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Acidified water glass in the selective flotation of scheelite from calcite, Part I: performance and impact of the acid type

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Abstract: To improve the performance of sodium silicate in scheelite flotation and allow the selective separation of scheelite from other semi-soluble salt-type minerals such as calcite, three acids, sulfuric, oxalic and for the first time hydrochloric are used to acidify sodium silicate (also called water glass). A literature review of previous usage of acidified water glass shows that no comparison between acids was made before, that comparisons with alkaline water glass were limited and that the idea that acidified water glass is more efficient at lower dosages has not been proven in scheelite flotation. As a consequence, the impact of the acid type, the ratio between acid and sodium silicate and acid dosage is tested in single mineral flotation and batch flotation experiments. All three acids allow a higher performance of acidified water glass compared to alkaline water glass at lower dosages and with little addition of acid: the tungsten recovery and grade are improved while silicates and to a lesser extent calcium-bearing minerals float less. The dosage of acid is less determining than the mass ratio of the acid to sodium silicate, except in the case of hydrochloric acid. Overall, the acid type does not matter as all three acids perform well in flotation, whereby oxalic and hydrochloric acid are better.

Keywords: acidified water glass, scheelite calcite separation, froth flotation

1. Introduction

Scheelite (CaWO_4) is one of the main mineral resources of the critical raw material tungsten for the mostly high-tech industry. Froth flotation of scheelite is quite straightforward and the typical reagent regime, called "lime flotation process" involves sodium carbonate and sodium silicate as modifiers after the addition of lime and a fatty acid type as the main collector, and has been existing since at least the 1970s (Vazquez et al., 1976). However, the main challenge in scheelite flotation is still the contamination of the concentrate by other semi-soluble salt minerals, mainly calcite, fluorite and apatite, as these minerals display analogous flotation behavior to scheelite due to similar surface properties (Kupka and Rudolph, 2018a). Indeed, ~50 % of the articles on scheelite flotation published in the last decade are specifically dedicated to this problem (calculation based on data from Kupka and Rudolph (2018a)).

Sodium silicate and quebracho (a tannin) are the main depressants for calcite and fluorite used in the scheelite flotation industry (Martins and Amarante, 2012). The dosages are typically very high (in kg/t) for sodium silicate, also called water glass, even though selectivity is limited (Yongxin and Changgen, 1983). Indeed, water glass also depresses scheelite when the dosage becomes too high (Gao et al., 2016; Han et al., 2017). Therefore, simple sodium silicate can be considered insufficient.

Researchers have tried to improve the performance of sodium silicate in scheelite flotation by modifying it, through a mixture with polyvalent metals salts (Foucaud et al., 2019; Patil and Nayak, 1985; Wei et al., 2018) or through acidification with sulfuric or oxalic acid (Feng et al., 2015; Martins and Amarante, 2012). Acidified water glass (AWG) is supposed to have higher polymerizing ability, stronger hydrophilicity and stronger depressing effect on gangue at lower dosages than alkaline water

glass (Berlinskii and Klyueva, 1972; Fuerstenau et al., 1968; Yang et al., 2016; Yongxin and Changgen, 1983).

The preparation of the AWG solution however varies in terms of acid type, sodium silicate type, ratio between acid and sodium silicate and overall approach. In its first part, this article aims at:

- Reviewing the existing approaches, including in other flotation systems;
- Estimating the impact of the acid type by comparing oxalic, sulfuric and for the first time hydrochloric acid;
- Comparing the performance of acidified water glass to that of alkaline sodium silicate;
- Determining if acidified water glass can outperform alkaline water glass at lower dosages.

Any observable difference between the types of water glass and acidified water glass will be linked to the species generated in solution. The identification of said species, their interactions and their impact are discussed in Part II of this article.

2. Materials and methods

2.1. Single minerals and microflotation

Scheelite and calcite were the feed materials for single mineral flotation (Hallimond tube 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 μm – 63 μm . X-ray diffraction determined that the sample was composed of 96 % (w/w) scheelite with pyrite, molybdenite and other minerals as contaminants. Calcite came from Straßberg, Germany and the 63 μm – 100 μm fraction was selected. Purity of the calcite sample was determined by X-ray diffraction and showed that it was composed of 97 % (w/w) of calcite, 1 % (w/w) of quartz and minor amounts of fluorite, ilmenite and others.

Microflotation was conducted in a Hallimond tube designed at the TU Bergakademie Freiberg. 1 g of the single minerals is added to an aqueous solution of 10^{-2} M KCl, stirring on a magnetic stirrer with a rotation speed of 400 min^{-1} . 3 to 5 minutes are allocated to pH conditioning with HCl and NaOH. After achieving a stable pH, the depressant is added before the collector with a conditioning time of 2 and 3 minutes, respectively. The flotation suspension is transferred to the Hallimond tube and agitated for another 3 minutes with a rotational speed of 800 min^{-1} using a magnetic stirrer. Airflow rate is set to 20 cm^3/min and microflotation lasts 2 minutes. The filtered flotation products are dried in an oven overnight at 50°C - 60°C and flotation recovery and loss are calculated based on said dried weights. All experiments were conducted at least twice and the errors shown correspond either to the differential difference or to the standard deviation.

2.2. Batch flotation

The ore used for batch flotation tests contains 0.51 % (w/w) scheelite, 1.70 % calcite, 0.28 % apatite and various silicates (quartz, phyllosilicates, plagioclases and hornblende) according to MLA. The ore was ground with a rod mill to a $d_{80,3}$ 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 had only a rougher stage, lasted seven minutes and involved three concentrates with a 5 second scraping rate, 450 min^{-1} impeller speed and an air flowrate of 5 L/min. The filtered flotation products were dried in an oven overnight at 50°C - 60°C and the mass pull was calculated based on said dried weights. The flotation tests were repeated until standard deviation on the mass pulls was lower than 4 %, tests that lead to an increase in standard deviation over 4 % were rejected. The three points on the diagrams represent the cumulative concentrates taken at $t = (1, 3, 7)$ min. The calcium contained in scheelite was removed from the calcium recoveries displayed in the graphs. Mass balance of the tests for the mass and water flows and elemental assays was conducted with HSC Sim 9.1.1 (Outotec, Finland) with the Non-Negative-Least-Square Method (NNLS).

2.3. Elemental assays

Elemental assays for the concentrates were conducted by ALS Global® by method number ME-MS81d which combines ICP-AES (Inductively coupled plasma atomic emission spectroscopy) and ICP-MS

(Inductively Coupled Plasma – Mass Spectroscopy) for tungsten. If the assay of tungsten exceeds the detection limit of ICP-MS, ALS Global runs an X-Ray fluorescence analysis (XRF, method XRF12k).

Tailings were analyzed in-house with XRF, whereby the lower detection limit for tungsten was 0.1 %. XRF Analytics were done using a PANalytical Axios max spectrometer (Malvern PANalytical, Almelo, Netherlands). Two grams of wax (Fluxana) was added to approx. 10 g of dried sample material and thoroughly mixed by means of a Retsch swing mill (MM400, Retsch, Haan, Germany), adding two agate balls. Pressed pellets were produced using a Herzog HTP 40 press (Herzog, Osnabrück, Germany). Pellets were immediately measured and evaluated using PANalyticals fundamental parameters programme OMNIAN which was supported by an additional matrix-matched calibration for tungsten, set up prior to the actual measurements.

2.4. Reagents

Sodium oleate ($C_{17}H_{33}COO-Na^+$) 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 Kupka and Rudolph, 2018b. Analytical grade sodium hydroxide (NaOH) was used as a pH modifier. Acidified water glass was produced using analytical grade of sodium metasilicate nonahydrate ($Na_2O_3Si_2 \cdot 9H_2O$) with a modulus of 1:1 from Aldrich Chemistry mixed with three different acids: sulfuric acid (H_2SO_4), oxalic acid ($C_2H_2O_4$) and hydrochloric acid (HCl) from Carl Roth.

3. Review of existing approaches

A summary of the acidified water glass types used by previous authors in flotation is shown in Table 1. The essential parameters in the preparation of acidified water glass are: the type of acid (oxalic or sulfuric), the stirring time (basically the time allocated to the reaction) and the general approach, i.e. authors either mix sodium silicate and the acid until the solution reaches a certain pH or aim for a ratio between the two solutions.

The performance of acidified water glass was tested very differently depending on the authors (Table 2). In the ten articles presented, only six actually compared AWG to alkaline sodium silicate and only three in batch flotation.

The results are also different:

- Yang et al. (2016) compared AWG with alkaline sodium silicate in batch-scale locked cycle tests and demonstrated that the recovery and grade of the Ti concentrates increased by 7.74 % and 3.82 %, respectively, while decreasing depressant consumption by two-fifths.

Table 1. Types of acidified water glass used by other authors in scheelite flotation

Source	Target mineral	Gangue mineral	Modulus	Acid type	pH of solution	Ratio type	Ratio	Stirring time
Deng et al. (2019)	Barite	Calcite	2.4		-	-	-	-
Zhou et al. (2013)		Carbonates	2.8		-	-	1:1	1 h
Zhou and Lu (1992)	Fluorite		2.4		1 to 4	-	-	-
Tian et al. (2019)		Calcite and Celestine	2.4	Sulfuric Acid	8.2	-	-	-
Martins and Amarante (2012)			3.1		2 to 3	-	-	-
Liu et al. (2016)	Scheelite	Calcite	2.4		-	-	1:1	15 min
Kang et al. (2018)			-	-	-	1:1	-	
Feng et al. (2015)			Nonahydrate	-	-	3:1	-	
Dong et al. (2018)			Hexahydrate	-	-	3:1	-	
Yang et al. (2016)	Illmenite	Olivine	2.8	Oxalic Acid	-	-	3:1	1 h

Table 2. Methods to evaluate the performance of acidified water glass

Source	Target mineral	Acid type	Flotation Type			Comparison to	
			Single Mineral	Mixed Mineral	Batch	Water glass	Other depressant
Deng et al. (2019)	Barite		x	x		x	
Zhou et al. (2013)					x		x
Zhou and Lu (1992)	Fluorite	Sulfuric Acid			x		
Tian et al. (2019)			x	x			
Martins and Amarante (2012)					x	x	
Liu et al. (2016)			x		x	x	x
Kang et al. (2018)	Scheelite	Oxalic Acid			x	x	
Feng et al. (2015)			x	x		x	
Dong et al. (2018)			x				
Yang et al. (2016)	Illmenite		x	x	x	x	

- Martins and Amarante (2012) conducted batch flotation with a circuit involving prior sulfides removal. When using AWG, they increased the tungsten concentrate grade by 14.8 % and their tungsten recovery by 2.6 % compared to using pure sodium silicate only in the presence of sodium carbonate. Without sodium carbonate, the concentrate tungsten grade was increased by 3.8 % but the recovery fell by 12.3 %.
- Kang et al. (2018) showed a large improvement in flotation efficiency whereby, for example, at 600 g/t, the tungsten recovery with AWG decreases by 2.5 % as compared to alkaline water glass but the tungsten grade increases by 0.4 % and the flotation efficiency by 2.6, also in the presence of sodium carbonate.

These observations show that sodium carbonate might be necessary in the reagent regime but more importantly, that no comparison between acids was made on the same ore before, that comparisons with alkaline water glass were limited and that the idea that acidified water glass is more efficient at lower dosages has not yet been proven in scheelite flotation.

4. AWG in action: comparison to sodium silicate

4.1. Preparation of AWG

Three acids are used in this article, oxalic acid and sulfuric acid, both of which can be used in hydrometallurgy for the leaching of scheelite (Ilhan et al., 2013; Xuin et al., 1986) and hydrochloric acid. Oxalic acid is the simplest dicarboxylic acid, sulfuric acid is a mineral acid whose acidity is only exceeded by superacids (Miessler et al., 2019) and hydrochloric acid is simply strongly acidic. Hydrochloric acid was selected as a point of comparison to determine the importance of the acid type and if any acid can be used to produce acidified water glass. Further information on the three acids are found in Table 3.

In terms of a general approach, mass ratios were deemed a more reproducible method than acidification pH, as comparison between acids is more complex since the dosages are different between each acid and that method is complicated to reproduce in a possible future application in a plant. The acidification pH also can lead to an overdosage of the acid, which is deleterious to the process especially with respect to the froth phase (Chinbat, 2017; Kupka et al., 2017).

Table 3. Methods to evaluate the performance of acidified water glass

	Oxalic Acid	Sulfuric Acid	Hydrochloric Acid
Type	Organic	Mineral	Mineral
Formula	HOOC-COOH	H ₂ SO ₄	HCl
Acid dissociation constant (pKa)	1.25	-3	-6.3
Molar mass (g/mol)	90.034	98.078	36.461

Batch flotation tests were conducted to determine the importance of the type of acid, the mass ratio and the dosage of AWG. In this case, the dosage of sodium silicate is fixed and the dosage of the acid is varied. The base reagent regime is based on previous experiments (presented in Kupka and Rudolph (2018b)) and consists of sodium carbonate at 100 g/t, sodium silicate at 500 g/t, sodium oleate at 200 g/t and a frother at 20 g/t.

Comparison tests were also conducted without sodium silicate and with 350 g/t sodium silicate. They resulted in tungsten recoveries below 75 % and grades below 1 %, so that all tests presented here outperformed them. This is why they are not represented on the diagrams for more clarity. Further tests involved higher dosages of sodium silicate as is usually operated in classical scheelite flotation processes, including dosages at 800 g/t, 1 kg/t and 2 kg/t. Said tests resulted in very low tungsten recoveries (below 65%) which explains why the dosages were maintained low in this testwork.

Finally, by acidifying sodium silicate, the authors expect the silica species in solution to change, e.g. generating a higher production of the specific species supposed to depress the gangue minerals. The type of silica species is dependent on the pH of the sodium silicate solution and on its concentration (Yang et al., 2018). In this work, the solution pH is varied through the mass ratio between sodium silicate and the acid and by the acid type but this pH could also be influenced by the stirring time. Solutions of acidified water glass at a mass ratio of 3:1 and 5:1 of sodium silicate with oxalic acid, sulfuric acid and hydrochloric acid were prepared and their pH was measured at different stirring times (Fig. 1). The solution pH appears very stable over time and microflotation also showed that the mineral recoveries remain stable after 30 minutes of stirring (Chinbat, 2017). Therefore, AWG is mixed for 30 minutes before being added to the flotation cell.

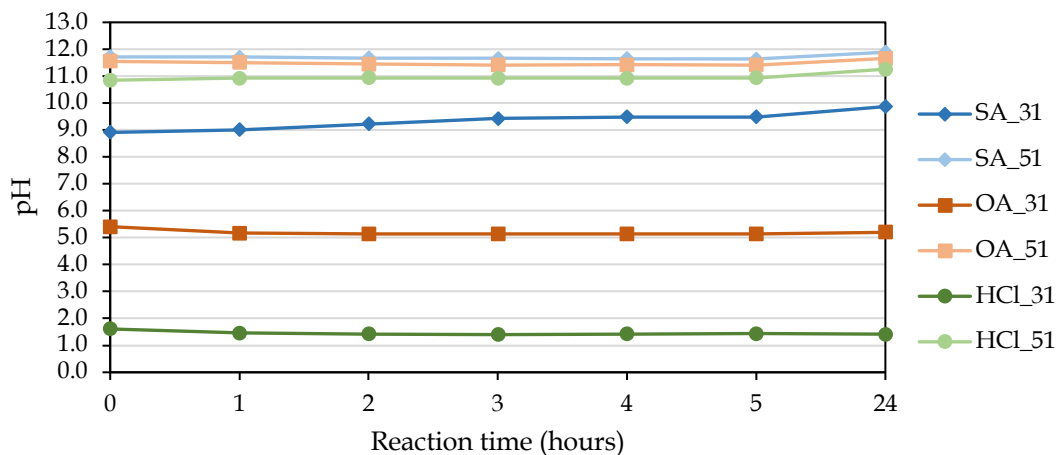


Fig. 1. Evolution of the solution pH depending on the reaction time (X1: mass ratio of X:1 sodium silicate to the acid, SA: sulphuric acid, OA: oxalic acid, HCl: hydrochloric acid)

The consequences of the pH, the solution concentration and the type of acid on the species generated in solution and the identification of said species and their interactions are discussed in Part II of this article. However, it can already be noted that the large differences in pH depending on the type of acid already indicate a clear influence of the acid type in the species generated. Batch flotation tests will determine if this influence translates well in the typical grade and recovery curves.

4.2. Sulfuric acid

The protocols of the flotation tests involving sulfuric acid are shown in Table 4. A comparison of the mass and water pulls depending on the dosage of sodium silicate with sulfuric acid are presented in Fig. 2a. SA31_500 and SA51_350 show no difference with the blank while SA51_500 displays a slightly lower mass pull and SA31_350 a distinctively higher mass pull. SA31_350 is therefore the least performing test of the set (Fig. 2b). SA31_500 is identical to WG_500 while the tests at a mass ratio of 5:1 perform better.

SA51_350 however only shows higher selectivity for silicates while SA51_500 reveals higher selectivity both for calcium-containing minerals and silicates (Fig. 3). SA31_500 remains very close to

Table 4. Batch flotation testwork with sulfuric acid

Test number	pH	Regulators (g/t)		Acid (g/t)		Collector (g/t)	Frother (g/t)
		Sodium carbonate	Sodium silicate	Ratio acid : water glass	Sulfuric acid	Sodium oleate	Flotanol 7197
WG_500	9	100	500	-	-	-	-
SA31_350	9	100	350	1:3	117	200	20
SA51_350	9	100	350	1:5	70	200	20
SA31_500	9	100	500	1:3	167	200	20
SA51_500	9	100	500	1:5	100	200	20

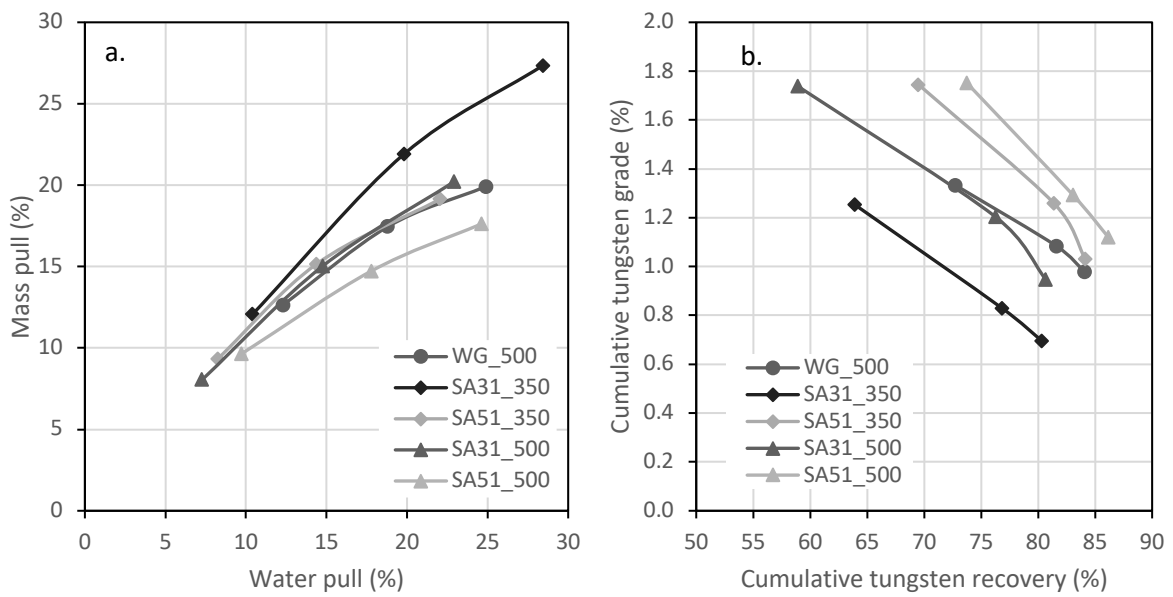


Fig. 2. a) Cumulative mass and water pulls and b) Cumulative tungsten grade and recovery of the sulfuric acid tests (at flotation times 1, 3 and 7min)

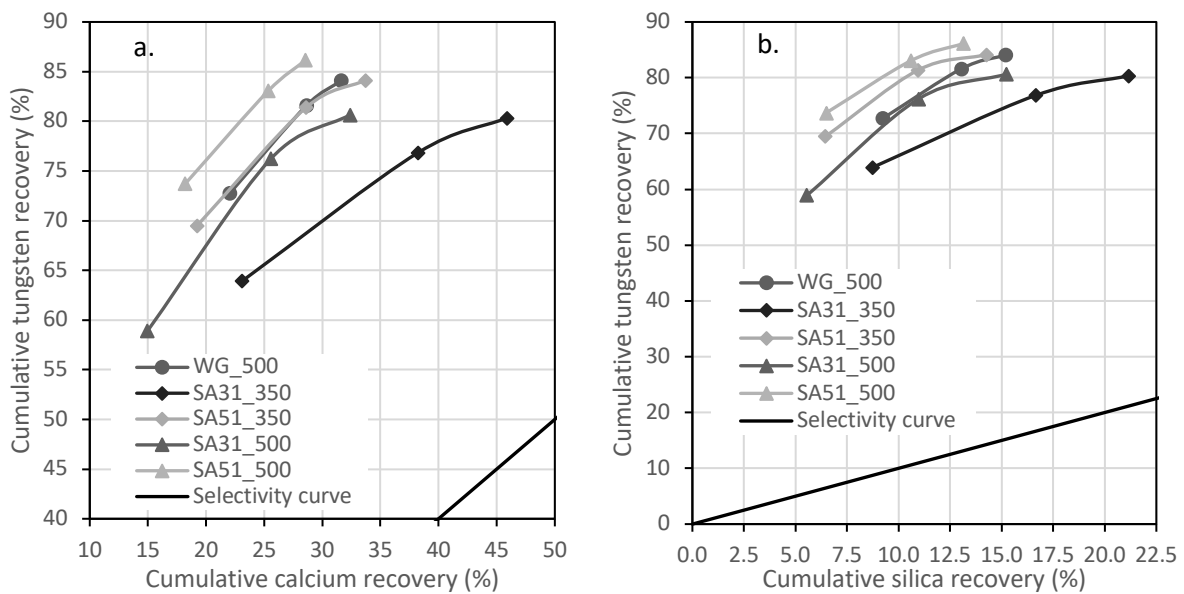


Fig. 3. a) Cumulative tungsten recovery against calcium recovery and b) Cumulative tungsten recovery against silica recovery of the sulfuric acid tests (at flotation times 1, 3 and 7min)

to WG_500. It seems the dosage of the acid itself is less determining than the mass ratio to sodium silicate. Furthermore, similar results to sodium silicate can be achieved at a lower dosage with the addition of acid.

The flotation rate constant k and the associated maximum recovery at infinite flotation time R_{\max} were calculated for tungsten, calcium and silicon based on the classical first order kinetics equation (Sutherland, 1948) (Table 5). They confirm the previous observations and truly show that a little addition of sulfuric acid impact the recovery of calcium- and silicon-bearing minerals.

Table 5. Calculated flotation rate constant k and associated maximum recovery at infinite flotation time R_{\max}

Test	k (min ⁻¹)			R_{\max} (%)		
	W	Ca	SiO ₂	W	Ca	SiO ₂
WG_500	2.075	1.237	0.922	82.4	27.3	14.0
SA31_350	1.662	0.673	0.502	78.5	38.9	21.0
SA51_350	1.814	0.828	0.539	82.4	27.6	14.0
SA31_500	1.350	0.572	0.396	79.1	27.8	15.9
SA51_500	2.020	1.023	0.627	84.2	23.8	13.1

4.3. Oxalic acid

The protocols of the flotation tests involving oxalic acid are shown in Table 6. In terms of mass and water pulls, OA51_350 and OA31_500 display a similar behaviour like WG_500, with OA51_500 relati-

Table 6. Batch flotation testwork with oxalic acid

Test number	pH	Regulators (g/t)		Acid (g/t) Ratio acid : water glass	Collector (g/t)		Frother (g/t) Flotanol 7197
		Sodium carbonate	Sodium silicate		Oxalic acid	Sodium oleate	
WG_500	9	100	500				
OA31_350	9	100	350	1:3	117	200	20
OA51_350	9	100	350	1:5	70	200	20
OA31_500	9	100	500	1:3	167	200	20
OA51_500	9	100	500	1:5	100	200	20

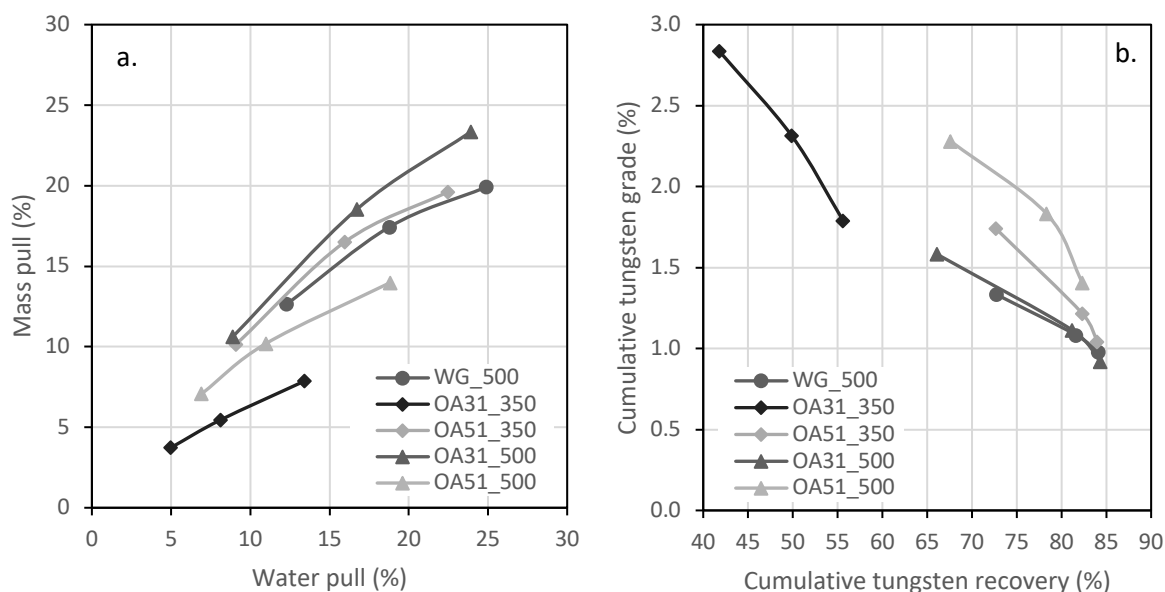


Fig. 4. a) Cumulative mass and water pulls and b) Cumulative tungsten grade and recovery of the oxalic acid tests (at flotation times 1, 3 and 7min)

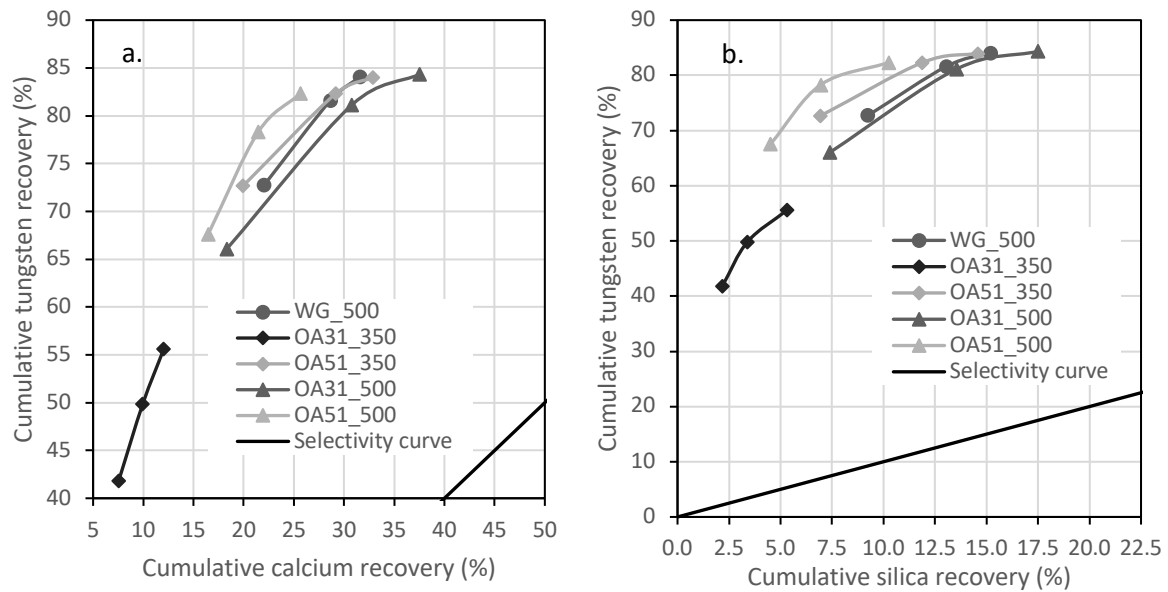


Fig. 5. a) Cumulative tungsten recovery against calcium recovery and b) Cumulative tungsten recovery against silica recovery of the oxalic acid tests (at flotation times 1, 3 and 7min)

vely close and OA31_350 having an important impact on both (Fig. 4a). This appears in the tungsten grade relatively recovery curves as well (Fig. 4b). Tests at a mass ratio of 5:1 result in a higher quality concentrate while tests at a mass ratio of 3:1, which is the mass ratio recommended in the literature, underperforms in this case. This shows that acidified water glass is a complex reagent to use.

In terms of selectivity for calcium and silica, the results are more contrasted (Fig. 5). OA51_500 is the best performing test, showing selectivity against both calcium-containing minerals and silicates, proving that a little addition of oxalic acid is enough to impact the results. OA51_350 shows higher selectivity only in the case of silicates but is identical to WG_500 for calcium. A mass ratio of 3:1 is in this case deleterious to the flotation.

The flotation rate constant k and the associated maximum recovery at infinite flotation time R_{\max} for tungsten, calcium and silicon are presented in Table 7. They confirm the previous observations, showing however that OA51_350 could potentially perform better than WG_500.

Table 7. Calculated flotation rate constant k and associated maximum recovery at infinite flotation time R_{\max}

Test	k (min ⁻¹)			R_{\max} (%)		
	W	Ca	SiO ₂	W	Ca	SiO ₂
WG_500	2.075	1.237	0.922	82.4	27.3	14.0
OA31_350	1.541	1.085	0.381	52.5	9.1	5.3
OA51_350	2.055	0.925	0.605	83.7	27.6	14.7
OA31_500	1.632	0.649	0.513	82.8	30.4	16.9
OA51_500	1.799	1.044	0.441	80.8	20.8	10.5

4.4. Hydrochloric Acid

The protocols of the flotation tests involving hydrochloric acid are shown in Table 8. All tests with AWG-HCl display lower mass and water pulls than with sodium silicate (Fig. 6a). At 500 g/t, there is not difference between mass ratios 3:1 and 5:1 in terms of mass and water pulls but in tungsten grades and recoveries (Fig. 6b). HCl51_500 is the least performing test while all other tests, especially HCl31_350 and HCl31_500 work better than WG_500.

This can also be seen in the selectivity curves for calcium and silica (Fig. 7). All tests except HCl51_500 show higher selectivity, with HCl31_350 as the best result. Similarly to sulfuric and oxalic acids, this demonstrates that even a little addition of hydrochloric acid is enough to impact the flotation

Table 8. Batch flotation testwork with hydrochloric acid

Test number	pH	Regulators (g/t)		Acid (g/t)		Collector (g/t)	Frother (g/t)
		Sodium carbonate	Sodium silicate	Ratio acid : water glass	Hydrochloric acid	Sodium oleate	Flotanol 7197
WG_500	9	100	500				
HCl31_350	9	100	350	1:3	117	200	20
HCl51_350	9	100	350	1:5	70	200	20
HCl31_500	9	100	500	1:3	167	200	20
HCl51_500	9	100	500	1:5	100	200	20

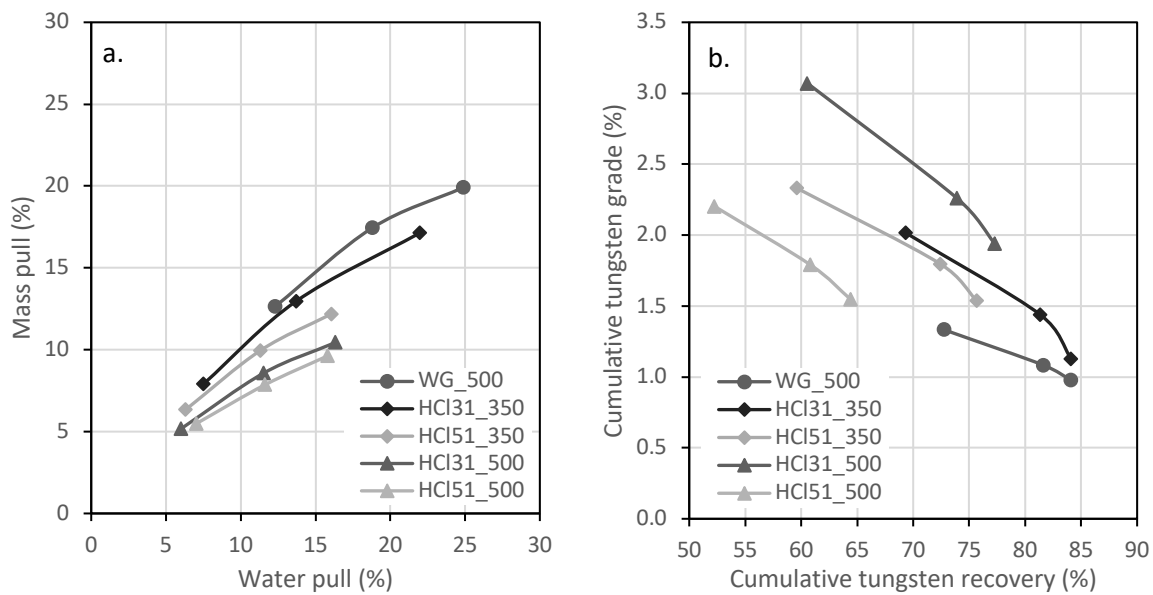


Fig. 6. a) Cumulative mass and water pulls and b) Cumulative tungsten grade and recovery of the hydrochloric acid tests (at flotation times 1, 3 and 7min)

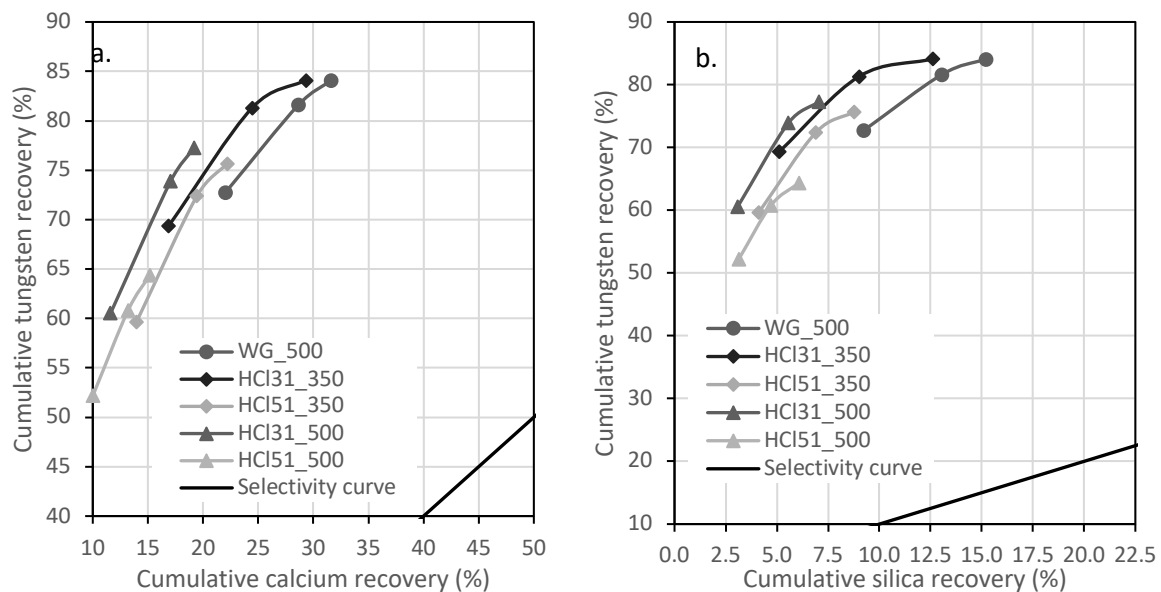


Fig. 7. a) Cumulative tungsten recovery against calcium recovery and b) Cumulative tungsten recovery against silica recovery of the hydrochloric acid tests (at flotation times 1, 3 and 7min)

results and to improve the performance of acidified water glass as compared to alkaline water glass. Moreover, the dosage of hydrochloric acid is as important as the mass ratio, as the tests with higher dosages of hydrochloric acid perform better.

The flotation rate constant k and the associated maximum recovery at infinite flotation time R_{\max} for tungsten, calcium and silicon are presented in Table 9. They confirm the previous observations, showing clearly that water glass acidified with hydrochloric acid impacts more silicates than calcium-bearing minerals.

Table 9. Calculated flotation rate constant k and associated maximum recovery at infinite flotation time R_{\max}

Test	k (min ⁻¹)			R_{\max} (%)		
	W	Ca	SiO ₂	W	Ca	SiO ₂
WG_500	2.075	1.237	0.922	82.4	27.3	14.0
HCl31_350	1.784	0.826	0.430	82.4	24.2	13.1
HCl51_350	1.617	1.010	0.581	74.4	18.0	8.5
HCl31_500	1.621	0.952	0.548	75.9	15.7	6.9
HCl51_500	1.741	1.090	0.634	62.8	12.7	6.1

5. Dosage and mass ratio as determining parameters

Previous experiments have highlighted that the mass ratio of the acid to sodium silicate is a crucial parameter when using acidified water glass. Sulfuric acid was chosen as a focal point of the flotation tests to determine the impact of the mass ratio of sodium silicate to the acid. The protocols are shown in Table 10.

The mass and water pulls are presented in Fig. 8a. There seems to be a cyclic effect of the dosage of sulfuric acid, where SA11 and SA41, SA21 and SA51 and finally SA31 and SA101 form respective pairs. This effect also translates onto the tungsten grade and recovery curves (Fig. 8b). Ratios of 2:1, 5:1 and 10:1 produce identical results. Ratios 1:1 and 4:1 are also very close and are the highest performing tests, requiring however some optimization to compensate for the loss in recovery. The mass ratio of 3:1 found in literature is the least performing one in this case while SA101 performs just as well as the control test WG_500 with very little addition of acid and lower dosage of sodium silicate.

Table 10. Batch flotation testwork with sulfuric acid

Test number	pH	Regulators (g/t)		Acid (g/t)		Collector (g/t)	Frother (g/t)
		Sodium carbonate	Sodium silicate	Ratio acid : water glass	Sulfuric acid	Sodium oleate	Flotanol 7197
SA11_350	9	100	350	1:1	350	200	20
SA21_350	9	100	350	1:2	175	200	20
SA31_350	9	100	350	1:3	117	200	20
SA41_350	9	100	350	1:4	87	200	20
SA51_350	9	100	350	1:5	70	200	20
SA101_350	9	100	350	1:10	35	200	20

Fig. 9 shows that the higher grades are mostly due to higher selectivity for silica and to a lesser extent to higher selectivity for calcium-bearing minerals for SA11 and SA41. It also shows more contrasted results: SA101 performs similarly to WG_500 only with silica but not with calcium. SA21 and SA51 are closer to it in terms of selectivity.

The flotation rate constant k and the associated maximum recovery at infinite flotation time R_{\max} for tungsten, calcium and silicon are presented in Table 11. They confirm the previous observations but also show that SA21 could potentially perform better than WG500 while SA51 is almost identical.

This cyclic effect is also observed for hydrochloric acid in single mineral flotation of scheelite and calcite as seen in Fig. 10, but not for oxalic acid. The microflotation experiments show that hydrochloro-

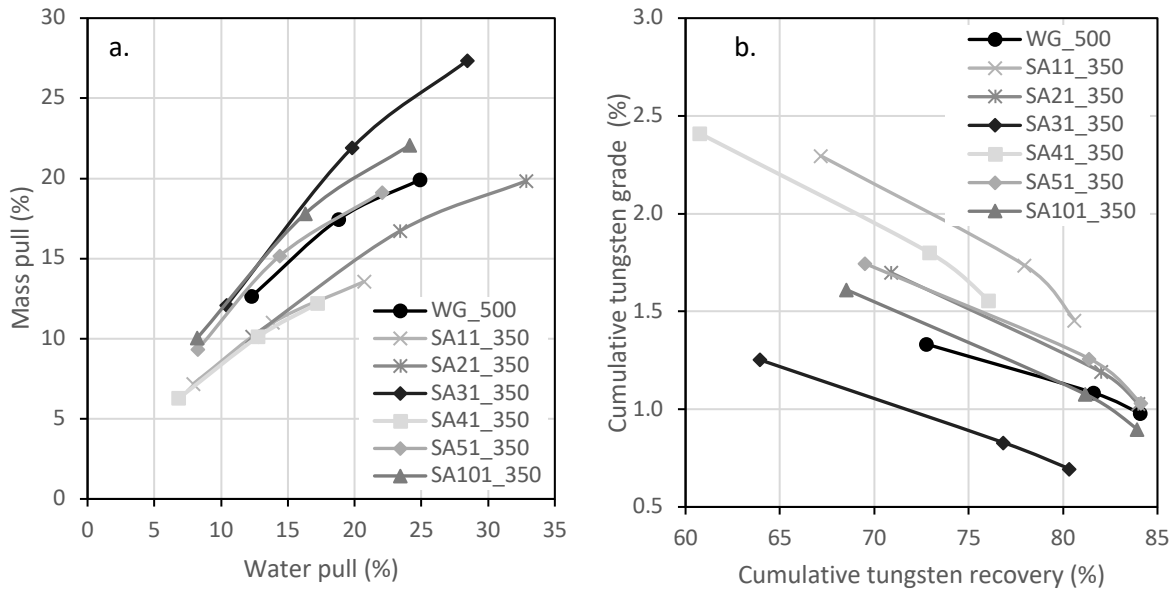


Fig. 8. a) Cumulative mass and water pulls and b) Cumulative tungsten grade and recovery of the sulfuric acid tests with a varying mass ratio and a dosage of 350 g/t sodium silicate (at flotation times 1, 3 and 7min)

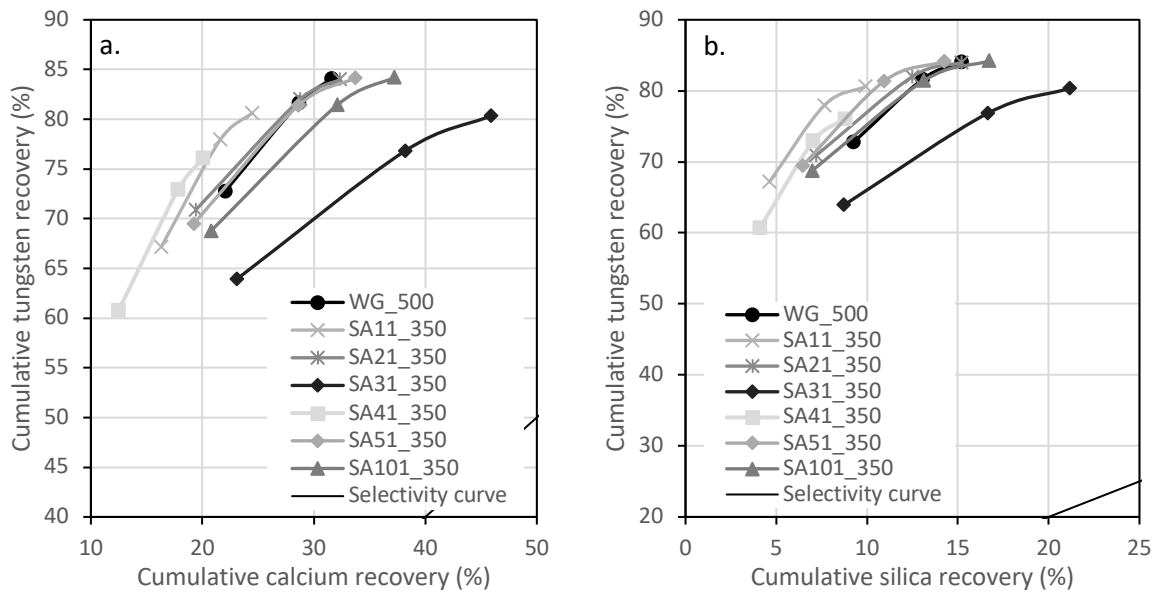


Fig. 9. a) Cumulative tungsten recovery against calcium recovery and b) Cumulative tungsten recovery against silica recovery of the sulfuric acid tests with a varying mass ratio and a dosage of 350 g/t sodium silicate (at flotation times 1, 3 and 7min)

Table 11. Calculated flotation rate constant k and associated maximum recovery at infinite flotation time R_{max}

Test	k (min ⁻¹)			R_{max} (%)		
	W	Ca	SiO ₂	W	Ca	SiO ₂
WG_500	2.075	1.237	0.922	82.4	27.3	14.0
SA11_350	1.913	1.183	0.580	79.5	19.3	9.4
SA21_350	1.955	0.940	0.620	83.0	26.3	14.6
SA31_350	1.662	0.673	0.502	78.5	38.9	21.0
SA41_350	1.686	0.998	0.599	74.9	16.6	8.4
SA51_350	1.814	0.828	0.539	82.4	27.6	14.0

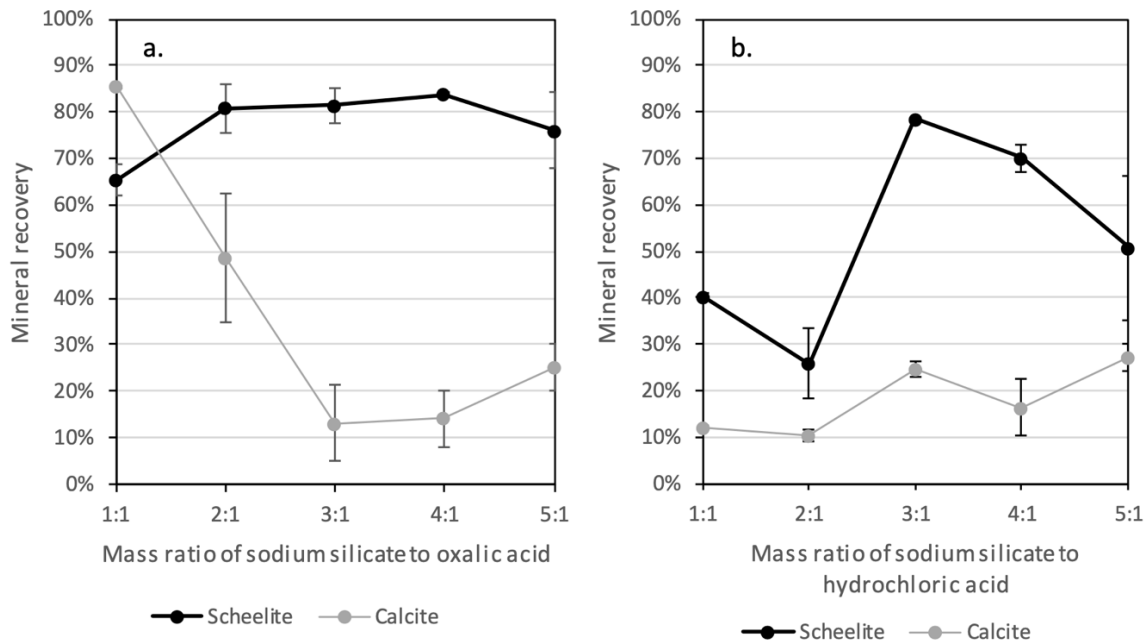


Fig. 10. a) Single-mineral flotation results for sodium silicate acidified with a) oxalic acid and b) hydrochloric acid at different mass ratios of sodium silicate to the acid (error bars correspond to the 95 % confidence interval)

ric acid has a large impact not only on calcite but also on scheelite and correspond well to the batch flotation themselves, e.g. a mass ratio of 5:1 is not performing as well as the ratio of 3:1.

Overall, when using acidified water glass, the mass ratio of sodium silicate to acid is by far the first parameter that will require optimization and remains acid dependent.

6. Does the type of acid matter?

The addition of acid results in equivalent or better performances than sodium silicate alone or sometimes at lower dosages. Unlike what was expected from literature where only sulfuric acid and oxalic acid are used, hydrochloric acid also performs well. This begs the question: does the type of acid matter?

Fig. 11 presents the tungsten grade recovery curves of all tests, with tests at 500 g/t of sodium silicate in black and 350 g/t in light grey. At the lowest dosage of acid, the type of acid is irrelevant as the results

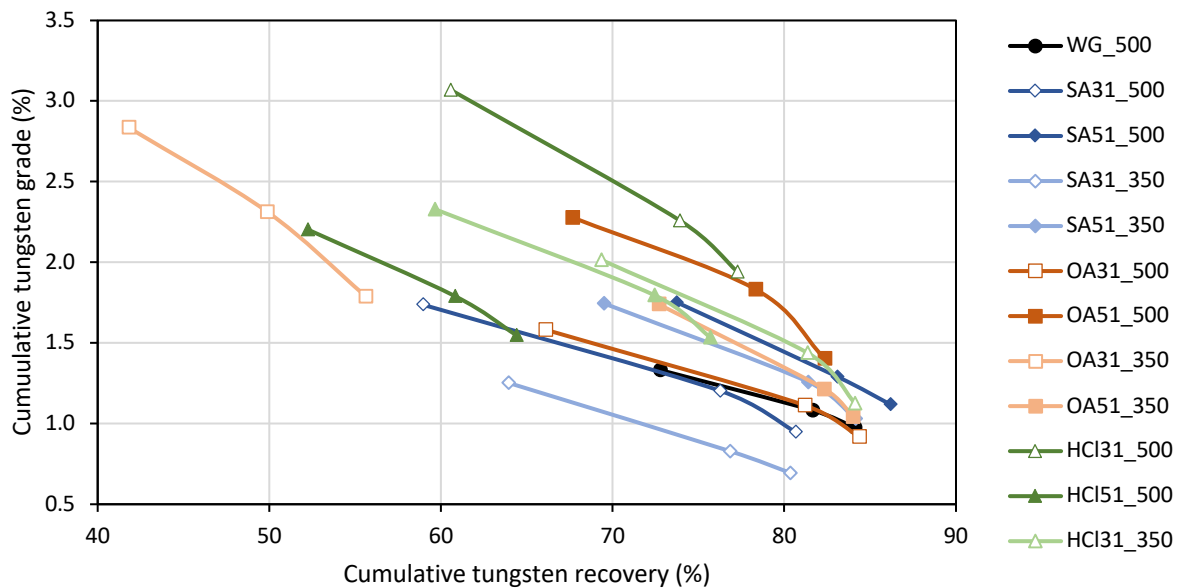


Fig. 11. Tungsten grade recovery curves for all tests

are identical. As the dosage increases, the type of acid becomes increasingly important. On one hand, sulfuric acid and oxalic acid behave similarly: a mass ratio of 3:1 works roughly as well as WG_500 while a mass ratio of 5:1 performs better than WG_500. On the other hand, hydrochloric acid is dosage dependent and requires higher dosages than the other acids to outperform them. Overall, oxalic acid and hydrochloric acid are the best performing acids.

In terms of selectivity for calcium, it appears that HCl31_350, HCl31_500, OA51_500 and SA51_500 have a higher selectivity than WG_500 and only SA31_350 and OA31_350 are worse, all others are equivalent. For silica, all tests have higher than or equivalent selectivity like WG_500 except HCl51_500, SA31_350 and OA31_350 (see Figs. of §4). Therefore, acidified water glass outperforms alkaline water glass mostly through its higher selectivity for silica while hydrochloric acid at a mass ratio of 3:1 and oxalic acid and sulfuric acid at 5:1 and 500 g/t actually offer higher selectivity for calcium-bearing minerals.

In general, the type of acid does not matter as all three acids do perform well, the crucial parameters are the dosage of the acid and its mass ratio towards sodium silicate.

7. Conclusions

Acidifying sodium silicate in order to improve the selectivity of sodium silicate in the selective flotation of scheelite from calcite was investigated. Three acids were tested, oxalic acid and sulfuric acid, both of which can be used in hydrometallurgy for the leaching of scheelite, and for the first time, hydrochloric acid, as a point of comparison. A literature review of previous usage of acidified water glass showed that no comparison between acids was made on the same ore before, that comparisons with alkaline water glass were limited and that the idea that acidified water glass is more efficient at lower dosages had not yet been proven in scheelite flotation.

This article shows that acidified water glass does outperform alkaline water glass in terms of selectivity: it increases mainly the grade by further depressing silicates and calcium-bearing minerals. In most cases, it requires lower dosages to do so and sometimes very little addition of acid. The type of acid is not relevant as all three acids perform well, with a higher performance of oxalic acid and hydrochloric acid in this particular case. The parameters crucial to the preparation of acidified water glass with a real impact on flotation are the dosage of acid and its mass ratio to sodium silicate.

Further measurements were undertaken to understand why acidified water glass can outperform alkaline water glass and to explain the actual mechanism of AWG. As mentioned before, these differences arise from the species generated in solution. This is the subject of Part II of this article.

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