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Kupka, N.; Rudolph, M.;

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Role of sodium carbonate in scheelite flotation – a multi-faceted reagent

Nathalie Kupka^{1,a}; Martin Rudolph¹

¹*Helmholtz Institute Freiberg for Resource Technology, Helmholtz Zentrum Dresden-Rossendorf, Chemnitz
Straße 40, 09599 Freiberg, Germany*

^an.kupka@hzdr.de

Abstract

Even though sodium carbonate is a reagent frequently used in flotation, its role is mostly described as a buffering pH modifier and a pulp dispersant. In the case of scheelite flotation, it has been hinted that sodium carbonate improves both grade and/or recovery but the mechanism itself is ambiguous at best or at least has not been distinctly reported in the literature. Furthermore, the addition of depressants such as sodium silicate or quebracho could be triggering additional mechanisms. Through batch flotation testwork on a skarn scheelite ore with high calcite content, single mineral flotation and contact angle measurements, this article aims at demonstrating that sodium carbonate is a multi-faceted reagent, which serves as a buffering pH modifier, a pulp dispersant precipitating calcium and magnesium ions in suspension, a depressant for calcite and calcium silicates and also a promoter for scheelite. It acts mostly synergistically and partially antagonistically with other depressants, notably sodium silicate and quebracho.

Keywords: sodium carbonate, scheelite flotation, mechanism

1. Introduction

A typical reagent regime for scheelite flotation is called the “lime flotation process”, which involves the addition of lime and sodium carbonate as co-pH modifiers, sodium silicate as a depressant and oleic acid (or sodium oleate) as the main collector [1, 2].

The presence of lime could be considered as ill-advised as it was commonly observed that calcium had deleterious effects in fatty acid flotation systems [3]. Indeed, Arnold et al. [4] and Gao, Z. et al. [5] showed that scheelite recovery could decrease drastically at very high concentrations of Ca^{2+} or Mg^{2+} when using sodium oleate as a collector, especially since it is sensitive to water hardness [6].

This is where sodium carbonate comes along: this reagent precipitates calcium and magnesium ions into CaCO_3 and MgCO_3 if the pH is high enough, as well as heavy metal ions [7-12], limiting their presence in the pulp. Additionally, sodium carbonate, namely its carbonate ion, is sensitive to pH and can end up precipitating onto mineral surfaces [7, 9] such as fluorite [13, 14] or calcite [1]. This means it could end up depressing said minerals.

Sodium carbonate (or soda ash) is therefore a buffering pH modifier [8, 10, 15], a pulp dispersant [7-10] and a depressant at the same time [7]. In the case of scheelite flotation, it has been shown that sodium carbonate improves both grade and/or recovery [16-19] but the mechanism itself is ambiguous or at least has not been distinctly reported in the literature for scheelite. Furthermore, the addition of depressants such as sodium silicate or quebracho could be triggering new mechanisms [3, 16, 17].

As a consequence, this article aims at describing the effects of sodium carbonate in order to identify or at least hypothesize its role in froth flotation of scheelite.

2. Material and Methods

Single minerals Scheelite and calcite were the feed materials for single mineral flotation (microflotation). Scheelite came from the Mittersill mine, Austria, and was concentrated through gravity separation, sulphide flotation and magnetic separation. The target size fraction was 32-63 μm . X-ray diffraction determined that the sample was composed of 96 wt% scheelite with pyrite, molybdenite and other minerals as contaminants. Calcite came from Sträßberg, Germany and the 63-100 μm fraction was selected. Purity of the calcite sample was determined by X-ray diffraction and

1 showed that it was composed of 97 wt% of calcite, 1wt% of quartz and minor amounts of fluorite,
2 ilmenite and others.

3 **Microflotation** was conducted in a Hallimond tube designed at the TU Bergakademie Freiberg. 1g of
4 the single minerals is added to an aqueous solution of 10^{-2} M KCl, stirring on a magnetic stirrer with a
5 rotation speed of 400rpm. 3 to 5 minutes are allocated to pH conditioning with HCl and NaOH. After
6 achieving stable pH, the depressant is added before the collector with a conditioning time of 2 and 3
7 minutes respectively. The flotation suspension is transferred to the Hallimond tube and agitated for
8 another 3 minutes with a rotational speed of 800rpm using a magnetic stirrer. Airflow rate is set to 20
9 cm^3/min and microflotation lasts 2 minutes. The filtered flotation products are dried in an oven
10 overnight at 50-60°C and flotation recovery and loss are calculated based on said dried weights. All
11 experiments were conducted at least twice, up to five times, the number of repetitions being driven
12 by the mass loss, which had to be strictly inferior to 10%.

13 **Batch flotation** The ore used for batch flotation tests contains 0.51% scheelite, 1.70% calcite, 0.28%
14 apatite and various silicates (quartz, micas, plagioclases and hornblende). The ore was ground with a
15 rod mill and has a d_{80} of 63 μm after milling. Froth flotation tests were conducted with 500g of ore at
16 33% pulp density in a Magotteaux® bottom-driven flotation cell and at constant pH of 9.5. Each had
17 only a rougher stage, lasted seven minutes and involved three concentrates with a 5 second scraping
18 rate, 450 rpm impeller speed and an air flowrate of 5L/min. The filtered flotation products are dried in
19 an oven overnight at 50-60°C and mass pull is calculated based on said dried weights. All samples were
20 split and send to ICP-MS and XRF for chemical assays (done by ALS Global®). It should be noted that all
21 calcium grades given in this article have been recalculated by removing calcium contained in scheelite.
22 The feed and tailings water samples were sent to ICP-OES for cation assays (done by the Technische
23 Universität Bergakademie Freiberg, Germany). Finally, automated mineralogy conducted on the feed
24 of flotation (after milling) showed that minerals are well liberated, with a surface liberation of 96% for
25 scheelite.

26 **Contact angles** Contact angle measurements were conducted on epoxy resin grain mounts of scheelite
27 and calcite with a Dataphysics OCA 50 instrument equipped with the SCA 20 software. The pure
28 scheelite crystal came from Malakka, India whereas the pure calcite crystal came from Mittersill,
29 Austria. The single crystal is conditioned in a background solution of 10^{-2} mol/l KCl and the reagents
30 (also prepared with KCl) are added one after the other after setting the pH at 9 with NaOH. The grain
31 mount is then dried with an air blower and placed on the instrument. Measurement is done with the
32 sessile drop method with water droplets of a constant volume of 1 μL . Once the measurement is
33 complete, the substrate is polished and cleaned in a plasma cleaner before being used again. Each
34 point displayed on the diagrams corresponds to at least 12 to 20 measurements unless the angle is
35 lesser than 10°, then it corresponds to 5 measurements.

36 **Reagents** Sodium oleate ($\text{C}_{18}\text{H}_{33}\text{NaO}_2$) of >90% purity from Carl Roth® was used as a collector at a
37 single dosage of 200g/t in order to avoid multicomponent technical grade collectors with effects
38 difficult to evaluate. A complex mixture of glycols, Flotanol 7197® from Clariant Mining Solutions®, was
39 used as a frother at 20g/t. Four pH modifiers were used: analytical grade sodium hydroxide (NaOH),
40 lime (CaO), and HCl from Carl Roth® and analytical grade sodium carbonate (Na_2CO_3) from Alfa Aesar®.
41 Analytical grade sodium chloride (NaCl) from Carl Roth® was used for microflotation. Depressants
42 included analytical grade of sodium metasilicate nonahydrate ($\text{Na}_2\text{O}_3\text{Si}\cdot 9\text{H}_2\text{O}$) from Aldrich Chemistry®
43 and extract of quebracho from Baeck GmbH & Co.

54 3. Impact as a co-pH modifier

55 Different pH modifiers can be used in scheelite flotation, such as sodium hydroxide, sodium carbonate
56 or calcium oxide. As described before, sodium carbonate can be considered a co-pH modifier, even
57 though its addition fulfills several roles. In a series of scheelite batch flotations, the authors compared
58 the impact of the pH modifier type by using NaOH and CaO alone or in combination with sodium
59 carbonate. The authors chose not to use sodium carbonate alone because:
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- Vazquez et al. [1] note in their scheelite flotation that sodium carbonate alone (without lime or NaOH) did not precipitate any dissolved calcium in their case and that these calcium ions did not have any impact on either grade or recovery anyways.
- By analyzing De Castro et al. [20]'s data, it appeared that sodium carbonate alone compared to sodium hydroxide did not offer higher grades or higher selectivity against calcite in the flotation of celestite (SrSO_4).

3.1. General observations

When looking strictly at mass pull and water pull curves (Figure 1, top left), it seems the type of pH modifier is irrelevant. The addition of sodium carbonate appears to slow down the flotation rate. It could be therefore considered that sodium carbonate does not interact with the froth whatsoever. The influence is much greater when considering the grade-recovery curves and the tungsten-calcium selectivity curves (Figure 1, top right, bottom left).

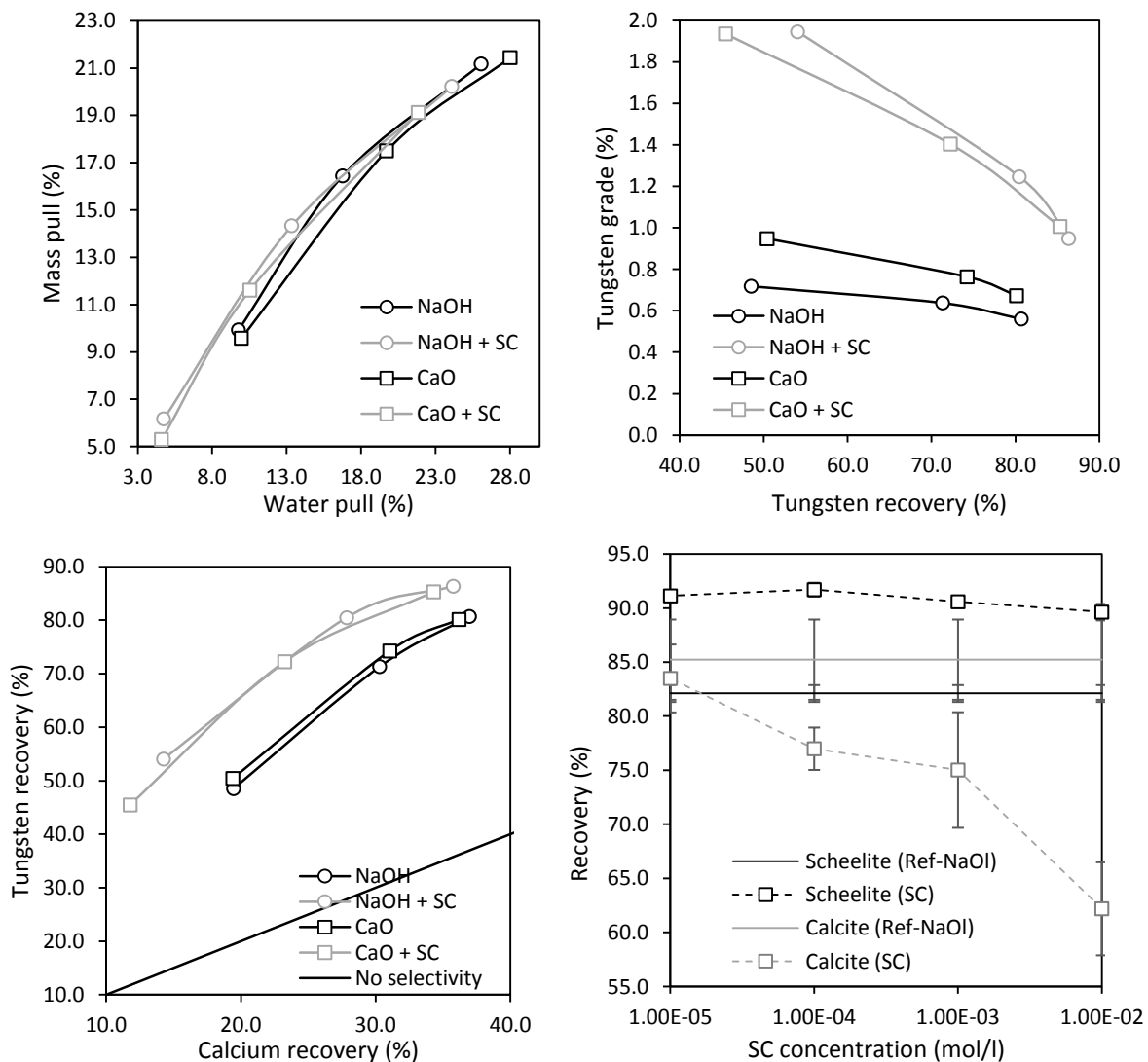


Figure 1: top left – mass pull against water pull depending on the pH modifiers in use, top right – grade-recovery curves, bottom left – selectivity curves and bottom right – Single-mineral flotation results for scheelite and calcite, pH is set at 9 with NaOH, sodium oleate is added at a dosage of 1×10^{-4} mol/l (Ref-NaOl are experiments without sodium carbonate)

The difference between CaO and NaOH is limited, using CaO does improve the grade but does not impact the recovery, which has been observed by Vazquez et al. [1] in the seventies. These authors had also stated that using NaOH produced a poor flotation response, which is not the case here. The presence of sodium carbonate has a deep impact on the grade and recovery of tungsten. It seemingly erases the difference between NaOH and CaO while improving the flotation performance and

selectivity against calcium-bearing minerals (except apatite which is not represented here) as well as silicates (also not represented here).

Taking into account the fact that in this ore, most of the calcium is contained in silicate minerals, it could be considered that sodium carbonate increases selectivity against calcium-containing silicates and have no interaction with calcite. However, single-mineral flotation showed this was not the case (Figure 1, bottom right) as sodium carbonate promotes scheelite and depresses calcite specifically. This additional selectivity against calcite between NaOH and sodium carbonate was signaled by Klassen and Mokrousov [21] in the sixties without specifying for which flotation type.

These microflotation results are the exact opposite of those obtained by Patil and Nayak [22], whose scheelite single-mineral flotation is affected in the presence of high concentrations of sodium carbonate. In their case, calcite recovery remained unaffected. They worked however at higher pH (10), lower collector dosage and shorter flotation times.

3.2. Calcium and magnesium ions in the pulp

Figure 2 shows the enrichment rate in calcium and magnesium ions between the feed water and the tailings water depending on the pH modifier in use. Iron has also been measured but is ignored as the values were too close to zero to be reliable. It has been stated before that sodium carbonate limits calcium and magnesium ions in the pulp. Comparing NaOH to NaOH + SC, it appears clearly that the Ca^{2+} and Mg^{2+} have been reduced, calcium more intensely so. This had been observed by Dean and Schack [23] in the batch flotation of five different calcareous scheelite ores from the USA, who stated that “sodium carbonate was more effective than sodium hydroxide as an overall pulp-regulating reagent”. Between CaO and NaOH, it is clear that calcium is much more reduced since the input of calcium ions is higher when using lime. In their flotation of Co-Mo sulphide ores, Jeldres et al. [24] wrote that lime as an alkalinizing reagent is a “promoter of magnesium precipitation” whereas sodium carbonate precipitates calcium but the magnesium reduction is “conservative”. In the present case, when comparing CaO to CaO + SC, there indeed has been a magnesium reduction but the presence of sodium carbonate resulted in lower calcium reduction.

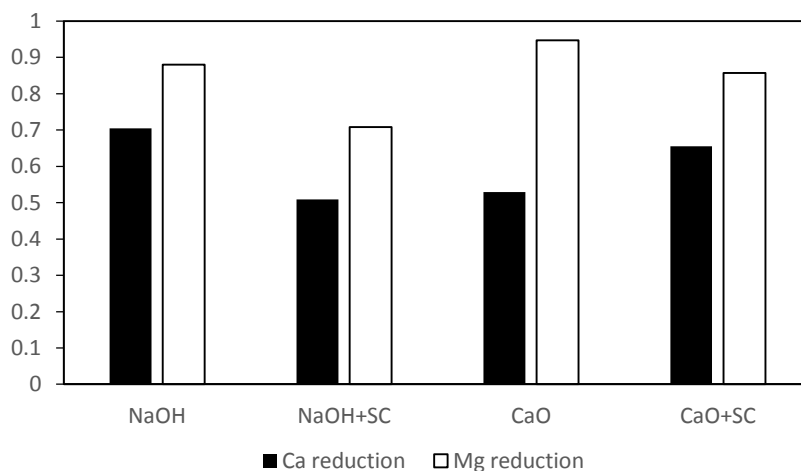


Figure 2: Calcium and magnesium ions reduction in the tailings water (SC being the abbreviation of sodium carbonate)

As a whole, these ions do not seem to play a role in the present flotation experiments and the pulp dispersing properties of sodium carbonate are not of primary importance here.

3.3. Flotation kinetics

Finally, the experimental flotation rate k and the associated maximum recovery at infinite flotation time R_{max} for tungsten, calcium and silica has been calculated based on the classical first order kinetics equation [25] (Figure 3). Interestingly, if the presence of sodium carbonate clearly slows down the flotation rate for calcium, it does not impact the R_{max} . This could mean that sodium carbonate first depresses calcite, and that the dosage is not enough to depress calcium silicates, which will end up in the slow-floating fraction or be entrained. For silica, R_{max} logically increases, because the non-floated

calcium-bearing minerals are replaced with the silica gangue, while the flotation rate constant still decreases because calcium silicates are slowed down. For tungsten, if sodium carbonate does improve the R_{max} , it either barely impacts its flotation rate or slows it down. The effect here is unclear. Its R_{max} appears correlated with the one from silicates, but this is only a coincidence since MLA (Mineral Liberation Analysis) conducted on the feed of flotation showed that scheelite was $\sim 96\%$ liberated.

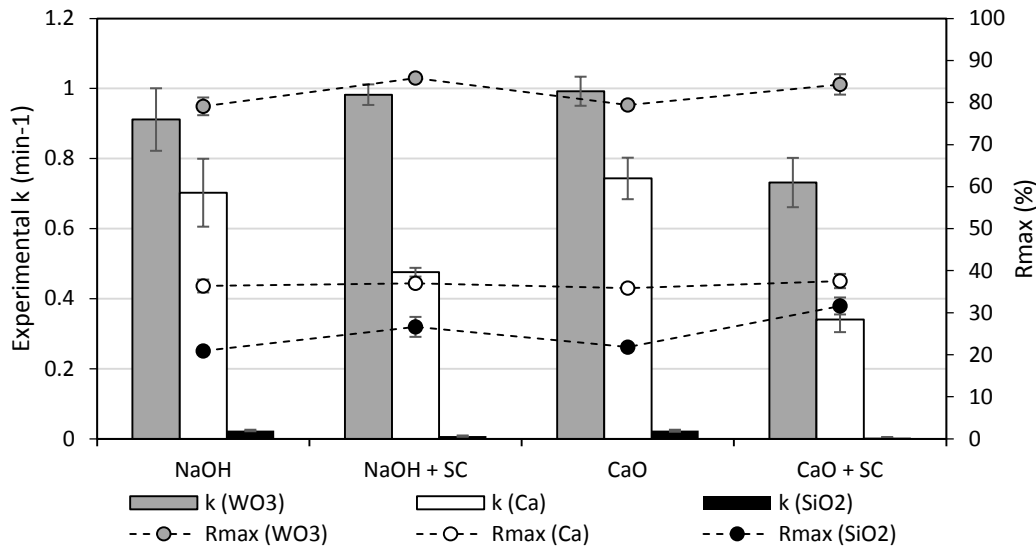


Figure 3: Flotation kinetics - experimental k and R_{max} of tungsten, calcium and silica

3.4. Short summary

As a summary, in the absence of depressants, the presence of sodium carbonate yields the following observations:

- The absence of impact on mass and water pull would support the idea that sodium carbonate does not interact with the froth in any way;
- It increases tungsten recovery and grade, clearly showing a promoting effect for scheelite. It also increases selectivity against calcium-bearing minerals, notably calcite, and silicates. This increase in selectivity could be linked to the fact that sodium carbonate delays the flotation of calcium minerals by depressing calcite and only a part of the calcium silicates, which will end up either entrained or in the slow floating fraction.
- Magnesium reduction always take place and is intensified by sodium carbonate. The behavior of calcium ions is inconclusive. Besides, their impact in the present flotation is virtually non-existent while using sodium carbonate. Between CaO and NaOH alone however, calcium ions in suspension might be improving concentrate grade.

4. Interaction with depressants: example of sodium silicate and quebracho

Sodium carbonate alone does behave as more than a pH modifier, it could be both a promoter for scheelite and a depressant for calcium-bearing minerals, especially calcite but excluding apatite. Yet, these effects might vary in the presence of additional depressants. In order to test this hypothesis, two classic depressants for scheelite flotation have been used, namely sodium silicate and quebracho, sodium silicate being the primary focus of this article and quebracho allowing for a comparison.

A flotation testwork was set up using DesignExpert® software (Version 10.0.5.0) from Stat-Ease, Inc, with three parameters with several levels: the type of pH modifier (4 levels: NaOH, lime and both with sodium carbonate), the type of depressant (2 levels: sodium silicate and quebracho) and the dosage of the depressant (3 levels). The dosages of water glass and quebracho were adapted based on previous flotation testwork conducted on the ore in use: dosages of sodium silicate were 500, 1000 and

2000g/t and quebracho 15, 30 and 60g/t, while sodium carbonate was added at a constant dosage of 100g/t.

This flotation program bore in mind that Crozier et al. [26] considered that two levels for a variable would detect trends only, three would detect the existence of a response curve but not its shape, and more than three levels would progressively refine the shape. The testwork includes repetitions of the experiments. DesignExpert® was then used to analyze the data through ANOVAs and create response models with predictive properties, as can be seen in the following figures.

4.1. Mass pulls

First, in terms of mass pull (Figure 4), the presence of sodium silicate leads to an intense decrease in mass collected in the concentrates which is expected, similarly to quebracho, where the decrease is more moderate but still marked. Water pulls show the same trends and froth effects cannot be ignored. The trends are almost identical for both depressants: using CaO as a pH modifier is at the beginning less affecting the mass pull than NaOH is but then brings about a greater decrease in mass pull with increasing dosage of depressants. This difference between CaO and NaOH fades completely in the presence of sodium carbonate.

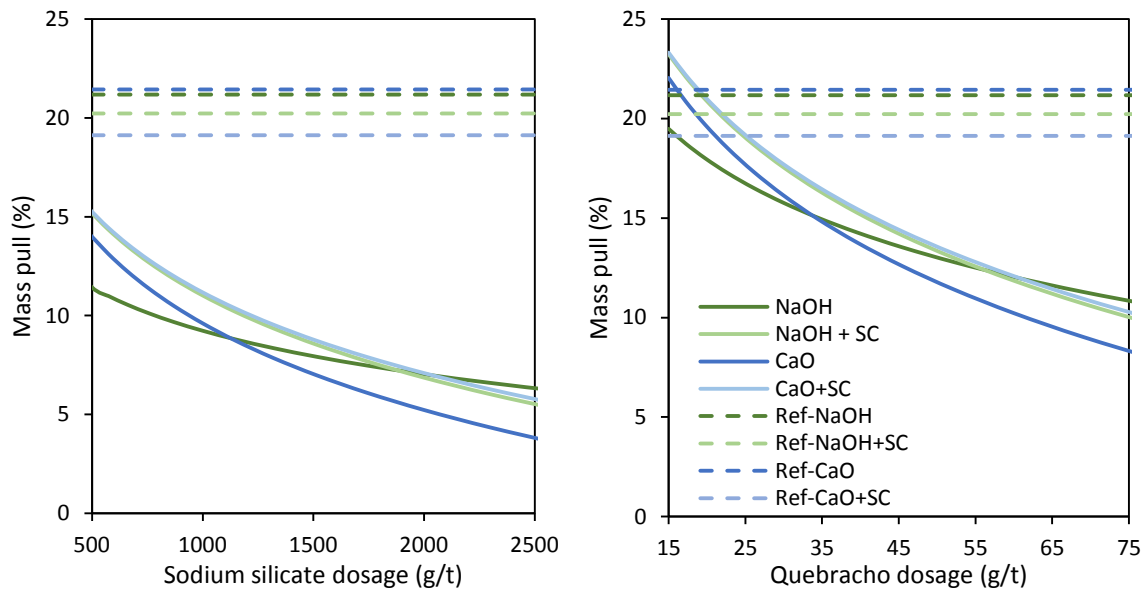


Figure 4: Mass pull depending on the type of pH modifier and the depressant dosage with left sodium silicate and right quebracho, as a result of statistical analyses of the experimental results, legend is the same for both diagrams, Ref is the reference value of the mass pulls for tests without depressants

4.2. Tungsten grade and recovery

Logically, when the mass pull decreases massively, the recoveries of minerals will follow. Therefore, it is not surprising to see that sodium silicate induces an intense decrease in tungsten recovery with higher dosages (Figure 5). This decrease is much more limited for quebracho. In the case of sodium silicate, the tungsten grade is doubled to quadrupled for the same recovery as the reference tests. Interestingly, even though quebracho is often regarded as a better depressant in scheelite flotation than sodium silicate, it does not seem to be superior to sodium silicate in its lower dosages for this ore. If there is a slight improvement in grade, it's mostly in the fact that higher dosages do not impact the tungsten recovery as much that quebracho might be considered better. In the absence of sodium carbonate, NaOH appears as the better pH modifier compared to CaO, which is the opposite result of when no depressant is in play.

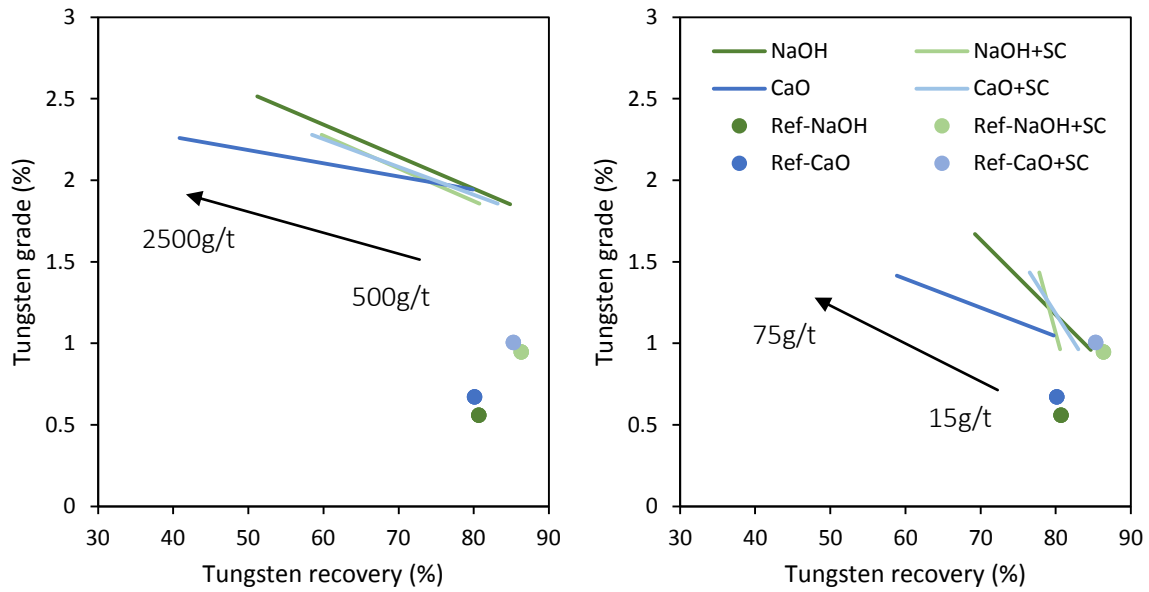


Figure 5: Tungsten grade-recovery curves depending on the type of pH modifier and the depressant dosage with left sodium silicate (dosages from 500 to 2500g/t increasing from l to left) and right, quebracho (dosages from 15 to 75g/t increasing from right to left), as a result of statistical analyses of the experimental results, legend is the same for both diagrams, Ref is the reference value of the tungsten grade-recoveries for tests without depressants

Single mineral flotation might provide part of an explanation to these observations (Figure 1 bottom right and Figure 6). When tested with only sodium oleate and sodium silicate, scheelite was slightly depressed by sodium silicate whereas calcite was almost completely depressed. For sodium oleate and sodium carbonate, scheelite is promoted while calcite is slightly depressed with increasing dosage. It's in presence of both sodium silicate and sodium carbonate that flotation seems most effective: on one hand, calcite flotation improves slightly and seems to reach an average between SS and SC alone at high sodium carbonate dosages but is yet depressed. On the other hand, any depression effect on scheelite disappears and the mineral is actually promoted. It would seem that sodium carbonate largely prevents interaction between scheelite and sodium silicate and more moderately between calcite and sodium silicate. These microflotation tests have not been conducted with quebracho.

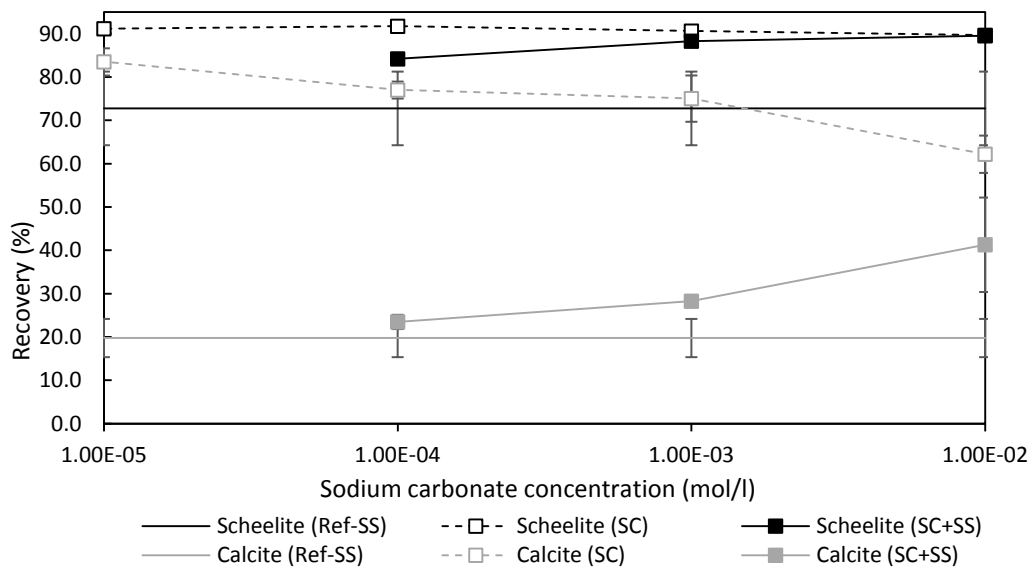


Figure 6: Single-mineral flotation results for scheelite and calcite, pH is set at 9 with NaOH, sodium oleate is used as a collector at a dosage of 1×10^{-4} mol/l, sodium silicate is used as a depressant at a dosage of 1×10^{-2} mol/l (Ref-SS referring to experiments without sodium carbonate and with sodium silicate)

4.3. Selectivity against calcium, phosphate and silica

Tungsten-calcium selectivity curves (Figure 7) provide additional information to the tungsten grade-recovery curves. The difference between NaOH and CaO is less marked in the selectivity against calcium when using sodium silicate than quebracho but follows the same trend of a moderate superiority of NaOH. According to Iskra et al. [27], quebracho adsorbs onto scheelite, fluorite and calcite surfaces via lattice and pulp calcium ions in different proportions depending on the mineral and therefore competing with the collector on the mineral surface. They consider therefore that excess calcium ions in the system will cause quebracho to bind to scheelite as well, which would fit with the present results with CaO.

As a consequence of the previous observations, it is only logical that the selectivity against calcium is much higher for sodium silicate than quebracho, as the mass pull and the tungsten grade-recoveries are much lower. Finally, as previously stated, the presence of sodium carbonate erases any difference between CaO and NaOH and improves the overall performance. At low dosages, sodium silicate performs better than quebracho but with increasing dosage, quebracho allows higher selectivity without losing any tungsten.

Selectivity against phosphate (represented only by apatite in this ore) has also been investigated. Similarly to the absence of depressant, regardless of the pH modifier and the depressant in play, selectivity against apatite is non-existent. The presence of sodium carbonate actually promotes apatite.

Selectivity against silica shows the same trends as with selectivity against calcium. Silicates, notably quartz, are activated in the presence of calcium ions on the basis of exchanges between Ca^{2+} and hydrogen ions on the silicates surface [19]. This would explain why selectivity is lower when using CaO on its own. Sodium silicate is much more selective against silicates than quebracho, which is logical based on the fact that sodium silicate is originally a depressant for silicates.

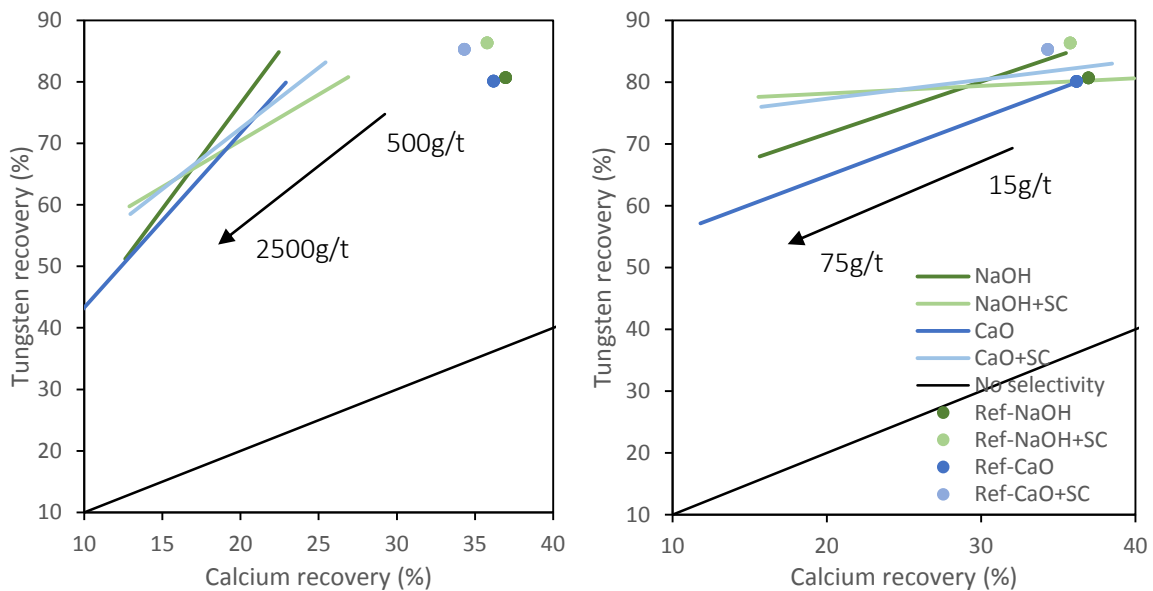


Figure 7: Selectivity curves of tungsten against calcium depending on type of pH modifier and the depressant dosage with left sodium silicate (dosages from 500 to 2500g/t increasing from right to left) and right, quebracho (dosages from 15 to 75g/t increasing from right to left), as a result of statistical analyses of the experimental results, legend is the same for both diagrams, Ref is the reference value of the selectivity curves without depressants

4.4. Calcium and magnesium ions in the pulp

Understandably, calcium ions behave differently in the presence of depressants. In the case of sodium silicate, the higher the dosage, the greater the calcium ion concentration in the tailings water, regardless of the pH modifiers in use. The concentration increases so greatly, that without any sodium carbonate, calcium ions are actually enriched instead of being reduced and if they are reduced, it's at

a higher rate than in the absence of depressants. It seems therefore that sodium silicate increases the solubility of calcium-bearing minerals, which could very well be the calcium-silicates.

As a consequence, the pulp dispersing properties of sodium carbonate play a greater role here and the possibility that it can reduce calcium ions is actually visible, especially in the case of CaO+SC, where the reduction is increased compared to CaO on its own or without depressant. It is also possible that sodium carbonate does not precipitate the calcium ions in suspension but simply prevents sodium silicate from increasing the solubility of calcium-bearing minerals. It could simply be a combination of both.

The behavior of calcium ions is entirely different with quebracho. Without sodium carbonate, calcium ions are slightly more or slightly less reduced for NaOH and CaO alone respectively. This reduction is unchanged throughout the dosage increase. It could be considered that either quebracho does not interact at all with ions in the pulp, hence the almost flat lines, or, based on the theory of Iskra et al. [27], quebracho consumes the calcium ions arising from solubility in a stable manner, which would assume that at higher dosages not all the quebracho is consumed or it consumes calcium ions (this is unlikely). Interestingly, the fact that the calcium reduction remains unchanged with the dosage also means that sodium oleate does not interact with calcium ions at all, as they are not floated with the concentrate. Sodium carbonate causes a moderate intensification of the reduction, greater for CaO than for NaOH. Similarly to the case with sodium silicate, there are three possibilities: either sodium carbonate also competes on the mineral surface with quebracho, preventing its absorption and forcing its precipitation with ions in the pulp, or it reduces calcium ions directly or it does a bit of both.

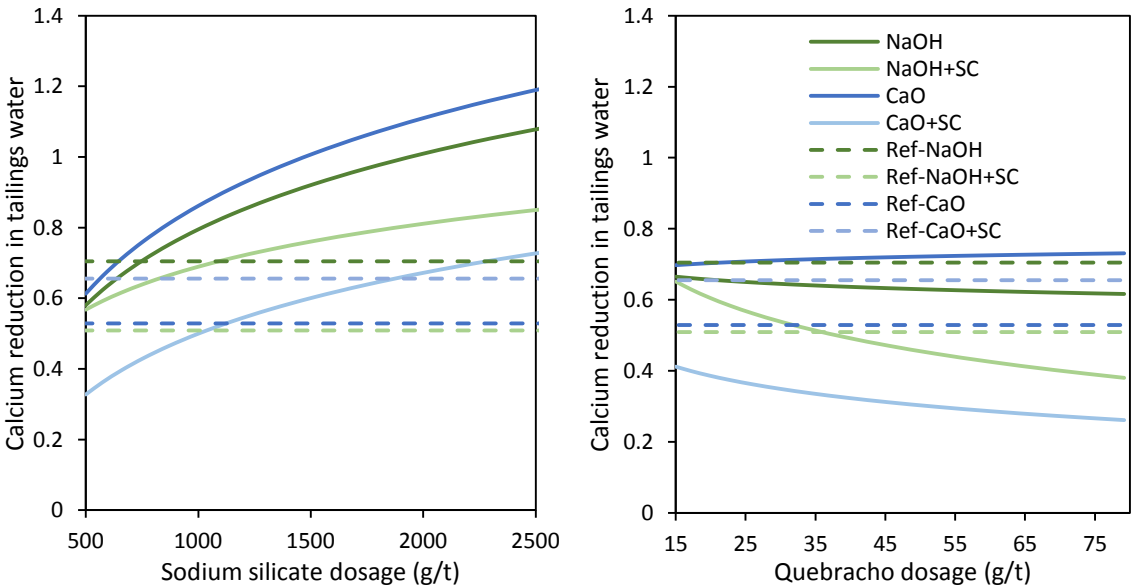


Figure 8: Calcium ions reduction in tailings water compared to flotation feed water depending on the type of pH modifier and the dosage of depressant with left, sodium silicate and right, quebracho, as a result of statistical analyses of the experimental results, legend is the same for both diagrams, Ref is the reference value of the calcium reduction in tailings water for tests without depressants

It could be expected that the behavior of magnesium ions in the presence of depressants would be similar if not the same like calcium ions (Figure 9). In the case of quebracho, it almost holds true. With the fact that without sodium carbonate the curves remain flat and very close to those without quebracho, it can be safely concluded that quebracho does not interact with magnesium ions in the pulp and that these do not float with the concentrate or interact with sodium oleate. The main difference resides in the fact that both combinations of CaO+SC and NaOH+SC behave similarly, which implies a much greater magnesium reduction in the presence of quebracho as compared to CaO+SC without depressant and an increase then a decrease in magnesium reduction in the presence of quebracho as compared to NaOH+SC without depressant. This would imply that sodium carbonate does reduce magnesium ions in the pulp.

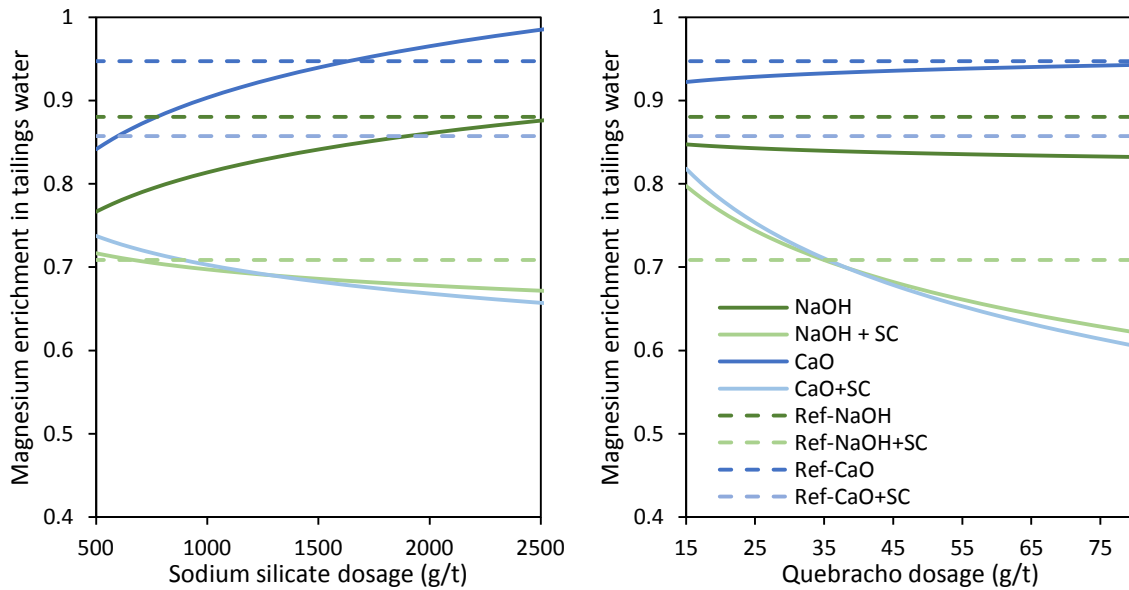


Figure 9: Magnesium ions reduction in tailings water compared to flotation feed water depending on the type of pH modifier and the dosage of depressant with left, sodium silicate and right, quebracho, as a result of statistical analyses of the experimental results, legend is the same for both diagrams, Ref is the reference value of the magnesium reduction in tailings water for tests without depressants

In the case of sodium silicate, the behavior of magnesium ions does not correspond to that of calcium ions. Magnesium reduction is intensified in the presence of sodium silicate but the intensity decreases with increasing dosage until it doesn't seem to affect it anymore above 2000g/t. With the presence of sodium carbonate, magnesium reduction is intensified only for CaO+SC and even though NaOH+SC behaves quite similarly, it is too close to the point without depressant to draw any conclusions.

4.5. Short summary

In the presence of depressants, very different observations are collected:

- Sodium silicate impacts the mass pull much more intensely than quebracho, yielding poorer recoveries but higher tungsten grades and a greater selectivity against calcium. Any interaction with the froth cannot be excluded based on the current flotation tests.
- Sodium silicate only outperforms quebracho in its lower dosages, any increase in dosage clearly demonstrates the superiority of quebracho as a depressant for this ore.
- Contrary to the absence of depressants where CaO improved tungsten grade, with depressants, NaOH performed better as a pH modifier, allowing a higher tungsten grade and even a higher selectivity when used with quebracho. This could be linked to the fact that in calcium-enriched pulps, quebracho may bind to scheelite surfaces, ending up in its depression.
- The presence of sodium carbonate limits or prevents any loss in tungsten while improving tungsten grade in the case of quebracho and also erases any previous differences between CaO and NaOH especially for tungsten-grade recoveries, selectivity against calcium and silica, and magnesium ions reduction, with the exception of calcium ions reduction.
- Sodium silicate causes an enrichment in calcium ions in the tailings water, which could mean that it increases the solubility of calcium-minerals. Based on literature, fluorite and calcite would not be concerned but scheelite. It is highly possible that sodium silicate increases the solubility of calcium silicates in particular.
- Quebracho on its own does not interact with calcium or magnesium ions in the pulp.

5. Mechanisms of sodium carbonate, a multi-faceted reagent

Sodium carbonate is clearly a crucial reagent in scheelite flotation, with a large range of combined impacts beyond pH setting. The role of sodium carbonate is therefore not limited to precipitating and limiting calcium and magnesium ions in the pulp or to buffering pH, and not just depressing gangue but also promoting scheelite.

A flotation involving semi-soluble salt type minerals such as scheelite, calcite, fluorite and calcium silicates, and calcium and magnesium ions in the pulp coupled to the use of several reagents leads to a very complex speciation system. This chapter aims at identifying the potential mechanisms of sodium carbonate in such a flotation environment, based on thermodynamics calculations available in the literature and the observations made throughout this article's testwork. The authors remind that all flotation tests were conducted at a constant pH of 9.5. This affects the interpretation of the mechanisms and said mechanisms might vary at lower and higher pH values.

5.1. Sodium carbonate on its own

Sodium carbonate has a distinct depressing effect on calcium minerals of the gangue, which would include not only calcite but also calcium silicates. The most logical mechanism seems to be surface precipitation of sodium carbonate through its anion HCO_3^- , as it is its main anion in solution at pH 9.5 according to Feng and Luo [11] (Figure 10, left) and Fuerstenau, D. W. et al. [28] and it was stated that it specifically adsorbs at the calcite/ aqueous solution interface [28]. The CO_3^{2-} anion would also have this ability.

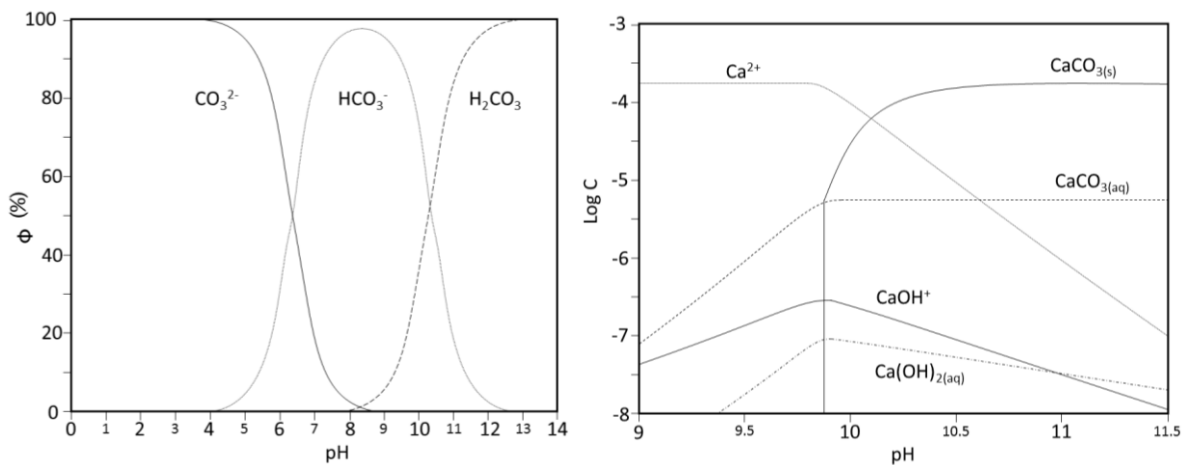


Figure 10: Right - distribution coefficients of various species in Na_2CO_3 solution as a function of pH modified from [11] and left - Species distribution diagram of calcium (for a calcium concentration of 2×10^{-4} mol/l, in the present flotation testwork, calcium concentration varied between 7.73×10^{-4} mol/l in the feed water to 4.82×10^{-4} mol/l in the tailings water) modified from [29]

Vazquez et al. [1] observed that adding lime would tend to reverse the surface charge of fluorite, calcite and scheelite through the adsorption of Ca^{2+} which would be followed by increased precipitation of CaCO_3 when adding sodium carbonate to adjust pH. More importantly, the surface charge would not be affected in the same way, as scheelite's surface remains negative unless the lime dosage becomes too important, inducing calcite precipitation onto scheelite. This would be compatible with the results of Arnold and Warren [30], who showed that calcium ions and sodium carbonate had little effect on the zeta potential of synthetic scheelite over a pH range of 4 to 12 whereas magnesium ions would lead to a sign reversal above pH 10 (which is outside the current scope of the article). Furthermore, calcium silicates in this article's ore include mostly anorthite and titanite and both have a positive surface charge at pH 9 [31], so sodium carbonate could also precipitate onto them, if it was only a question of charge.

In the present testwork however, this depression occurs regardless of the main pH modifier in use, NaOH or CaO. This concurs with Rahimi et al. [32] who also showed surface precipitation of sodium

carbonate onto negatively-charged calcite through zeta potential, contact angle and FT-IR measurements while setting the pH with NaOH in their cationic flotation of pyrolusite. This does partially contradict Vazquez et al. [1] since surface charge positivity does not seem to be a requirement but could be a facilitating parameter.

This would mean that sodium carbonate already selectively precipitates on other calcium minerals than scheelite. Calcite and fluorite (anecdotal in this ore) exhibit a stronger reactivity and higher calcium surface site density at its mineral surface than scheelite [33-35] meaning that it can accommodate the adsorption of more sodium carbonate, “neutralizing” the mineral by precipitating as CaCO_3 through HCO_3^- (and CO_3^{2-}). Based on the kinetics, calcite would be the first mineral to be depressed, followed by calcium silicates but to a lesser extent (calcium surface site density for these minerals is unknown). Additionally, calcium ions can activate silicates on their surface through $\text{Ca}(\text{OH})^+$ [19], which exists at pH 9.5 (Figure 10, right) in smaller proportions than Ca^{2+} . Sodium carbonate could prevent this not only precipitating onto the silicates surface into CaCO_3 as aforementioned but also by neutralizing calcium ions in the pulp.

Lastly, since other calcium mineral surfaces are not reactive anymore, sodium oleate adsorbs preferentially onto scheelite surfaces through its oleate anion RCOO^- ([36] in [18]), which is its main species in solution along with the oleate homodimer (Figure 11). The impact of other anionic oleate species is unknown or was not reported on. Aqueous species such as $\text{Ca}(\text{OH})(\text{RCOO})_{(\text{aq})}$, which could be resulting from the interactions between the pulp calcium species and the oleate anion, may be responsible for quartz flotation for example [37]. The effects are therefore multiple. Of course, adsorption of sodium carbonate onto scheelite is still possible, otherwise its overdosage would not conduct to tungsten depression as reported by Dean and Schack [23] and Wu et al. [38]. Apatite has a similar calcium density at its surface as scheelite [35], which would also fit with the fact that apatite could not be depressed regardless of the reagent regime.

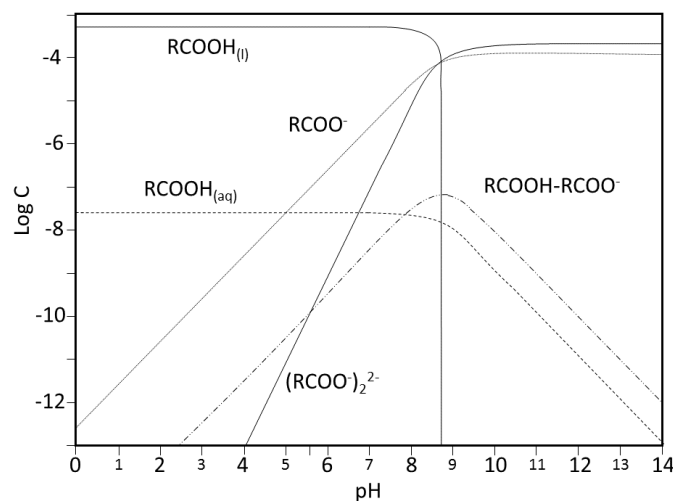


Figure 11: Species distribution diagram of sodium oleate at a concentration of 5.26×10^{-4} mol/l modified from [39] (in the flotation testwork, concentration of sodium oleate at the beginning of the tests was of 2.65×10^{-4} mol/l)

The depression mechanism of sodium carbonate would then be clear. It however does not explain why the reagent also promotes scheelite compared to using the collector on its own. It could be simply considered that because sodium carbonate depresses calcite and calcium silicates, more sodium oleate is available to float scheelite and therefore, tungsten is indirectly promoted in flotation. Yet, the mechanism cannot be as simple, because single mineral flotation (Figure 1 bottom right) as well as contact angle measurements performed on scheelite (Figure 12) show that sodium carbonate interacts with scheelite and impacts its contact angle, hence its wettability. This promotion effect would also happen if calcite is the only mineral available (Figure 13).

There is a clear inflection point at 1×10^{-3} mol/l of sodium carbonate for scheelite, with or without sodium silicate, which shows consistency. Atademir et al. [40] stated that above this concentration,

sodium carbonate starts precipitating onto scheelite to form calcium carbonate. It could be that part of the scheelite surface turns into calcium carbonate and starts behaving like calcite, which yields a new increase in wettability with a further increase in the sodium carbonate concentration, since the contact angle at 1×10^{-2} mol/l sodium carbonate is similar for calcite and scheelite.

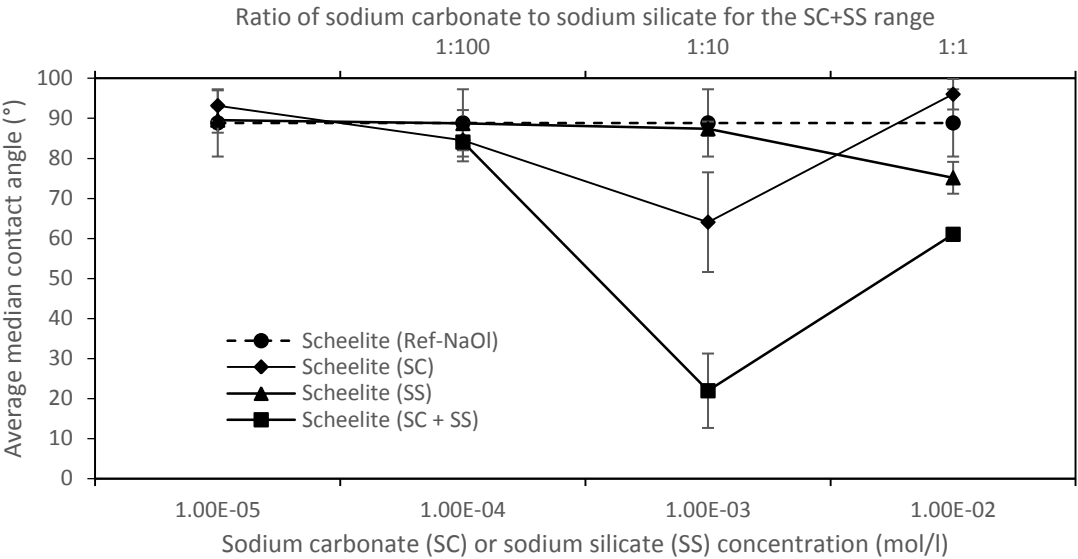


Figure 12: Contact angle measurements on scheelite depending on the sodium carbonate concentration (sodium oleate concentration is fixed at 1.10^{-4} mol/l, which is the same as in single mineral flotation, sodium silicate concentration is fixed at 1.10^{-2} mol/l for the SC+SS range, pH is 9 and fixed with NaOH)

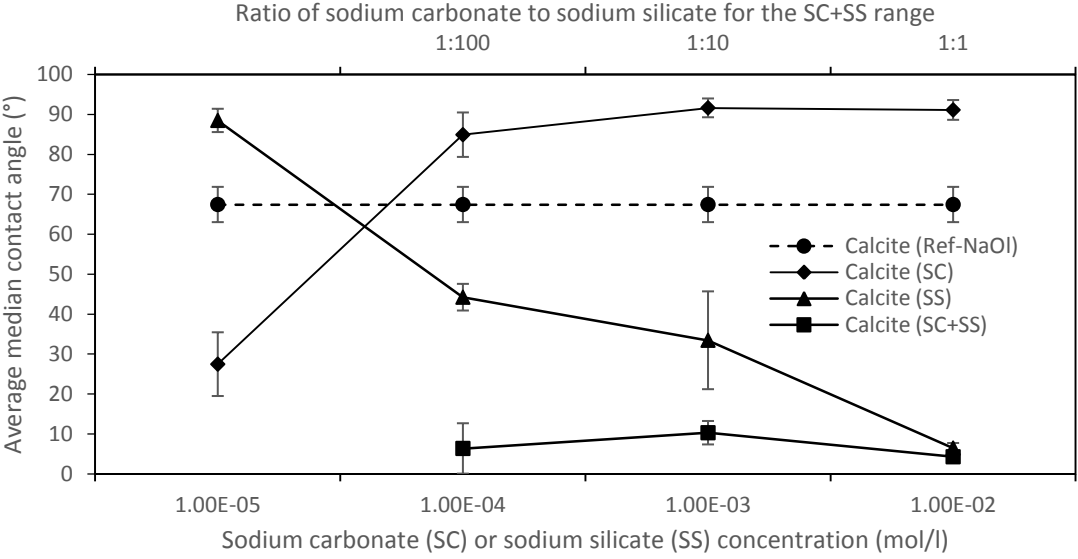


Figure 13: Contact angle measurements on calcite depending on the sodium carbonate concentration (sodium oleate concentration is fixed at 1.10^{-4} mol/l, which is the same as in single mineral flotation, sodium silicate concentration is fixed at 1.10^{-2} mol/l for the SC+SS range, pH is 9 and fixed with NaOH)

Single mineral flotation experiments with various concentrations of sodium chloride have been conducted on scheelite and show absolutely no impact of the sodium ion on scheelite recovery. This would mean interactions between sodium carbonate and scheelite are through the carbonate species. The promotion effect for scheelite is unclear and needs to be further investigated.

5.2. Sodium carbonate and depressants

The addition of depressants adds a new layer of complexity to sodium carbonate's role. Indeed, synergistic and antagonistic effects between sodium silicate or quebracho with sodium carbonate are apparent. As sodium carbonate can precipitate onto mineral surfaces bearing calcium, it is likely that sodium carbonate competes with the depressants on the mineral surfaces, preferentially on calcite or

1 calcium silicates and even general silicates in the case of sodium silicate. This could be seen in single
2 mineral flotation (Figure 6).

3 Sodium silicate, in solution, yields colloidal silica, which can depress calcite [19, 41], as well as
4 $\text{SiO}(\text{OH})_3^-$ and $\text{Si}(\text{OH})_4$, which can depress calcite, fluorite and dolomite [42-44]. Azizi and Larachi [42]
5 determined that $\text{SiO}(\text{OH})_3^-$ absorbs through covalent or hydrogen bonding whereas $\text{Si}(\text{OH})_4$ only
6 absorbs through hydrogen bonding, $\text{SiO}(\text{OH})_3^-$ being the main adsorbate. Sodium silicate logically also
7 yields Na^+ , which increases the zeta potential of quartz, and in turn, the silicates form insoluble salts
8 with ions replaced from the mineral surface [45].
9

10 Based on the observations, it was possible that sodium silicate increases the solubility of calcium-
11 bearing minerals. In literature however, it is stated that sodium silicate reduces the solubility of calcite
12 and fluorite as well as their zeta potential, e.g. makes it more negative, whereas it increases the
13 solubility of scheelite and at a high pH of 9-11, silicate ions adsorb on scheelite, also increasing its
14 negative charge [40, 46, 47]. Sodium silicate could nevertheless increase the solubility of calcium
15 silicates by exchanging Na^+ ions with Ca^{2+} ions, which is likely especially in the case of anorthite, as it is
16 part of the plagioclases series where impoverishment in calcium always is compensated by
17 enrichment in sodium. By precipitating onto silicate surfaces, sodium silicate could also prevent their
18 activation with $\text{Ca}(\text{OH})^+$, leaving more calcium ions in the pulp. In these two mechanisms that are
19 complementary and as they both possess the sodium ion, sodium carbonate synergistically enhances
20 sodium silicate depressing effects. The sodium carbonate anions left in the pulp can then precipitate
21 the pulp calcium and magnesium.
22
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25 For calcite and scheelite, both reagents would again react synergistically, as it is also known that
26 sodium carbonate increases the solubility of scheelite at high dosages [40]. On the basis of calcium
27 surface site density, sodium silicate anions would, similarly to sodium carbonate, preferentially
28 depress calcite over scheelite. Therefore, when sodium carbonate precipitates CaCO_3 at the silicates
29 surface, it increases yet again sodium silicate's depressing effect. This synergy is confirmed by contact
30 angles measurements made on calcite (Figure 13), which show that a minimal addition of sodium
31 carbonate to sodium silicate is already sufficient to strongly decrease the wettability of the mineral.
32
33

34 In single mineral flotation (Figure 6), it appeared that sodium carbonate prevented sodium silicate
35 from depressing scheelite and also calcite to a certain extent, even though the first was added after
36 the second. This had also been observed in single mineral flotation of celestite and calcite by de Castro
37 et al. [48]. This would mean that sodium carbonate can displace sodium silicate from the scheelite
38 surface and maintain a high recovery. Nonetheless, if sodium silicate is in too high dosages, it will still
39 depress scheelite as sodium carbonate loses progressively the competition against sodium silicate on
40 the scheelite surface. The effects are antagonistic in this case, which is also apparent from the contact
41 angle measurements made on scheelite (Figure 12). When scheelite starts behaving like calcite at
42 1×10^{-3} mol/l of sodium carbonate, the depressing effect of sodium silicate is enhanced by sodium
43 carbonate, but as the concentration increases to 1×10^{-2} mol/l (so for a ratio of 1:1 of both reagents),
44 the wettability increases in a similar way than if only sodium carbonate was being used.
45
46

47 The case of quebracho seems much simpler. Similarly to sodium carbonate and sodium silicate,
48 quebracho will preferentially depress calcite over scheelite based on the calcium surface site density.
49 This depressing effect is enhanced by sodium carbonate as the latter precipitates as calcite onto the
50 mineral surfaces. Even if they compete on the surface of such minerals, sodium carbonate will mostly
51 enhance quebracho's depressing power. Quebracho is not as selective as sodium silicate against
52 silicates, because it lacks the sodium ion. It should only depress silicates when those are activated by
53 calcium ions in the pulp or carbonated by sodium carbonate, which is why concentrate tungsten
54 grades with quebracho are lower than with sodium silicate. This also explains why much lower
55 dosages of quebracho are required to achieve similar to better results than sodium silicate, especially
56 in terms of tungsten recovery. And because such low dosages are used, the risk of depressing
57 scheelite is limited.
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6. Conclusion

Sodium carbonate appears as a crucial reagent in scheelite flotation, increasing tungsten grade and recovery as well as selectivity against other calcium-bearing minerals. Through batch flotation testwork on a skarn scheelite ore with high calcite content, single mineral flotation and contact angle measurements, robust hypotheses on its mechanisms are drawn:

- 1) Sodium carbonate precipitates onto the surface of calcium-bearing minerals through its HCO_3^- , forming CaCO_3 layers on said minerals. Additionally, silicates may be activated by calcium ions in the pulp, which is either prevented by pulp precipitation or hindered by surface precipitation. Sodium carbonate will preferentially interact with calcite over scheelite, as its calcium surface site density is much higher and allows for more absorption of the reagent.
- 2) Sodium carbonate has a promoting effect on scheelite, increasing its wettability. The exact mechanism remains to be investigated.
- 3) Sodium carbonate interacts mostly synergistically with sodium silicate, as they both possess the sodium ion, which increases the solubility of calcium silicates, depressing them, while the excess calcium ions in the pulp are precipitated by the carbonate anion of sodium carbonate.
- 4) Sodium carbonate may also counter sodium silicate depressing effect on scheelite by displacing it from the mineral surface.
- 5) Sodium carbonate and quebracho act entirely in synergy as the surface carbonation of silicates and calcium minerals by sodium carbonate increases the depressing power of quebracho. However, lacking the sodium ion, quebracho will not depress non-calcium-bearing silicates without the presence of sodium carbonate. This explains why higher grades are achieved with sodium silicate but also why quebracho is a superior depressant, as it will increase tungsten recovery even at lower dosages.

Sodium carbonate is therefore a multi-faceted reagent, which serves as a buffering pH modifier (which should not be used on its own), a pulp dispersant precipitating calcium and magnesium ions in suspension, a gangue depressant and a promoter for scheelite. It acts mostly synergistically and partially antagonistically with other depressants, notably sodium silicate and quebracho.

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