite and dolomite recoveries versus sodium silicate concentration (sodium oleate = 2.5 × 10⁻⁵ M and pH 9.47 ± 0.04). Error bars represent the 95% confidence interval of the average values.

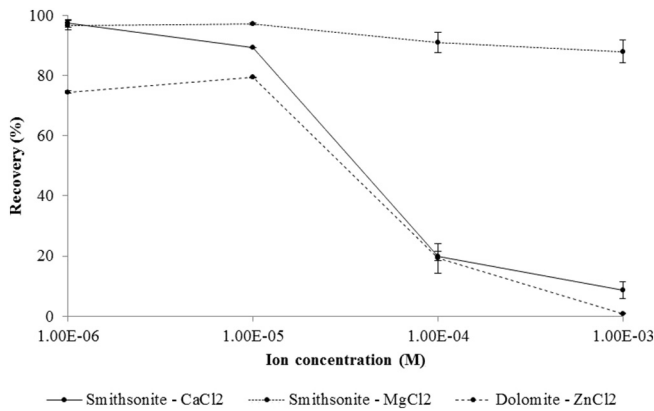


Fig. 3. Smithsonite recovery versus CaCl₂ and MgCl₂ and dolomite recovery versus ZnCl₂ concentration (sodium oleate = 2.5×10^{-5} M and pH 9.49 ± 0.13). Error bars represent the 95% confidence interval of the average values.

silicate has no effect on the depression of smithsonite is probably because of the existence of smaller positive sites number on smithsonite surfaces compared with those present on dolomite surfaces.

Fig. 3 shows that the depressant effect of Ca²⁺ ions on smithsonite was more significant than that of Mg²⁺ ions. At the highest concentration of 1.0×10^{-3} M, smithsonite recovery decreased from 98% in the tests without ions in solution (Fig. 1) to 8.60% and to 87.0% (Fig. 3) in the tests with CaCl₂ and MgCl₂, respectively. On the basis of the Ca²⁺ species distribution diagram, the predominant species at pH 9.5 are Ca²⁺ cations, whereas the predominant magnesium species are Mg²⁺ cations, followed by MgOH⁺ (Butler, 1964 apud Fuerstenau et al., 1985). The decrease in the recovery of smithsonite conditioned with CaCl₂ and MgCl₂ is probably because of the formation of Ca and Mg oleates in the solution (Xiao and Chen, 1992). The higher depression power of Ca²⁺ cations compared with that of Mg²⁺ cations can be ascribed to a smaller concentration of Mg²⁺ being present in the solution. Therefore, the consumption of oleate anions when forming calcium oleate is higher than that needed to form magnesium oleate.

As shown in Fig. 3, at low ZnCl₂ concentrations of 1.0×10^{-6} M and 1.0×10^{-5} M, dolomite recovery increased from 68.57% to 74.52% and 79.36%, respectively, indicating that the Zn²⁺ ions acted as activator of the mineral surfaces. Using X-ray photoelectron spectroscopy analysis, Shi et al. (2013b) concluded that the Zn²⁺ cation is adsorbed onto calcite surfaces by exchanging Ca²⁺ cations at low Zn²⁺ concentrations ($<1.0 \times 10^{-5}$ M). This mechanism, proposed for calcite, may also be valid for dolomite.

However, at higher concentrations of ZnCl₂ (1.0×10^{-4} M and 1.0×10^{-3} M) (Fig. 3), dolomite recovery reduced to 19.19% and 0.85%, respectively. On the basis of the zinc species diagram (1.0×10^{-3} M), the Zn(OH)_{2(s)} species is formed at pH 9.5 (Albrecht et al., 2011). In accordance with Shi et al. (2013b), at high Zn²⁺ concentrations ($>1.0 \times 10^{-5}$ M), the interaction between Zn²⁺ cations and CO₃²⁻ and OH⁻ anions from the calcite lattice leads to the formation of the insoluble species hydrozincite [Zn₅(OH)₆(CO₃)₂] and/or [Zn(OH)₂], which precipitate on the mineral surfaces (slime coating phenomenon), and prevent oleate adsorption. This mechanism can also be valid for dolomite as the same ions occur in the solution, i.e. Zn²⁺, CO₃²⁻ and OH⁻.

As shown in Fig. 4, smithsonite recovery showed no significant variation compared with the tests performed without Ca²⁺ and Mg²⁺ (98.35%) at the lowest concentration studied (1.0×10^{-6} M). However, at the highest concentration (1.0×10^{-3} M), smithsonite was completely depressed to 0.28% and 18.56% recovery in the presence of Ca²⁺ and Mg²⁺, respectively. The calcium and magnesium species present at pH 9.5, i.e. Ca²⁺, Mg²⁺ and Mg(OH)⁺, were adsorbed onto the smithsonite surface and favoured the interaction of the mineral with sodium silicate which showed great affinity with dolomite in previous

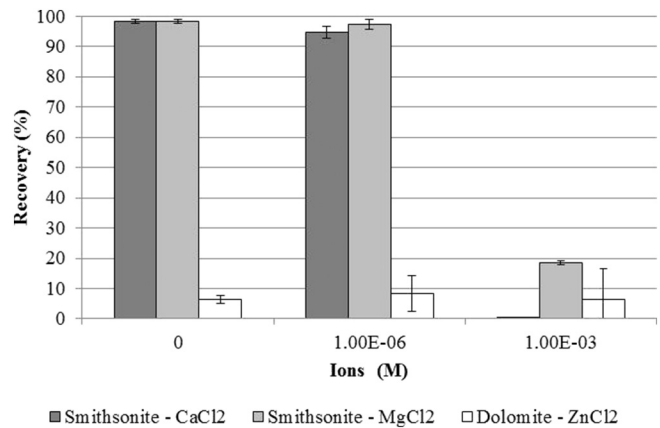


Fig. 4. Smithsonite recovery versus CaCl₂ and MgCl₂ concentration and dolomite versus ZnCl₂ concentration (sodium silicate = 10.0 mg/L; sodium oleate = 2.5×10^{-5} M and pH 9.52 ± 0.13). Error bars represent the 95% confidence interval of the average values.

microflotation tests (Fig. 2). In tests involving dolomite, sodium silicate depressed the mineral, independent of the ZnCl₂ concentration.

3.2. Zeta potential

Fig. 5 shows that the zeta potential values of smithsonite, with an indifferent electrolyte, becomes more negative with the increase in pH, consistent with the findings of Hosseini and Forsberg (2006a) and Shi et al. (2012). These authors determined the isoelectric point (IEP) of smithsonite between pH 7.7 and 8.0. As can be seen in Fig. 5, the IEP of smithsonite is close to pH 8.8. Araújo (2016) determined a similar value for 24 h-aged smithsonite suspensions. The difference in these IEP values may be associated with differences in the chemical composition and origin of the mineral used in this study.

The zeta potential of dolomite without reagent (Fig. 5) showed negative values at pH below 11.5. Studies indicate that the IEP of dolomite ranges from pH 6.3 to pH 7.8 (Chen and Tao, 2004; Gence and Ozbay, 2006; Kosmulski, 2009). In this study, the zeta potential measurements of dolomite were conducted at different pH values from 8 to 12. At pH 8 the zeta potential was approximately -18.0 mV, indicating that an IEP exists at pH values below 7. Positive zeta potential values for dolomite at pH >11.5 can be attributed to the precipitation of Mg(OH)_(s), which is formed under alkaline pH conditions and has an IEP of pH 12.0 (Parks, 1965; Prédali and Cases, 1973; Chen and Tao, 2004; Gence and Ozbay, 2006).

With sodium oleate, the zeta potential for pH values measured for smithsonite and dolomite (Fig. 5) became more negative compared with the values measured in the absence of a collector. At pH 9.5, the predominant species of oleate in solution are the R-COO⁻ ion and its dimer (R-COO)₂⁻ (Somasundaran, 1984; Ejtemaei et al., 2014). In accordance with the mechanism proposed by Shi et al. (2012), at pH values lower than the IEP of smithsonite, the ZnOH₂⁺_{<sur>} sites react with oleate anions and form zinc oleate. At pH values above this IEP, the hydrocarbon chains of oleate anions in the solution and the oleate anions previously adsorbed onto positive sites form Van der Waals bonds (species R-COO₂⁻) on the surface. In addition, positive sites occur by the adsorption of Zn²⁺, Ca²⁺, Mg²⁺ and Fe²⁺ species into the internal Helmholtz plan. These species arise from the dissolution of the studied minerals and react with oleate anions to form oleates of calcium, magnesium and iron on the mineral surfaces, thereby decreasing their zeta potentials after conditioning with a collector.

Hosseini and Forsberg (2006b) by FTIR, using diffuse reflectance of oleic acid adsorbed onto smithsonite verified the absence of a band around 1690 cm^{-1} and 1718 m^{-1} , ascribed to the $\nu\text{C}=\text{O}$ stretching vibration of undissociated oleic acid ($-\text{COOH}$) for dimer ((R-COO)₂⁻) and monomer (R-COO⁻). This indicates that only the monomer is

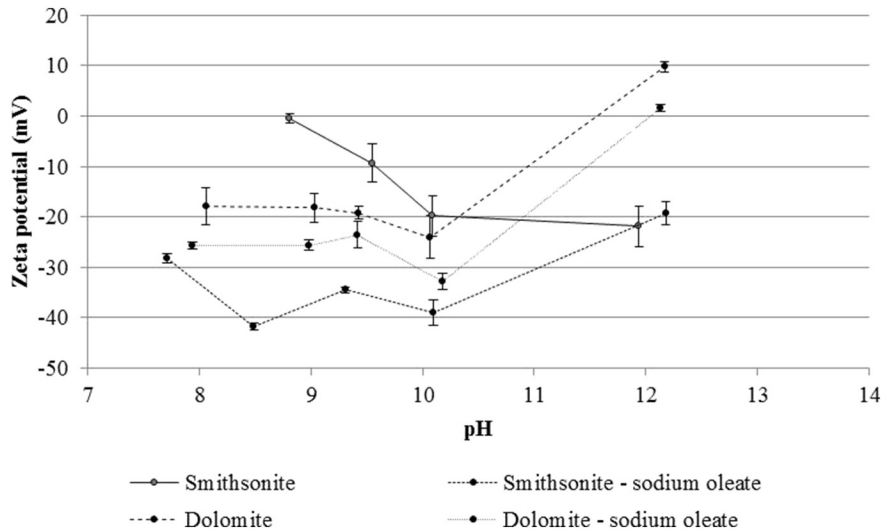


Fig. 5. Smithsonite and dolomite zeta potential with and without 2.5×10^{-5} M sodium oleate versus pH ($\text{NaCl} = 1.0 \times 10^{-4}$ M). Error bars represent the 95% confidence interval of the average values.

chemically adsorbed onto the mineral surface and not the dimer. Using FTIR spectroscopy, Ince et al. (1991) studied the adsorption of oleic acid species onto dolomite at pH values of 4 and 10, and, on the basis of the intensity of the carboxyl stretching band at 1735 cm^{-1} , concluded that the predominant species on the dolomite surfaces was oleate.

Fig. 6 shows that after conditioning the minerals with sodium silicate at pH 9.5, the zeta potential of smithsonite (-20 mV to -50 mV) and dolomite (-25 mV to -35 mV) became more negative compared with the values obtained without the reagent, i.e. -9.5 mV for smithsonite and -20 mV for dolomite (Fig. 5). At pH 9.5, the predominant silicate species is $\text{Si}(\text{OH})_4$ followed by $\text{SiO}(\text{OH})_3^-$ (Sjoberg and Ohman, 1985; Rao and Forsberg, 2007; Matis and Gallios, 1989). These results suggest that the anionic species $\text{SiO}(\text{OH})_3^-$ gets adsorbed onto both minerals surfaces. Marinakis and Shergold (1985) assumed that the surface of calcite contains cationic sites analogous to those in solution such as Ca^{2+} , which are involved in the adsorption process with $\text{SiO}(\text{OH})_3^-$. The same assumption can be applied to the positive sites of the studied minerals (Ca^{2+} , Zn^{2+} , Fe^{2+} and Mg^{2+}). Comparing the curves in Fig. 6 based on the sodium silicate content in both

minerals, the smithsonite zeta potential presents more negative values than dolomite. For studies conducted using apatite ($\text{Ca}_5(\text{PO}_4)_3(\text{F}, \text{OH}, \text{Cl})$), Mishra (1982) demonstrated that sodium silicate molecules may adsorb onto a mineral, making its zeta potential values less negative, and form a hydrophilised layer, promoting mineral depression. At pH 9.5, dolomite exhibited a more negative surface charge than smithsonite (see Fig. 5). Therefore, the anionic species of sodium silicate may undergo repulsion at its surface, explaining the adsorption of neutral molecules onto dolomite. Because of this, the zeta potential of dolomite did not present values as negative as those of smithsonite in the presence of sodium silicate.

The zeta potential of dolomite after conditioning with sodium silicate and sodium oleate was compared with that of dolomite conditioned with sodium silicate (Fig. 6). As can be observed its negative zeta potential decreased. Marinakis and Shergold (1985) reported that the low adsorption of oleate ions by calcite previously conditioned with sodium silicate was because of Ca^{2+} sites not being available for oleate adsorption. The same reason may be applicable to dolomite, after the $\text{SiO}(\text{OH})_3^-$ adsorbed on the positive Ca^{2+} and Mg^{2+} sites. For

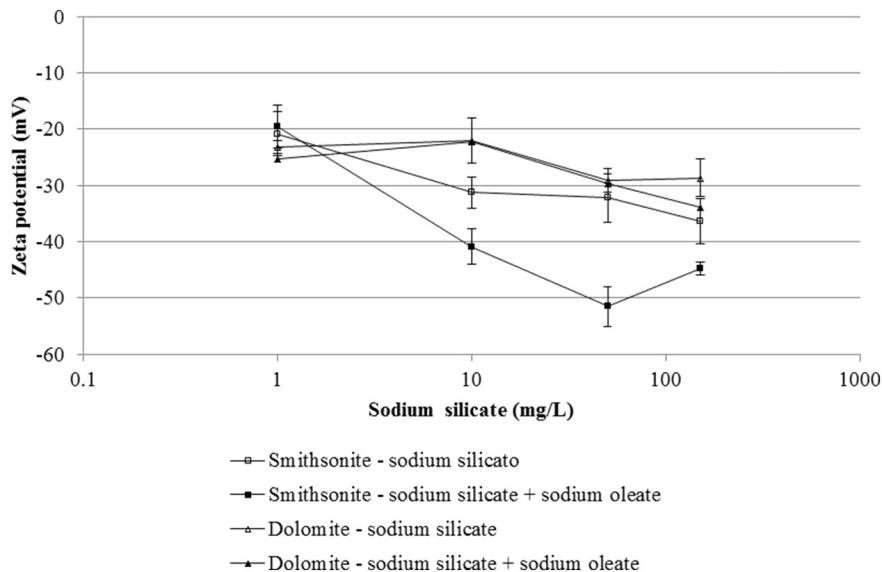


Fig. 6. Smithsonite and dolomite zeta potential versus sodium silicate concentration with and without 2.5×10^{-5} M sodium oleate ($\text{NaCl} = 1.0 \times 10^{-4}$ M and $\text{pH} 9.48 \pm 0.11$). Error bars represent the 95% confidence interval of the average values.

smithsonite, the negative zeta potential significantly increased after conditioning with sodium oleate, suggesting high adsorption by the collector, as shown in Fig. 6.

Fig. 7 shows that the zeta potential of smithsonite conditioned with CaCl_2 and MgCl_2 became less negative as the concentration of these salts increased, compared with the value measured with an indifferent electrolyte (NaCl_2 : 10^{-4} M) at pH 9.5 (-9.29 mV). This result may be related to the adsorption of the calcium and magnesium species that predominate at pH 9.5 (Butler, 1964 apud Fuerstenau et al., 1985), i.e. positively charged Ca^{2+} , Mg^{2+} and MgOH^+ which are electrostatically attracted by the negative sites of smithsonite at pH 9.5. The larger effect of calcium ions on zeta potential compared with magnesium ions can be attributed to the higher concentration of Ca^{2+} ions in the solution. The curves present more negative zeta potential values after sodium oleate conditioning, indicating that the collector was adsorbed onto the smithsonite in the presence of cations.

Fig. 8 shows that the zeta potential of dolomite conditioned with ZnCl_2 became less negative with increasing concentration of the salt, compared with the value obtained with an indifferent electrolyte (NaCl_2 : 10^{-4} M) at pH 9.5 (-19.2 mV). This behaviour is related to the deposition of $\text{Zn}(\text{OH})_2$ which displays an IEP close to pH 9.5 (Albrecht et al., 2011). Shi et al. (2013a, b) concluded that when the concentration of Zn^{2+} in the solution is higher than 1.0×10^{-5} M, the insoluble species hydrozincite and/or zinc hydroxide are formed and precipitated onto calcite. With sodium oleate being added, the zeta potential values became more negative, suggesting that the collector was adsorbed onto the dolomite surface. However, for the highest concentration studied (1.0×10^{-3} M), the zeta potential values were found to be less negative compared with the measurement made with ZnCl_2 probably because of the high concentration of $\text{Zn}(\text{OH})_2$.

As shown in Fig. 9, at low cation concentrations (1.0×10^{-6} M), addition of sodium silicate (10 mg/L) and sodium oleate (2.5×10^{-5} M) resulted in more negative zeta potential values for both minerals compared with the values obtained when they were conditioned with CaCl_2 and MgCl_2 for smithsonite, and ZnCl_2 for dolomite at pH 9.5 (-40.0 mV for smithsonite and -25 mV for dolomite). This suggests that the two reactants were adsorbed onto the mineral surfaces. For smithsonite at 1.0×10^{-3} M (high concentration), the zeta potentials were less negative than those at low ion concentrations. As mentioned before, the cations (Ca^{2+} and Mg^{2+}) in the solution and the oleate anions formed CaOl or MgOl , thus decreasing the oleate anions available for adsorption onto the mineral.

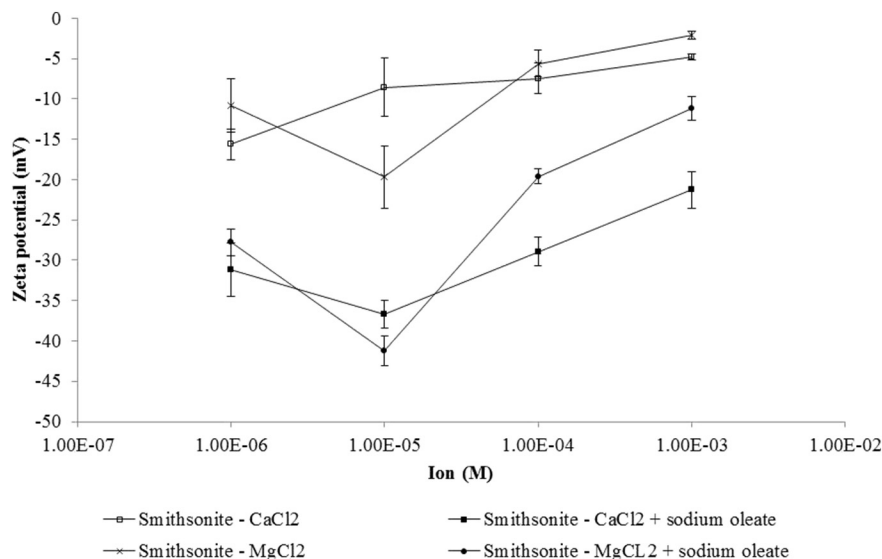


Fig. 7. Smithsonite zeta potential versus ion concentrations with and without 2.5×10^{-5} M sodium oleate ($\text{NaCl} = 1.0 \times 10^{-4}$ M and $\text{pH} 9.45 \pm 0.10$). Error bars represent the 95% confidence interval of the average values.

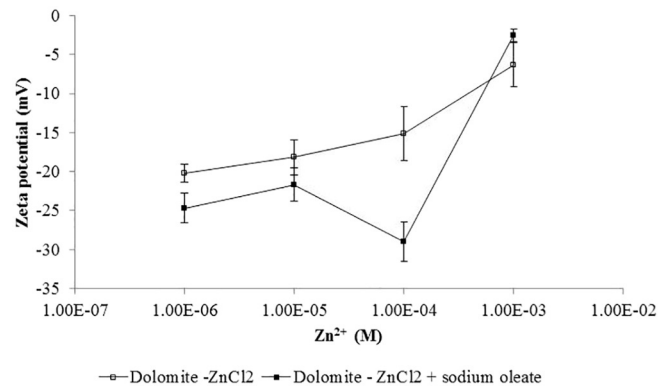


Fig. 8. Dolomite zeta potential versus ion concentrations with and without 2.5×10^{-5} M sodium oleate ($\text{NaCl} = 1.0 \times 10^{-4}$ M and $\text{pH} 9.45 \pm 0.09$). Error bars represent the 95% confidence interval of the average values.

4. Conclusions

On the basis of the results and discussion presented above, we conclude that selective flotation of smithsonite and dolomite is possible at pH 9.5. Sodium silicate has a higher effectiveness to depress dolomite than smithsonite, probably because of the larger number of divalent cation sites on dolomite surfaces involved in the adsorption of $\text{SiO}(\text{OH})_3^-$. The Ca^{2+} cation, as the predominant species at pH 9.5, is more effective for smithsonite depression than Mg^{2+} and MgOH^+ . The performance of Ca^{2+} is associated with the reaction of the Ca^{2+} species in the solution with the oleate anions, thereby decreasing the collector concentration for adsorption onto the smithsonite. Depression of both minerals was observed when the solution had a high ion concentration, so the concentration must be controlled below 1.0×10^{-6} M to promote selective separation of the two minerals. From zeta potential measurements at pH 9.5, we conclude that the predominant species from the oleate and sodium silicate gets adsorbed onto both minerals, and the silicate species prevented the adsorption of oleate anions onto dolomite. The decrease in negative zeta potential of both minerals after cation conditioning can be related to their electrostatic attraction by the negative sites on minerals surfaces. At a concentration of 1×10^{-6} M of Ca^{2+} and Mg^{2+} , the negative zeta potential of smithsonite was found to increase. The opposite happened at 1×10^{-3} M, which can be related to a lower number of oleate anions being available for adsorption.

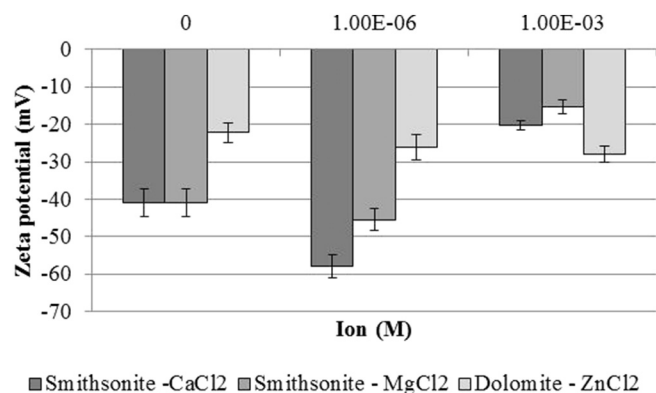


Fig. 9. Smithsonite and dolomite zeta potential versus ion concentrations ($\text{NaCl} = 1.0 \times 10^{-4}$ M, sodium silicate = 10 mg/L, sodium oleate = 2.5×10^{-5} M and pH 9.51 ± 0.16). Error bars represent the 95% confidence interval of the average values.

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