

Cationic flotation of smithsonite and dolomite from Brazilian Ambrósia Norte Deposit

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Abstract

The flotation of low-grade oxidized zinc ores has been commonly used to produce marketable concentrates for many years. Several flotation routes are being successfully used: cationic, anionic and a mixture of anionic and cationic. The choice of the route taken is dependent on the major zinc-bearing minerals in the deposit of interest and its associated gangue. Since both the mineralogical composition of zinc ores and the chemical composition of smithsonite and dolomite vary between deposits, the physico-chemical conditions under which selective flotation processes are determined must be established for each unique case. In this study, cationic flotation tests were performed using smithsonite and dolomite samples from an unstudied oxidized zinc deposit in Brazil, using Na₂S as the sulfidizing agent, sodium silicate as the depressant and amine as the collector. The surface charges of both minerals were investigated with and without reagents. These tests showed that the optimum conditions of flotation were reached at pH 11. Na₂S allowed a significant increase in the recovery of smithsonite, which implies lower amine consumption. Sodium silicate functioned as a dolomite depressant at concentrations up to 6.0 mg/L. The results for both flotation and the zeta potential of the minerals were analyzed using specimen diagrams of the reagents and compared with studies published in previous literature.

keywords: Smithsonite, dolomite, cationic flotation, sodium sulphide, sodium silicate, amine, Ambrósia Norte deposit.

1. Introduction

Zinc is the fourth most consumed metal in the world and its uses include galvanization (50% of total consumption) and the manufacturing of alloys (40% of total consumption). The remaining 10% is used in the industries of paint, chemicals and pharmaceuticals, amongst others (International lead and zinc study group, 2016). In zinc sulfide deposits, the major ore-bearing mineral is sphalerite (ZnS), which occurs in association with sulfides of lead, copper, silver and other metals. The main mineral ores of oxidized zinc deposits are willemite (Zn₂SiO₄), smithsonite (ZnCO₃), zincite (ZnO), hydrozincite (Zn₅(CO₃)₂(OH)₆) and franklinite (ZnFe₂O₄), and they are associated with several gangue minerals such as; carbonates, oxides, and silicates (Wet and Singleton, 2008, Etjemae *et al.*,

2014, Khaleghi *et al.*, 2016).

The zinc extraction process is comprised of leaching, zinc solvent extraction and electrowinning to produce high-grade zinc (Wet and Singleton, 2008, Khaleghi *et al.*, 2016). However, in order to decrease the consumption of acid, it is necessary to use ores or ore concentrates with grades between 25 and 35% Zn (Etjemae *et al.*, 2014). Flotation is widely used to concentrate low-grade zinc ores (using anionic, cationic, or mixture of anionic/cationic routes). The choice of route depends on the main zinc-bearing mineral in the deposit and its associated gangue mineral. Cationic flotation at pH 11 using a soluble sulphide and amine as a collector is the most common flotation route for oxidised zinc ores, whose zinc-bearing minerals (silicates and carbonates) occur together

with calcite, dolomite and/or other gangue minerals (Abkoshk *et al.*, 2014, Etjemae *et al.*, 2014, Khaleghi *et al.*, 2016).

The ore from a previously unstudied Brazilian zinc deposit (Ambrósia Norte) is comprised of smithsonite associated with the following gangue minerals: goethite (Fe₂O₃ · H₂O), quartz (SiO₂), kaolinite (Al₂(Si₄O₁₀)(OH)₈), calcite (CaCO₃), and dolomite (Mg,Ca(CO₃)). Bench anionic flotation was performed at a pH 9.5 using 10.7% Zn together with sodium silicate as a depressant (500 g/tonne) and sodium oleate as a collector (500 g/tonne), produced a rougher concentrate with Zn content and Zn recovery above 30% and 75%, respectively (Araújo and Lima, 2017; Ferreira, 2018).

Due to depletion of the zinc deposit of the Vazante region, the Ambrósia Norte

ore will be blended with Vazante ore within the next two years. In the Vazante ore, the major zinc-bearing minerals are willemite and hemimorphite, which are concentrated by cationic flotation. It is important to investigate the behavior of

smithsonite and dolomite from the Ambrósia Norte deposit during the cationic flotation process in order to understand the physico-chemical conditions required for selective separation between the carbonates, which have similar surficial

properties. In this study, the cationic flotation of smithsonite and dolomite from the Ambrósia Norte deposit were studied using sodium sulfide as the sulfidization agent, sodium silicate as the depressant, and amine as the collector.

2. Materials and methods

2.1 Sample of minerals and reagents

The preparation of the smithsonite and dolomite samples from Ambrósia Norte deposit, used in this study were comprised in comminution followed by size classification into

-212 +75 μm . The smithsonite sample was purified in a Frantz magnetic isodynamic separator with a field of 18.000 Gauss.

Figure 1 presents the X-ray dif-

fraction patterns of purified samples and indicates that there is a trace of quartz in both samples. Table 1 presents the chemical compositions of both the smithsonite and dolomite samples.

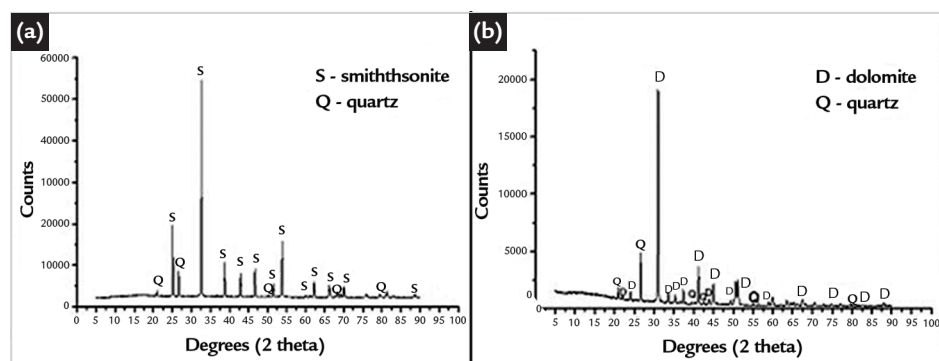


Figure 1
X-ray diffraction patterns of purified smithsonite (a) and dolomite (b). (Souza, 2018).

Mineral sample	Chemical composition and LOI (%)									
	ZnO	PbO	Fe ₂ O ₃	CaO	MgO	Ag ₂ O	CuO	SiO ₂	LOI	Others
Smithsonite	54.77	0.54	1.26	0.21	1.01	0.0002	0.001	10.97	30.88	0.36
Dolomite	0.22	0.01	1.12	24.96	19.7	-	-	-	39.99	13.93

Table 1
Chemical composition and loss of ignition (LOI) of mineral samples.

The reagents used in the microflotation tests and the zeta potential measurements were etherdiamine (Tomamine®) as the collector, sodium silicate (Na₂SiO₃)

modulus 3.33 (Quimidrol) as the depressant, sodium sulfide (Na₂S) as the sulfidizing agent, sodium chloride (NaCl) of analytical purity as an indifferent

electrolyte, and hydrochloric acid (HCl) (F Maia) and sodium hydroxide (NaOH) (Synth), both of analytical purity, as well as pH controls.

2.2 Microflotation tests

Microflotation tests (performed three times for each condition with a maximum standard deviation of 5%) were conducted in a Hallimond cell with a volume of 250 mL. For each microflotation test, 1 g of either smithsonite (mean particle size = 145 μm) or dolomite (mean particle size = 137 μm) mineral sample was transferred to the cell and conditioned with reagent solu-

tions (total volume 50.0 mL) at a speed of 600 rpm. The conditioning times of the minerals previously determined by Souza (2018) with a depressant (sodium silicate) or a sulfidizing agent (sodium sulphide) were 3 min. Following this initial conditioning stage, amine (18.5 mg/L) was added and conditioned for 7 min more. Thereafter, the cell volume was raised to 250 mL using

distilled water with a pH 11. Finally, a commercial nitrogen gas reservoir was opened and allowed to flow through the dispersion (at a flow rate of 60 mL/min) and flotation was performed for 1 min. Particles that floated and sank were then collected separately and filtered, dried, and then weighed for further calculations of the flotation mass recovery relative to the feed (recovery).

2.3 Zeta potential determination

Zeta potential determinations were carried out using a Zetasizer Nano Z model zetameter. A suspension density (250 mL) of 0.01% (-10 μm) with NaCl 1.0×10^{-4} M was prepared for each test. This solution was left in equilibrium for 15 h, before 40 mL of each suspension was transferred to beakers where a pH adjustment was performed to the desired value using HCl

or NaOH solution (i.e. a determination of the zeta potential without reagent). Zeta potential was also determined as a function of pH for the minerals conditioned with the following reagents: ether diamine: 18.5 mg/L (7 min), sodium silicate: 6 mg/L (3 min), and sodium sulphide: 5.0×10^{-3} M (3 min). After the conditioning of each of the minerals, two samples of the suspen-

sions within each beaker were sequentially added to the equipment cuvette, which performed three readings for each sample. The zeta potential value considered was determined by the arithmetic mean of the six values read for each condition, assuming 5% as the maximum standard deviation between the determinations of the readings.

3. Results and discussion

3.1 Microflotation

Figure 2 presents the recovery curves of smithsonite and dolomite as a function of pH. The maximum recovery of smithsonite (80.0%) occurred at pH 11, which is in agreement with what have been found in previous studies (Hosseini, 2015, Ejtemari *et al.*, 2014). At this pH value, dolomite recovery was also at its maximum (57.4%). Notably, for pH values lower than 8, the recovery of dolomite was greater than that of smithsonite, which is coherent with the zeta potential values of both minerals, since the isoelectric point (IEP) of dolomite and smithsonite occurs

within the pH levels of 6.3 and approximately 8, respectively (Araújo and Lima, 2017). As the negative charge of dolomite in the pH range is more negative than that of smithsonite and the dominant reagent specimen is DiAm^{2+} , hence it was more attracted by the dolomite surface than the smithsonite surface. For pH values above 8, we found that the recovery of smithsonite was greater than that of dolomite, which can be related to the interaction of the DiAm species with surface zinc, forming zinc amino-complexes or zinc hydroxyl complexes on the surface of

smithsonite (Marabini *et al.*, 1984, Scott and Smith, 1991).

The maximum recovery of both dolomite and smithsonite at pH 11 (Figure 2) is related to the adsorption of the ionomolecular species $\text{DiAm} \cdot \text{DiAm}^+$, which decreases the electrostatic repulsion of the DiAm^+ species, increasing the hydrophobicity of the minerals. The recovery drop of both minerals at pH 12 is probably related to the predominance of the molecular species ($\text{DiAm}_{(s)}$ and $\text{DiAm}_{(aq)}$) in the solution (Marabini *et al.*, 1984, Scott and Smith, 1991).

Figure 2
Smithsonite and dolomite recovery with ether diamine, at 18.5 mg/L concentration, versus pH.

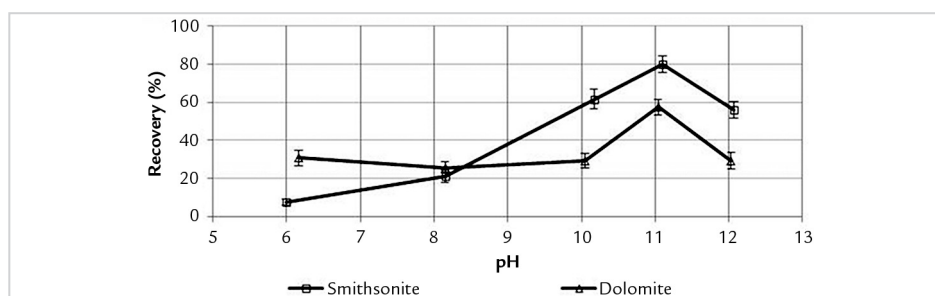
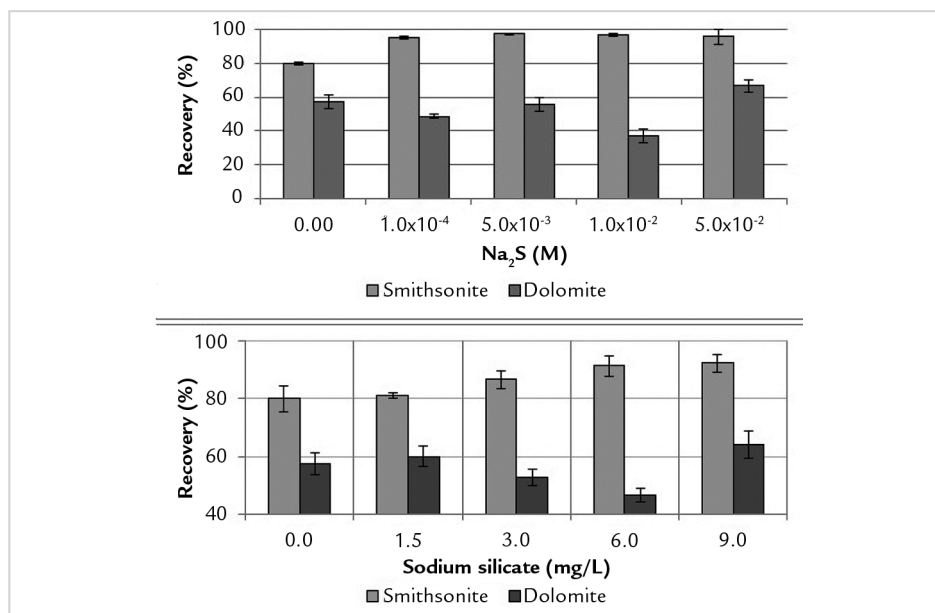


Figure 3 shows the recoveries of smithsonite and dolomite as a function of the concentrations of Na_2S and sodium silicate. This shows that the previous conditioning of smithsonite with Na_2S allows a significant increase (15 to 17%) in its recovery independent of the dosage applied. This implies that

a lower dosage of amine is sufficient to reach a higher recovery of this mineral. In accordance with the speciation diagram HS^- is the predominant form in the pH range between 9 and 11. At pH 11, S^{2-} begins to form (Hosseini and Forsberg, 2006). In accordance with previous studies, the earlier sulfidiza-

tion of smithsonite renders its surface less hydrophilic, due to the formation of a zinc sulphides film in addition to the partial substitution of CO_3^{2-} by S^{2-} in the crystalline lattice of the same, favouring the interaction between the cationic collector and the mineral surface (Wu *et al.*, 2015).

Figure 3
Recovery of smithsonite and dolomite versus Na_2S and sodium silicate concentrations at pH 11 (ether diamine = 18.5 mg/L).



The recovery of smithsonite increased with an increase in concentration of sodium silicate (maximum of 12% at 9 mg/L; Figure 3). However, for dolo-

mite, the inverse was observed up to a concentration of 6.0 mg/L (decrease of 11%), before an increase in the recovery of dolomite was seen at 9.0 mg/L. Based on

the speciation diagram of sodium silicate, the specimen ($\text{Si}(\text{OH})_3^-$) is predominant at pH 11 (Sjoeborg and Ohman, 1985; apud Rao and Forsberg, 2007). This

specimen could adsorb to the positive sites of both minerals, thus rendering their surfaces more negatively charged and consequently providing a greater adsorption of the cationic species of the collector by electrostatic attraction.

There was a slight drop observed in the dolomite recovery at Na_2S concentrations up to 1.0×10^{-2} M compared with its recovery using only ether diamine (Figure 3). This phenomenon

3.2 Zeta potential

Figure 4 depicts the zeta potential curves of smithsonite and dolomite as a function of pH, without reagent and conditioned with the reagents used in the microflotation tests.

The observed pH_{Iep} (isoelectric point) of smithsonite (without reagent) is around pH 8.3 (Figure 4), which is consistent with values reported in previous studies (Araújo and Lima, 2017; Hosseini and

may have occurred due to the high stability of the CaS species formed on the surface of dolomite, thus reducing the number of empty sites available for the interaction of the cationic and iono-molecular species of the collector and consequently decreasing its recovery (Araújo and Lima, 2017). The slight increase in dolomite recovery at concentration of 5.0×10^{-2} M may be due to the observed decrease of its hydrophilicity

Forsberg, 2006). After conditioning with ether diamine, the pH_{Iep} of smithsonite increased from 8.3 to approximately 10, which could be ascribed to the adsorption of the cationic ether diamine species in the Helmholtz internal plane. At pH 11, the zeta potential of smithsonite became less negative compared with the zeta potential of the mineral without reagent. This variation was not of great magnitude, suggesting

with increasing Na_2S . In accordance with Marabini *et al.* (1984), the DiAm species interacts with the surface zinc (ZnCO_3 or ZnS) through complex bonds at pH values of around 11, forming zinc amino-complexes or zinc hydroxyl complexes at the surface of smithsonite. This same effect could occur with CaS on the surface of dolomite, however, further investigations are necessary to confirm this hypothesis.

the adsorption of the amine species (DiAm⁺ and DiAm) present in the solution onto the mineral surfaces. It was also noted that when the pH was around 12, there was no significant variation of zeta potential values in relation to those of the mineral without reagent; this behavior is possibly related to the predominant molecular species of the collector in the solution for pH values from 11 (Scott and Smith, 1991).

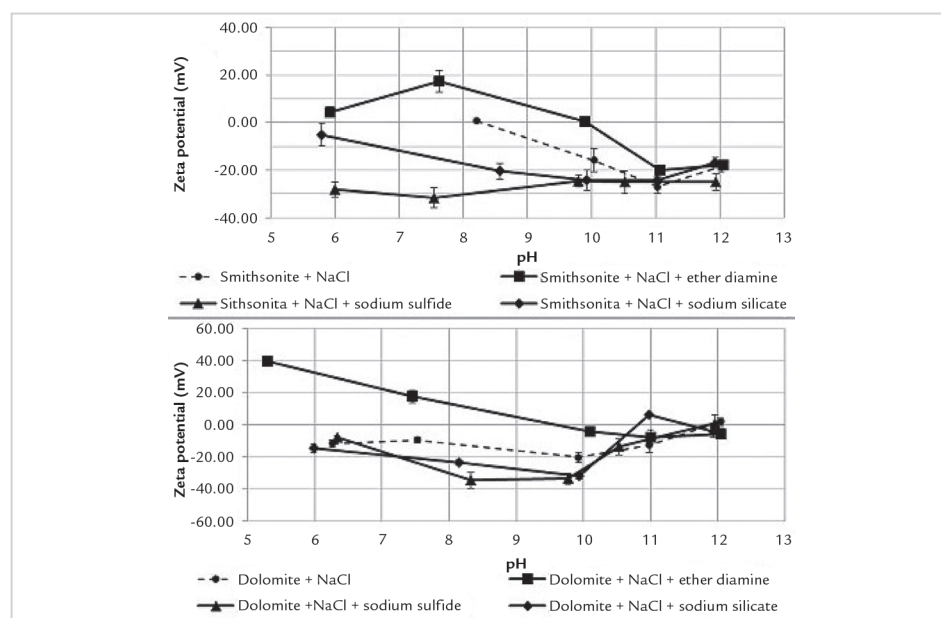


Figure 4
Zeta potential of smithsonite and dolomite versus pH both without reagents and conditioned with the following reagents: ether diamine (18.5 mg/L), Na_2S (5.0×10^{-3} M) and sodium silicate (6.0 mg/L).

As documented in Figure 4, the zeta potential values of smithsonite became more negative in the presence of sodium sulphide, which may be due to the interaction between the anions of HS^- , which is the predominant Na_2S species. Between pH 7 and 13, it has been reported that HS^- reacts with the Zn^{2+} cations at the surface of the mineral, forming a ZnS film (Hosseini and Forsberg, 2006; Ejtmaei *et al.*, 2014). The zeta potential of ZnS is more negative when compared with results obtained for smithsonite without reagent (Hosseini, 2008). Wu *et al.* (2015), using scanning electron microscopy coupled to energy dispersive scattering (SEM/EDS) and X-ray photoelectric spectroscopy

(XPS) concluded that the smithsonite surface was partially changed to a ZnS film after sulphide treatment; furthermore, they inferred that a reaction exchange between S^{2-} and CO_3^{2-} occurred within the crystal lattice of the mineral.

The zeta potential values of smithsonite conditioned with sodium silicate became more negative compared to the mineral without reagent. Based on the specimen diagram of sodium silicate (Rao and Forsberg, 2007), it could be inferred that the anionic species of sodium silicate – $\text{SiO}(\text{OH})_3^-$ and $\text{Si}_2\text{O}_3(\text{OH})_4^-$ – were adsorbed in the Helmholtz internal plane of the double electric layer of smithsonite.

Figure 4 shows the observed zeta po-

tential negative values of dolomite without reagent (Dolomite + NaCl), varying from –10 to –20 mV between pH values of 6 and 11. At a pH close to 12, the zeta potential was found to change from a negative to positive value. As dolomite is a weakly soluble mineral, cations of Mg^{2+} hydrolyse in aqueous solutions to form $\text{Mg}(\text{OH})_2$ at this pH region. Following this, this specimen deposits on the mineral surface and changes its surface charge from negative to positive, once its IEP occurs at pH 12 (Araújo and Lima, 2017; Gence, 2006).

The zeta potential values of dolomite became positive at pH values lower than 9.5 after conditioning with ether diamine (Figure 4). Based on the speciation dia-

gram of diamine (Scott and Smith, 1981), the specimen DiAm^{2+} was dominant up to pH 6, followed by DiAm^+ that reached its maximum concentration around pH 6 before continually decreasing and disappearing until pH values of approximately 11. The molecular DiAm formed when the pH values were approximately 5.5, reaching maximum concentration at pH 8, and becoming dominant at alkaline pH values. The positive zeta potential values of dolomite conditioned with amine up to pH 9.5 may be a result of the presence of the cationic species of the reagent (DiAm^+

and DiAm^{2+}) specifically adsorbed on the Helmholtz internal plane. Above pH 10, the zeta potential values of the mineral were negative and approximately constant (~ -5 mV), however, with a modulus lower than the values for the mineral without reagent, which can be attributed to a decrease of the cationic species of the reagent in the solution.

The zeta potential values of dolomite conditioned with Na_2S (Figure 4) became more negative compared with values obtained without reagent. It is probable that, as occurred in the case of smithson-

ite, there was an interaction between the HS^- anions and the Mg^{2+} and Ca^{2+} cations of the dolomite, concomitantly with the substitution of CO_3^{2-} by S^{2-} (Wu *et al*, 2015), which combines to make the zeta potential of the mineral more negative.

At pH levels below 10, the zeta potential values of the dolomite conditioned with sodium silicate were more negative in relation to the zeta potential values of the mineral without reagent, probably resulting from the adsorption of the anionic species $\text{SiO}(\text{OH})_3^-$ present in the solution (Figure 4).

4. Conclusions

Our results conclude that at pH 11, selective flotation between smithsonite and dolomite is possible when using diamine as a collector, Na_2S as the sulfidising agent of smithsonite, and sodium silicate as a dolomite depressant at concentrations of up to 6.0 mg/L. Na_2S significantly increased the recovery of smithsonite at all evaluated concentrations. The values of the zeta potentials of the minerals with amine contributed to the inference that the adsorption of

cationic species (DiAm^+ and DiAm^{2+}) occurred at the surface of both negatively charged minerals. The higher recovery of smithsonite at pH 11, when compared to dolomite, is due to the formation of zinc amino complexes at its surface. The zeta potential values of smithsonite conditioned with sodium silicate were more negative in relation to the zeta potential values of the mineral without reagent. The same behaviour was observed for dolomite at pH values up to 10. At pH

11 to 12, positive and less negative zeta potential values were observed, respectively, in relation to the values observed for the mineral in the absence of sodium silicate. The zeta potential values of the smithsonite conditioned with Na_2S were more negative than the values for the mineral without reagent at all pH values. In the case of dolomite, an increase in the negative values of zeta potential was only observed for pH values of 8 to 10.

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