

Technical Note

The Potential Role of Colloidal Silica as a Depressant in Scheelite Flotation

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Abstract: The main challenge in scheelite flotation lies in the contamination of the concentrate by other calcium-bearing minerals, mainly calcite. To remedy this problem, sodium silicate is frequently used as a depressant. According to the literature, one hypothesis for the mechanism of water glass consists in its absorption onto calcite through colloidal silica formation, preventing hydrophobization by the collector. This short communication presents research conducted on the direct use of colloidal silica as a depressant in scheelite flotation. Colloidal silica is shown to have an impact on scheelite flotation, especially by depressing silicates.

Keywords: scheelite flotation; colloidal silica; depressant

1. Introduction

The main challenge in scheelite flotation is the contamination of the concentrate with other semi-soluble salt minerals, mainly calcite, fluorite and apatite, as these minerals display flotation behavior analogous to scheelite due to similar surface properties [1]. Sodium silicate is one of the main depressants against calcite and fluorite used in the scheelite flotation industry [2]. The dosages are very high but selectivity is limited [3], meaning that sodium silicate can sometimes be considered insufficient. The literature describes how water glass can adsorb as colloidal silica in the case of calcite [2,4], preventing the adsorption of the collector. This short communication presents the primary results of research conducted on froth flotation using colloidal silica directly as a depressant.

2. Materials and Methods

The ore used for batch flotation tests contained 0.51% scheelite, 1.70% calcite, 0.28% apatite and various silicates (quartz, micas, plagioclases and hornblende) and was of the strata-bound type. Mineral liberation analysis conducted on the ground samples showed that 97.7% of the scheelite was over 80% liberated. As a consequence, mineral surface liberation and association did not play a major role in this flotation.

Methods regarding the sampling of pure minerals, microflotation, batch flotation tests and elemental assays are described in detail in Reference [5]. For batch flotation, the ore was ground with a rod mill to a d_{80} of 63 μm . Froth flotation tests were conducted with 500 g of ore at 33% pulp density in a Magotteaux[®] bottom-driven flotation cell. Each test comprised a single rougher stage, which lasted 7 min and involved three concentrates with a 5-s scraping rate, 450 min^{-1} impeller speed and an air flowrate of 5 L/min. The filtered flotation products were dried overnight in an oven at 50–60 °C, and the mass pull was calculated based on said dried weights. The flotation tests were repeated until the standard deviation of the mass pulls was lower than 4%, while tests that led to an increase in standard deviation over 4% were rejected. The three points on the diagrams are the cumulative concentrates taken at $t = 1, 3$ and 7 min. During each batch flotation test, pictures of the side of the transparent

flotation cell were taken at 2-s intervals with a MoticCam camera with 3 Mpx resolution. The pictures were then processed with ImageJ[®] in order to extract the froth and bubble information as described by Schach et al. [6]. Statistical analyses of the data were conducted with RStudio[®]. The diagrams present 30-s averages for more clarity.

The reagents used were as follows: sodium oleate ($C_{18}H_{33}NaO_2$) of >90% purity from Carl Roth was used as a collector at a single dosage of 200 g/t in order to avoid multicomponent technical grade collectors with effects difficult to evaluate; a complex mixture of glycols, Flotanol 7197[®] from Clariant Mining Solutions, was used as a frother at 20 g/t; sodium carbonate (Na_2CO_3) from Alfa Aesar was added before the depressant at a single dosage of 100 g/t, based on research presented in Reference [7]; analytical grade sodium hydroxide (NaOH) was used as a pH modifier; sodium metasilicate nonahydrate ($Na_2O_3Si_2 \cdot 9H_2O$) from Aldrich Chemistry was used as a reference depressant; three colloidal silica solutions from Nouryon (ex-AkzoNobel) were used, namely, Levasil CS30-324P[®], here referred to as CS1, Levasil CS45-38P[®], referred to as CS2, and Levasil CS50-34P[®], referred to as CS3.

3. Performance of Colloidal Silica in Scheelite Flotation

3.1. Proof of Principle

Single-mineral microflotation of scheelite and calcite was used to determine if colloidal silica would have any effect on the two minerals (Figure 1). It appears that colloidal silica prevents calcite from floating while scheelite is unaffected by the presence of the reagent, regardless of the dosage. Furthermore, even a small amount of colloidal silica shows an effect on calcite. Based on these results, the authors investigated several parameters related to colloidal silica, namely, its size, its dosage and the effect of pH.

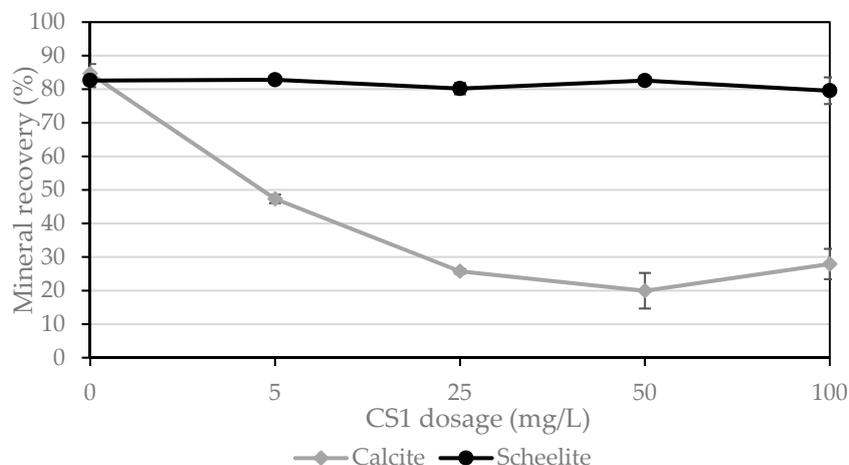


Figure 1. Single-mineral flotation recovery of calcite and scheelite depending on the Levasil CS30-324P[®] (CS1) dosage (at pH = 8, collector = 1×10^{-4} sodium oleate, error bars represent the 95% confidence interval).

3.2. Impact of Colloidal Silica Size

According to the manufacturer, the average colloidal silica sizes of CS1, CS2 and CS3 are 9, 30 and 55 nm, respectively. Single mineral microflotations were conducted with CS2 (Figure 2a) and CS3 (Figure 2b). CS2 also affects calcite but higher dosages of the reagent are required, while CS3 shows little effect regardless of the dosage. Based on these results, CS3 was left out of subsequent flotation tests.

To determine if the size of colloidal silica also influences froth flotation, batch flotation tests with CS1 and CS2 at 100 g/t were conducted and compared to tests with only sodium oleate as a collector

and with sodium silicate at 350 and 500 g/t (Table 1). Preliminary work with CS1 without repetitions, without sodium carbonate and at pH 8 had shown that dosages at 300 and 500 g/t were detrimental to flotation [8], hence the low dosages chosen for this study. The sodium silicate test at 350 g/t showed no difference from the reference test with only sodium oleate and is therefore not displayed on the diagrams. Higher dosages of sodium silicate (1 and 2 kg/t) resulted in an over-depression of the minerals [7], and 500 g/t of sodium silicate is considered optimal for this particular ore.

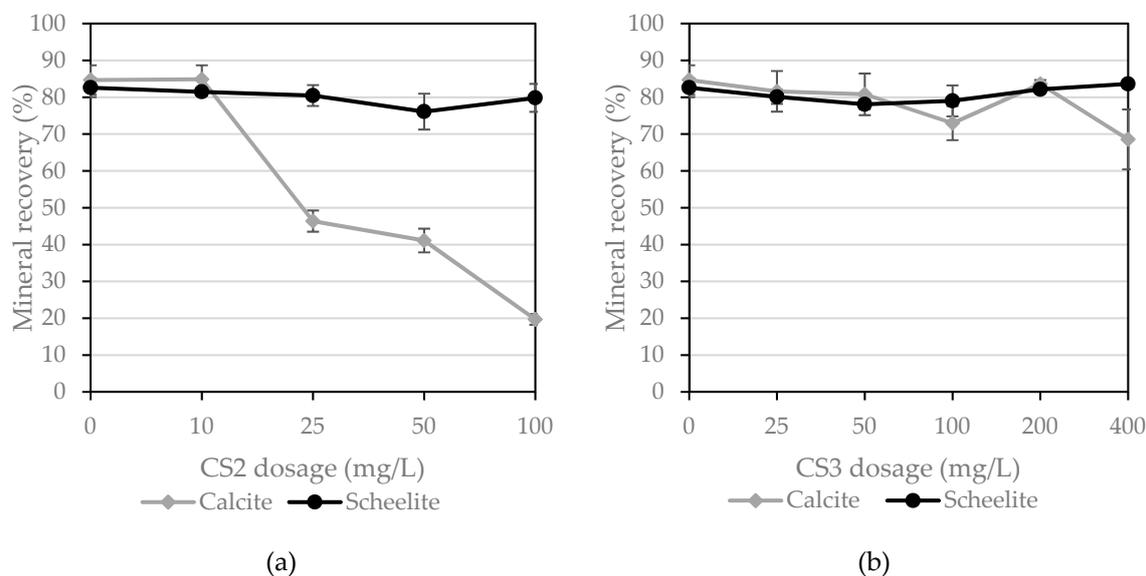


Figure 2. Single-mineral flotation recovery of calcite and scheelite depending (a) on the Levasil CS45-38P® (CS2) dosage and (b) on the Levasil CS50-34P® (CS3) dosage (at pH = 8, collector = 1×10^{-4} sodium oleate, error bars represent the 95% confidence interval).

Table 1. Batch flotation reagent regime.

Test	pH	Regulators (g/t)			Collector (g/t)	Frother (g/t)
		Sodium Carbonate	Sodium Silicate	Colloidal Silica	Sodium Oleate	Flotanol 7197 (Clariant)
Ref_NaOl	9	100			200	20
WG_500	9	100	500		200	20
CS1_100	9	100		100	200	20
CS2_100	9	100		100	200	20

Mass pulls, water pulls and tungsten grade-recoveries are presented in Figure 3. In general, the presence of a depressant leads to a more stable froth compared to Ref-NaOl, as for the same water pull, the mass pull is higher. This does not translate into a concentrate of lower quality: the tungsten grades and recoveries are higher, with a higher selectivity for sodium silicate.

Data on calcium and silicates show this higher selectivity for sodium silicate (Figure 4) and show that both colloidal silicas are not distinguishable from each other. The presence of colloidal silica at 100 g/t does not prevent the flotation of silicates even if the selectivity remains relatively high, including for calcium-bearing minerals.

Two froth properties are presented in Figure 5. Colloidal silica is associated with more stable froths as indicated by the average froth height, which is constantly higher than that of sodium silicate. The large variability in the CS2 data is potentially caused by the short scraping time (5 s), which might indicate a slower rebuild of froth. The corresponding average bubble diameter is indeed smaller for CS2 even though the froth is thicker, which indicates less bubble coarsening than with CS1 and with WG_500. Bubbles increase in size over time, with a constant increase for WG_500 and a sharp increase towards the end of the set time period for the other two tests. In general, this is related to the lower particle load within the froth as reflected in the mass/water recoveries with time, as these are batch tests.

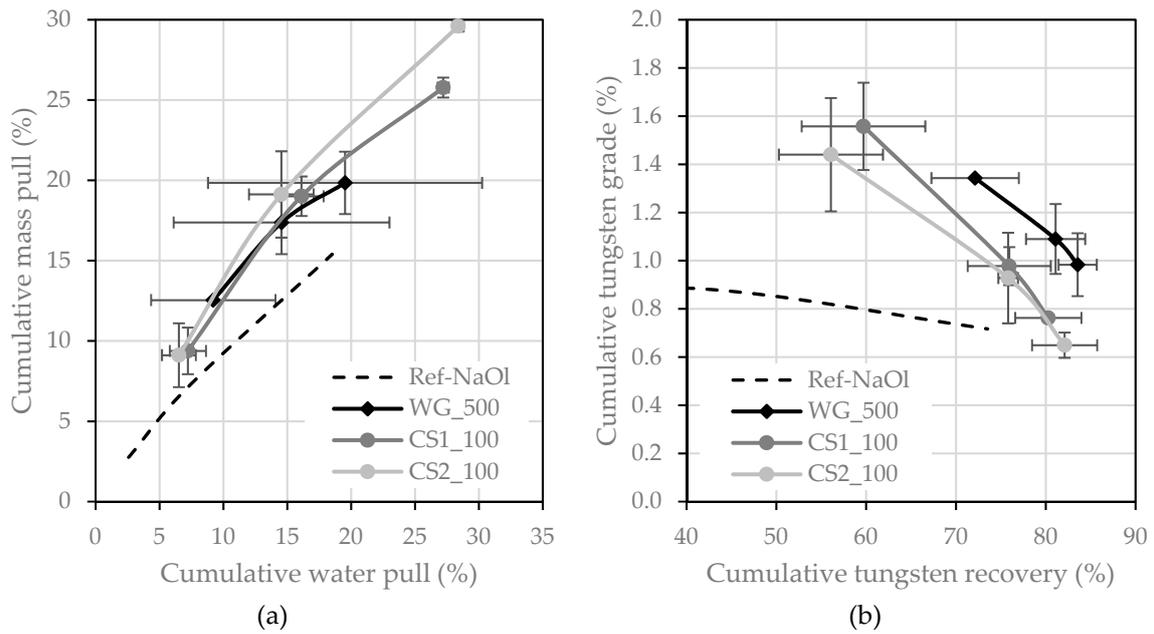


Figure 3. (a) Mass pull against water pull and (b) cumulative tungsten grade against recovery (error bars represent the 95% confidence interval).

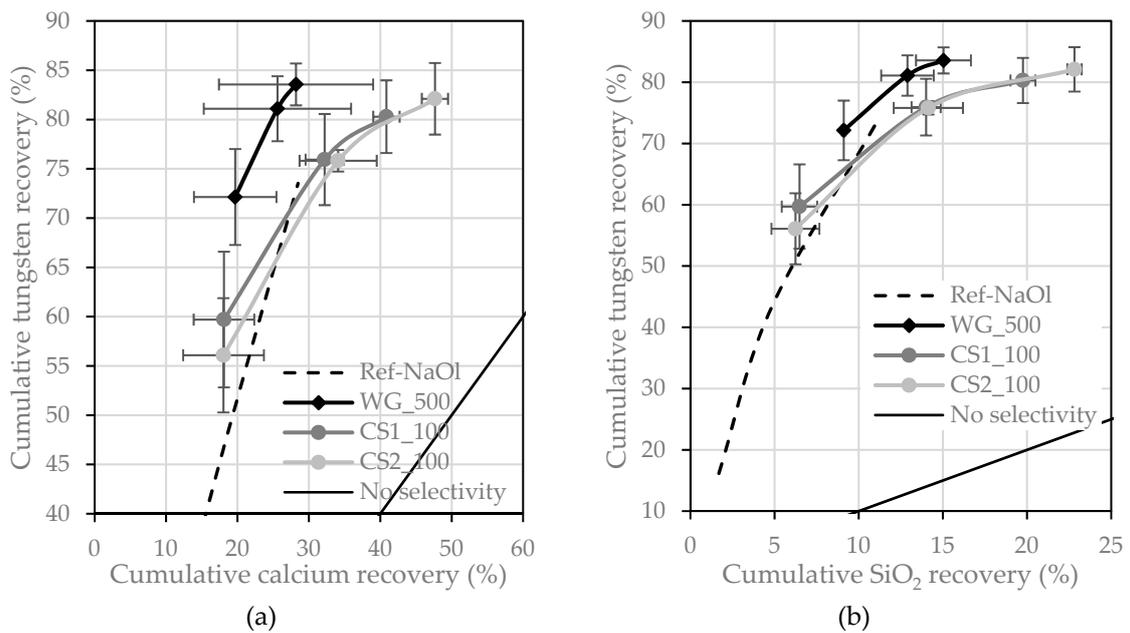


Figure 4. Selectivity curves of tungsten against (a) calcium (calcium contained in scheelite was subtracted) and (b) silica (error bars represent the 95% confidence interval).

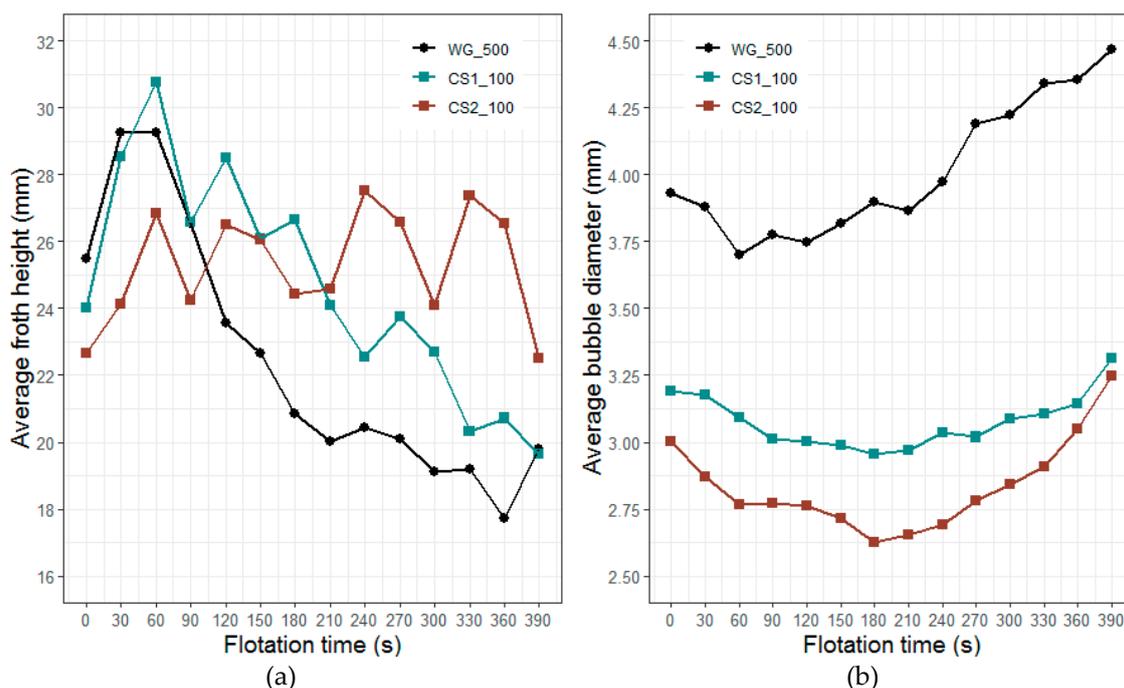


Figure 5. (a) Thirty-second average froth height and (b) average bubble diameter (by amount of bubbles) over flotation time for WG_500, CS1_100 and CS2_100.

3.3. Impact of Colloidal Silica Dosage

One set of tests with CS1 was conducted at a higher dosage of 200 g/t (Table 2) to determine the effect of the colloidal silica dosage.

Table 2. Batch flotation reagent regime.

Test	pH	Regulators (g/t)			Collector (g/t)	Frother (g/t)
		Sodium Carbonate	Sodium Silicate	Colloidal Silica	Sodium Oleate	Flotanol 7197 (Clariant)
Ref_NaOl	9	100			200	20
WG_500	9	100	500		200	20
CS1_100	9	100		100	200	20
CS1_200	9	100		200	200	20

CS1_200 is compared to the other tests in terms of mass and water pulls and tungsten grade-recovery curves in Figure 6. Doubling the dosage of CS1 results in mass and water pulls that are very close to those of the Ref-NaOl test. If the final tungsten recovery is very close, this shows a much higher grade and therefore a more efficient process with higher selectivity.

Indeed, CS1_200 differs from WG_500 by showing less selectivity against calcium-bearing minerals but the same selectivity against silica-bearing minerals (Figure 7). However, compared to the benchmark test with collector only, selectivity is only higher at the beginning of the flotation test.

Figure 8 shows that the froth of CS1_200 is not as thick as that from the other tests; it does not reach a peak at around 60 s but remains relatively constant. The average bubble diameter is stable over the flotation time and does not increase, where it should normally display higher bubble coarsening as the froth carries fewer particles with time. This is partially linked to the fact that the mass and water pulls are lower for CS1_200 than for the other tests.

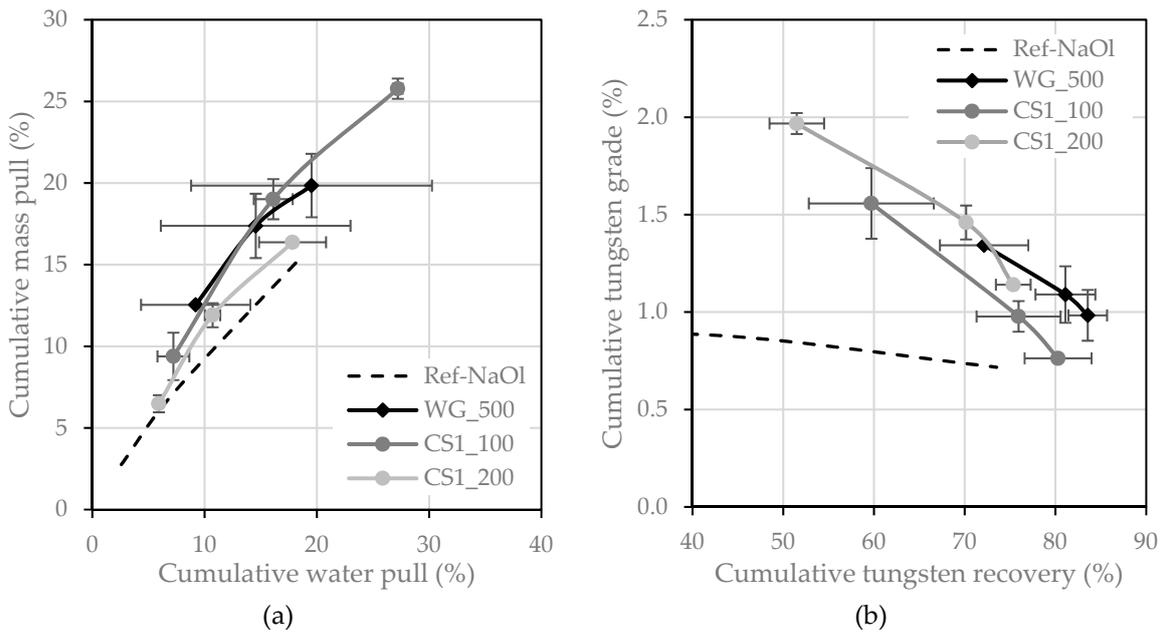


Figure 6. (a) Mass pull against water pull and (b) cumulative tungsten grade against recovery (error bars represent the 95% confidence interval).

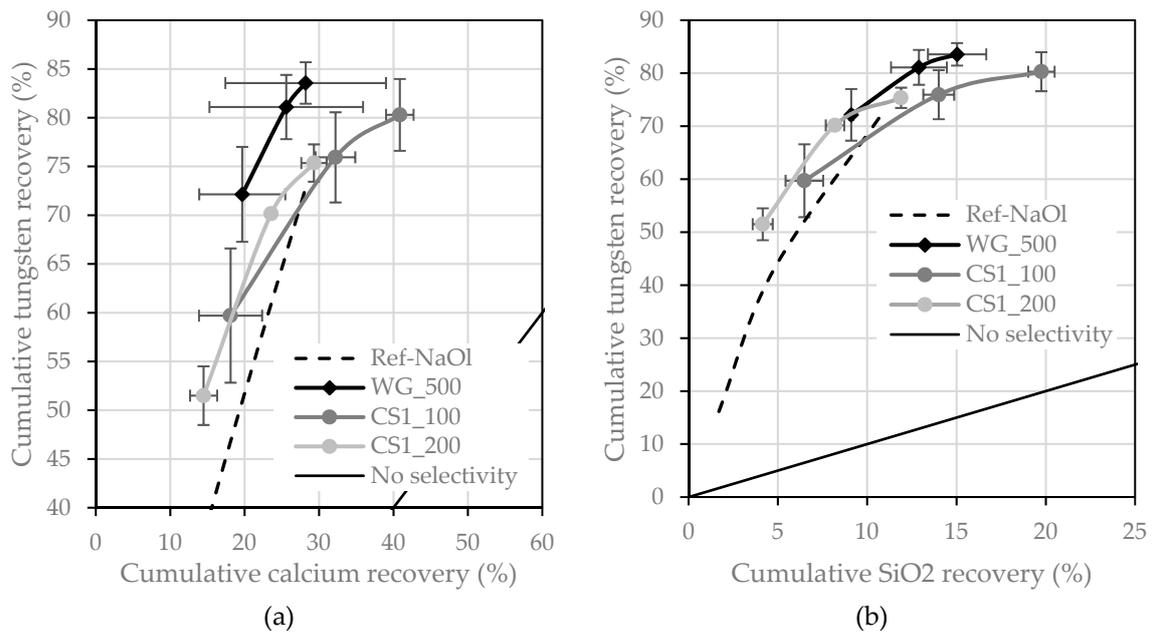


Figure 7. Selectivity curves of tungsten against (a) calcium (calcium contained in scheelite was subtracted) and (b) silica (error bars represent the 95% confidence interval).

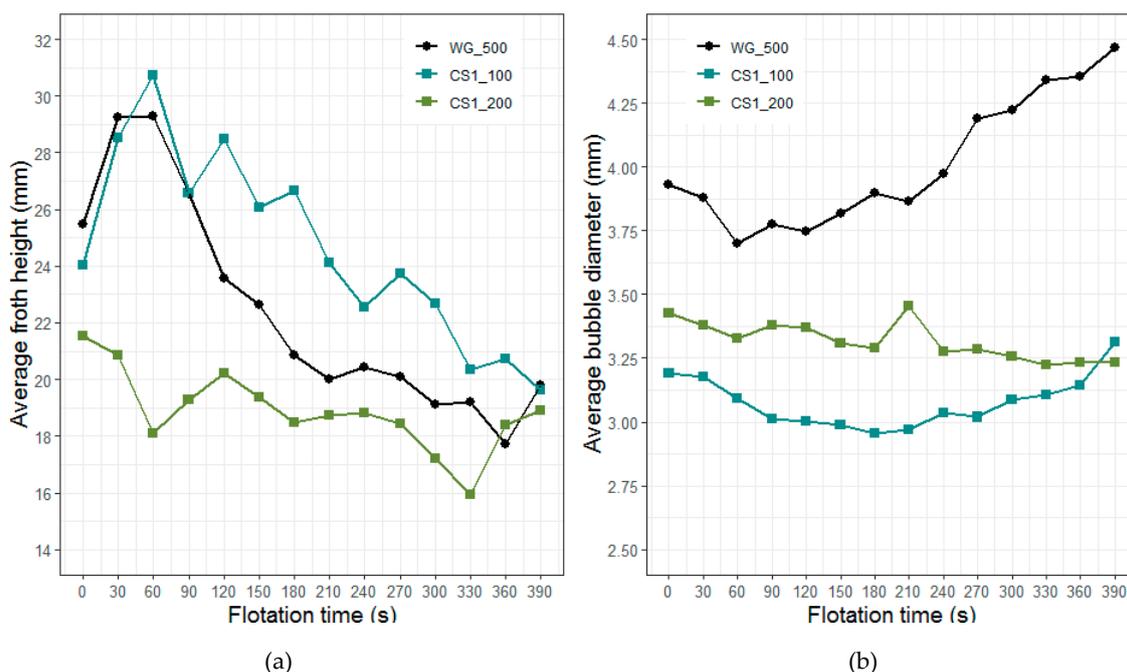


Figure 8. (a) Thirty-second average froth height and (b) bubble diameter over flotation time for WG_500, CS1_100 and CS1_200.

3.4. Effect of pH

Single mineral microflotations were conducted at different pH levels (Figure 9) as the classical scheelite flotation pH of 9 might be inappropriate. The recoveries of scheelite and calcite remain stable regardless of the pH. Batch flotation tests conducted in different conditions than the ones in this technical note with a CS1 dosage of 300 g/t and at pH 8, 9 and 10 also showed no impact on the flotation results [8]. Therefore, the action of CS1 can be considered independent of pH in the case of scheelite flotation.

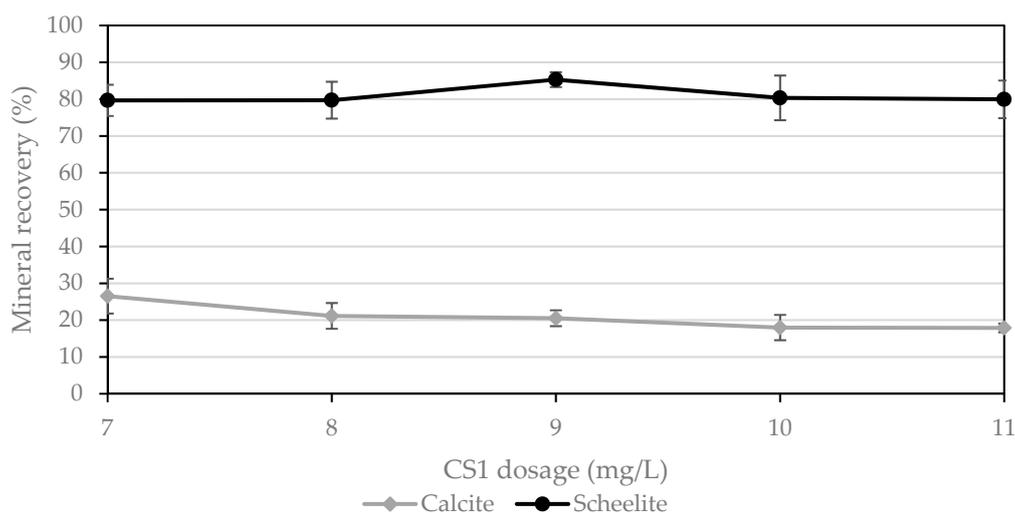


Figure 9. Single-mineral flotation recovery of calcite and scheelite depending on the pH (collector = 1×10^{-4} sodium oleate, depressant = 25 mg/L CS1, error bars represent the 95% confidence interval).

4. Link to Sodium Silicate

Silicic acid $\text{Si}(\text{OH})_4$ is the main silica species produced by alkaline water glass in solution at a pH below 9.4; above pH 9.4, it is $\text{SiO}(\text{OH})_3^-$, and above pH 12.6, it is $\text{SiO}_2(\text{OH})_2^{2-}$ [9–11]. Many authors have stipulated that these low molecular weight silica species are responsible for the depression effect of sodium silicate [10,12,13]. Fuerstenau et al. [4] suggested in the 1960s that colloidal silica would be the main species responsible for said depression effect.

In principle, the silica species bond with different minerals based primarily on their positive surface charge. In the case of calcium-bearing minerals, for example, the cation Ca^{2+} is indeed central to the adsorption of silica. Calcite and fluorite have been shown to exhibit a higher calcium surface site density on their surface than scheelite [14,15], meaning they can accommodate more of the silica on their surface. Furthermore, the Ca–O or Ca–F bond energies have different lengths depending on the mineral, e.g., the shorter the bond, the higher the expected reactivity of calcium. Calcite and fluorite have a similar Ca–X bond length while scheelite's is longer [16–19], so scheelite is not as reactive in the pulp. Finally, the calcium atom is more reactive at a higher dissociated energy of the dangling Ca–X bond. The Ca–O bond dissociative energy lies at 383.3 (\pm 5) kJ/mol, whereas it is at 529 kJ/mol for Ca–F [20]. Consequently, fluorite, then calcite are more attractive chemically than scheelite for the silica species.

Present research tends to show that if colloidal silica may participate in depressing silicates and calcium-bearing minerals, this is most likely a minor effect as compared to the low molecular weight silica species.

5. Conclusions

By directly using colloidal silica in the flotation, it was demonstrated that colloidal silica did have an impact on scheelite flotation, even at a low dosage. Required conditions include a fine enough size (below 40 nm) and an appropriate dosage, while pH does not seem to play a role. Further investigations are required before reaching definitive conclusions; however, it appears that froth stability is increased in the presence of colloidal silica. Some of these discoveries were patented in Germany under Patent Nr. 10 2017 129 673, as colloidal silica has the potential to become a depressant, and not only in scheelite flotation. However, as a synthetic nanopowder, colloidal silica is characterized by high production costs, hence a complementary economic evaluation of the product is planned in order to determine if these costs may be outbalanced by the very low dosages required.

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Conflicts of Interest: The authors declare no conflict of interest.

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