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THEMA:

Particle-based investigation of scheelite flotation using colloidal silica as a depressant

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Aufgabenstellung

The work investigates the flotation separation of scheelite from calcite using colloidal silica as a depressant with a particle-based approach. Based on previous batch flotation studies on a case study of a low grade scheelite ore, the work attempts to explain the behavior of the different colloidal silica modifications with respect to calcite and the main gangue minerals. The work is structured in three parts:

1. MLA measurements and data extraction and modeling (40 %, 10 weeks)

Based on batch flotation well defined concentrates and tailings of the investigated ore are prepared and measured with MLA. The extracted data will be used to link the effect of colloidal silica dosage and modification with particle properties (mainly mineral particle size) and to develop and train particle-based flotation kinetic models.

The work package includes sample preparation MLA measurement, data investigation, and model establishment and training.

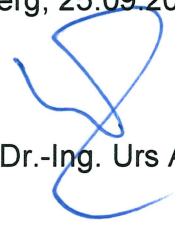
2. Micro flotation (35 %, 6 weeks)

To better understand the effect of colloidal silica on gangue minerals, microflotation experiments are carried out with hornblende (main silicate gangue mineral) and talc. The colloidal silica dosage, modification and specific surface area as parameters are studied using calcite supernatant. The work package includes sample preparation and micro flotation tests.

3. Implementation of the SOPAT system for the analysis of particle-bubble heterocoagulates. (25 %, 4 to 5 weeks)

Preparation experiments are carried out at HIF to study bubble generation. The reagent system consists of sodium oleate as collector and colloidal silica as a depressant. The pH value is adjusted to 8. Depending on the time period, 3 to 4 pure minerals are investigated (scheelite, calcite and hornblende/talc). Once the preparation tests are completed, the SOPAT system can be used at the TUBAF. The code development for the image processing is performed at HIF by Borhane Ben Said with the help of HIF colleagues. The work package includes sample preparation, preparation tests at HIF, measurements with SOPAT system at TUBAF, images processing at HIF.

Freiberg, 25.09.2023



Prof. Dr.-Ing. Urs A. Peuker

Eidesstattliche Erklärung

Ich versichere, dass ich diese Arbeit selbstständig verfasst und keine anderen Hilfsmittel als die angegebenen benutzt habe. Die Stellen der Arbeit, die anderen Werken dem Wortlaut oder dem Sinn nach entnommen sind, habe ich in jedem einzelnen Fall unter Angabe der Quelle als Entlehnung kenntlich gemacht. Diese Versicherung bezieht sich auch auf die bildlichen Darstellungen.

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Declaration

I hereby declare that I completed this work without any improper help from a third party and without using any aids other than those cited. All ideas derived directly or indirectly from other sources are identified as such. This declaration also refers to the representation of figures and visual material.

October 16, 2023

Bat-Ochir Battumur

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List of Acronyms

DoE	Design of experiments	18
MLA	Mineral liberation analyser	3
SSA	Specific surface area	3
PSD	Particle size distribution	4
ECD	Equivalent circular diameter	4
DLVO	Derjaguin–Landau–Verwey–Overbeek	6
MIBC	Methyl isobutyl carbinol	9
BHA	Benzo hydroxamic acid	11
SEM	Scanning electron microscope	15
BSE	Back-scattered electron	15
GXMAP	Grain-based x-ray mapping	15
XRD	X-ray powder diffraction	35
PSM	Particle-based separation model	16
LASSO	Least absolute shrinkage and selection operator	16
SOPAT	Smart online particle analysis technology	21
NaOl	Sodium oleate	23
C1	Concentrate 1	25
C2	Concentrate 2	25
C3	Concentrate 3	25
SSSM	Semi-soluble salt type minerals	2

1. Introduction

1.1. Motivation

Scheelite is one of the primary commercial tungsten sources, as scheelite deposits make up roughly two-thirds of its world reserves [1]. Tungsten itself has exceptional properties, which makes it suitable for various industrial applications, including tungsten alloys [2], and electrodes [3]. These properties include high melting point, high density, excellent wear resistance, and high tensile strength. Tungsten is recovered from the scheelite through consecutive processing, which usually involves combinations of ore beneficiation, hydro- and pyrometallurgical processes [4]. In coarser sizes, gravity separation is effective for the extraction of scheelite due to its high density. However, the liberation size of scheelite ore is often fine and current gravity separation methods exhibit poor performance for such particle sizes. Therefore, beneficiation of scheelite ore is often achieved by the combination of gravity separation and froth flotation [5]. Froth flotation is one of the main beneficiation process steps to recover scheelite concentrate from scheelite ore. Scheelite concentrate subsequently goes through tungstate extraction and purification to extract pure tungsten [6], as illustrated in Figure 1.

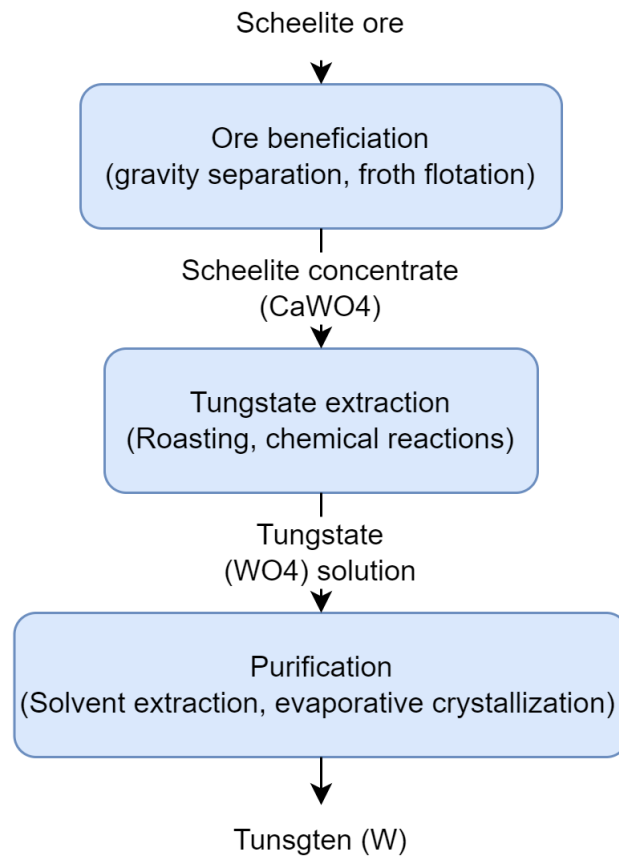


Fig. 1: A schematic diagram of common tungsten production route

Scheelite is considered a polar salt type material, thus naturally hydrophilic [7]. However, with the use of proper collectors, such as sodium oleate, scheelite flotation is possible. Nevertheless, the same mechanism appeared to be also true for the common gangue minerals in scheelite ore, such as calcite $CaCO_3$, silicates, and talc $Mg_3Si_4O_{10}(OH)_2$, which complicates the task to achieve industrial concentrate grade of 60 % WO_3 [7]. Scheelite and calcite belong to the same group of Semi-soluble salt type minerals (SSSM) and have similar surface properties [8]. Their selective separation by froth flotation is very challenging, thus finding an effective depressant for calcite is a big task [7]. Sodium silicate, known as water glass, is a common reagent used as a calcite depressant in scheelite flotation due to its accessibility and cost [9]. Nevertheless, effective depression of calcite is achieved at a high dosage, and a high concentration of water glass appears to depress scheelite as well, leading to limited selectivity [7]. Since water glass is deemed insufficient for calcite depression due to its moderate selectivity, the potential use of colloidal silica as a calcite depressant in scheelite flotation was introduced in 2020 by Kupka, Babel, and Rudolph [10]. However, the effect of CS modifications and their dosage on other gangue minerals, including silicates, and talc, need to be further studied.

Moreover, various papers reported the substantial effect of calcium species on the flotation recovery when using fatty acid as a collector [11][12]. Since calcite is one of the main gangue minerals in the scheelite ore, calcium species ions dissolved from calcite may form and influence the process behaviour. Therefore, the mentioned effect needs to be investigated for the other gangue minerals, including talc and silicate mineral groups.

Besides reagents, particle properties, such as particle size and shape, can affect the flotation behaviour of particles in scheelite froth flotation [13]. In addition, their interactions with bubbles significantly impact the process performance, depending on the bubble size distribution [14]. Therefore, the effect of bubble and particle size distributions and their interaction need to be investigated for scheelite froth flotation.

1.2. Objectives

This thesis focuses on the investigation of the selective flotation of scheelite from other gangue minerals using colloidal silica as a depressant. The thesis work comprises three main objectives.

The first objective is to understand the effect of colloidal silica on the main gangue minerals, hornblende (representative silicate mineral), and talc on a microflotation scale. The parameters, including colloidal silica modification, dosage, and specific surface area, are studied using calcite supernatant, as the possible impact of Ca^{2+} on the flotation behaviour of certain minerals was discovered in several studies [11][12].

The next task is to create particle-based kinetic models for scheelite flotation using Mineral liberation analyser (MLA) data extracted from batch flotation experiments. Previously proposed particle-based flotation model [15] provides extensive insight into the flotation kinetics of individual particles, including the response of each mineral type, and particle parameters. Moreover, MLA data from the samples performed in Design of Experiments (DoE) provide an insight into the effect of CS modification, dosage, and Specific surface area (SSA).

The third objective is to implement the use of an inline camera system, SOPAT for a qualitative investigation of particle-bubble coagulates in batch flotation. The possible effects of CS modification, dosage, and SSA on the particle-bubble coagulates are investigated in this work.

1.3. Methodology

The following methods are used in this thesis:

1. Review of relevant literature
2. Sample and reagent preparation
3. Microflotation of hornblende (representative silicate mineral) and talc
4. Particle-based kinetic model for scheelite batch flotation samples
5. Qualitative analysis on particle-bubble coagulates using the SOPAT system
6. Analysis, investigation, and interpretation of results

2. Theoretical background

2.1. Particle property parameters

Particle size distribution (PSD) is an essential design variable in any processing that deals with particles. PSD can be represented by a particle size descriptor, using the information from the two-dimensional images of individual particles obtained by MLA or image analysis. The most widely used particle size descriptor for PSD is equivalent circular diameter [16]. Equivalent circular diameter (ECD) employs the diameter of a circle that has the same value as the projected area of an irregular-shaped particle, as formulated below [16].

$$x_{ECD} = \sqrt{4 \frac{A}{\pi}} \quad (\text{Eq. 2.1})$$

x_{ECD} stands for equivalent circular diameter of a particle, and A represents the projected area of the particle.

Aspect ratio is the ratio of minimum to maximum Ferret diameter of the given particle. Circular-shaped particles have a value of 1, whereas the aspect ratio of needle-like particles approaches 0.

$$\Psi_A = \frac{x_{Ferret,min}}{x_{Ferret,max}} \quad (\text{Eq. 2.2})$$

Ψ_A stands for the aspect ratio of a particle, and $x_{Ferret,min}$ and $x_{Ferret,max}$ represent the minimum and maximum Ferret diameters of the particle, respectively.

Solidity is the ratio of the projected area to the convex hull area of the particle. A value of 1 indicates that the particle is solid, whereas a value of less than 1 indicates that the particle has an irregular boundary or contains holes. Solidity is a further measure if the particle shape is more convex or concave [17].

$$S = \frac{A}{A_{convex}} \quad (\text{Eq. 2.3})$$

S stands for the solidity of a particle, and A and A_{convex} represent the projected area and the convex area of the particle, respectively.

The mineralogical composition can be determined based on the area distribution from the 2D particle image. The degree of liberation is a representative parameter computed by the ratio of the mineral grain area of interest to the total particle area [18]. A value of 1 indicates that the particle is fully liberated, consisting of only one mineral.

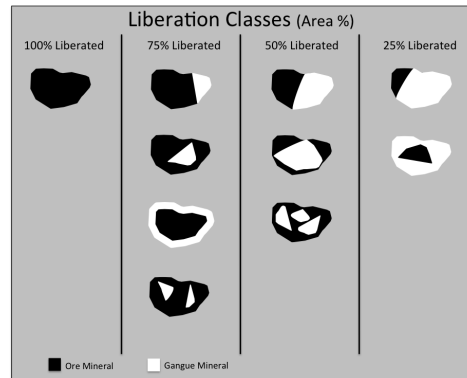


Fig. 2: An illustration of different liberation classes

2.2. Particle particle interactions

Particles possess properties that define the system and their interactions influence the process behaviour in the system. Particle interactions can be either attractive or repulsive and generally include the following interactions [19]:

1. Electrostatic interactions
2. Van der Waals interactions
3. Capillary interactions

Electrostatic interaction can be described by Coulomb's law. The interaction can be either attractive or repulsive depending on the charge of the particles. The energy of electrostatic interaction is formulated as below [20].

$$W(a) = \frac{q_1 q_2}{4\pi\epsilon_r\epsilon_0 a} \quad (\text{Eq. 2.4})$$

$W(a)$ stands for electrostatic interaction energy, ϵ_r for relative permittivity, ϵ_0 for absolute permittivity, a for particle separation distance, q_1 and q_2 represent point charges.

Van der Waals forces originate from the interactions on the atomic level and comprise three different types of interactions [21]. They include orientation forces, called Keesom interaction, and induction forces, known as Debye interaction. The third interaction is the dispersion force, named as London force. The Van der Waals interaction energy between two identical spheres can be formulated based on Hamaker's theory as shown below.

$$W(a) = \frac{rC_H}{12a} \quad (\text{Eq. 2.5})$$

$W(a)$ stands for Van der Waals interaction energy, C_H for Hamaker constant, r for the radius of sphere particles, and a represents particle separation distance.

For identical particles with the same composition, Van der Waals interaction is always attractive [22].

However, for particles with different compositions in a liquid environment, the interaction can be repulsive depending on the materials. The interaction of particles within the liquid phase is described by Derjaguin–Landau–Verwey–Overbeek (DLVO) theory, which superposes attractive Van der Waals interaction with repulsive electrostatic interaction within the double layer. Electrical double layer refers to a region, where the free ions are concentrated due to the particle charge, as illustrated in Figure 3 [23].

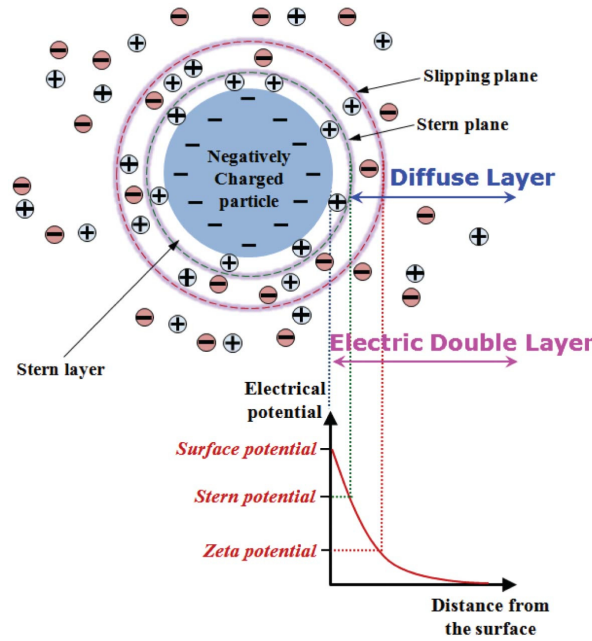


Fig. 3: A schematic diagram of electric double layer

The electric double layer consists of three parts, including surface charge, stern layer, and diffuse layer [23]. Surface charge refers to charged ions absorbed on the particle surface. The stern layer contains oppositely charged ions attached to the surface, whereas the diffuse layer contains free ions under the influence of electrostatic force. Zeta potential is the potential difference between the dispersion medium and the slipping plane and is a measure of the charge of particles in the suspension. Zeta potential is heavily influenced by the pH of the suspension. If alkali is added, there will be a high amount of negatively charged ions, decreasing zeta potential. Instead of alkali, acid addition increases the concentration of positively-charged ions, increasing zeta-potential [24]. Either the high positive or high negative zeta potential of these particles would allow stable suspension due to repulsion between each other and thus no coagulation. pH value, where the zeta potential is zero, is called isoelectric point (IEP). At this point, agglomeration of these particles happens, since Van der Waals attraction force becomes more dominant than repulsion forces. [24] On the other hand, the point of zero charge (PZC) refers to the pH value, where the overall particle charge is zero.

Debye length is the characteristic thickness of an electrical double layer and depends mostly on the ionic concentration in the liquid. Electric potential drops at the distance from the surface that equals the Debye length [20].

$$\kappa = \sqrt{\frac{e^2 \sum n_i z_i^2}{\varepsilon_r \varepsilon_0 k T}} \quad (\text{Eq. 2.6})$$

κ stands for Debye length, e for elementary electrical charge, n for number of ions, z for charge of the ion, ε_r for relative permittivity, ε_0 for absolute permittivity, k and T represent Boltzmann constant and temperature.

Capillary interactions are present when solid material is wetted by a liquid. The equilibrium wetting of a solid particle in the presence of water and air bubbles is described in Equation 2.7, known as the Young–Dupré equation.

$$\gamma_{SG} - \gamma_{SL} = \gamma_{LG} \cos \theta \quad (\text{Eq. 2.7})$$

Figure 4 shows the three interfacial tensions in equilibrium applied to the point and contact angle, also known as the wetting angle. Wetting angle is a measure to quantify the wettability of the material. The angle of 180° implies that the material is completely non-wetting, whereas 0° means perfect wetting [25].

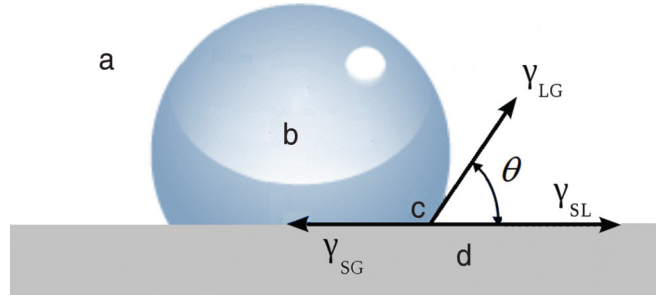


Fig. 4: A schematic diagram of the relationship between equilibrium contact angle and interfacial tensions (a) water; b) air bubble in water; c) three-phase contact point; d) hydrophobic solid [25]

2.3. Froth flotation

Froth flotation is a process used extensively in the mineral processing industry for the separation of fine materials [26]. The separation utilizes surface property differences of particles and rising bubbles, which the hydrophobic particles adhere to. Furthermore, the surface characterization of the desired mineral can be modified with the use of flotation reagents, which provides a possibility to achieve selective extraction of many other minerals [8]. Taking the limitation of natural resources into account, the significance of selective extraction by froth flotation becomes a great deal when handling low-grade deposits [27].

Flotation of the selected mineral in pulp is achieved by the supply of air bubbles, agitators, and chemical reagents. When a rising bubble from the bottom of the tank gets closer to a particle, particle-bubble interaction happens. Particle-bubble interaction involves micro-processes, including collision, attachment, and detachment. Attachment and detachment heavily depend on surface chemistry parameters of bubbles and particles, including zeta potential, contact angle, and so on [28]. In flotation, particles with a contact angle, $\theta > 10^\circ$ are typically considered a hydrophobic solid which can have a probability of floating [25]. These hydrophobic particles are more likely to attach to bubbles, as they are repelled by water and attracted to air bubbles. Surface interaction between a hydrophobic particle and a bubble is determined by Van der Waals, electrical double layer, and hydrophobic forces, which are investigated by atomic force microscopy [28].

The bubbles loaded with attached particles form a froth layer on the pulp surface, which can be separated. However, besides hydrophobic particles attached to bubbles by true flotation, hydrophilic particles can also be carried to the froth layer by entrainment with the rising bubbles [29]. There are numerous minerals, such as graphite, sulphur, molybdenite, talc, and coal, which are naturally hydrophobic. However, most minerals are hydrophilic by nature. Therefore, chemical reagents are utilized to change the surface properties of mineral particles for a desired outcome.

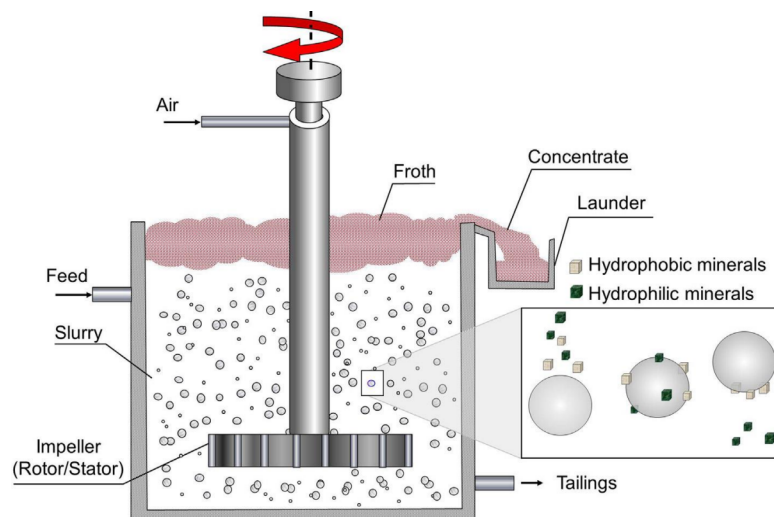


Fig. 5: A schematic diagram of a froth flotation cell

Based on their functionality, flotation reagents can be classified into the collector, frother, and auxiliary reagents [25]. Collectors include chemicals that create a hydrophobic layer on the mineral surface and can be divided into two groups of non-ionizing and ionizing compounds. The latter represents a chemical compound that dissociates in water and can be subdivided into anion and cation collectors. In contrast, non-ionizing compounds are non-polar hydrocarbons, which are insoluble in water. The classification of collector is summarized in Figure 6 [30].

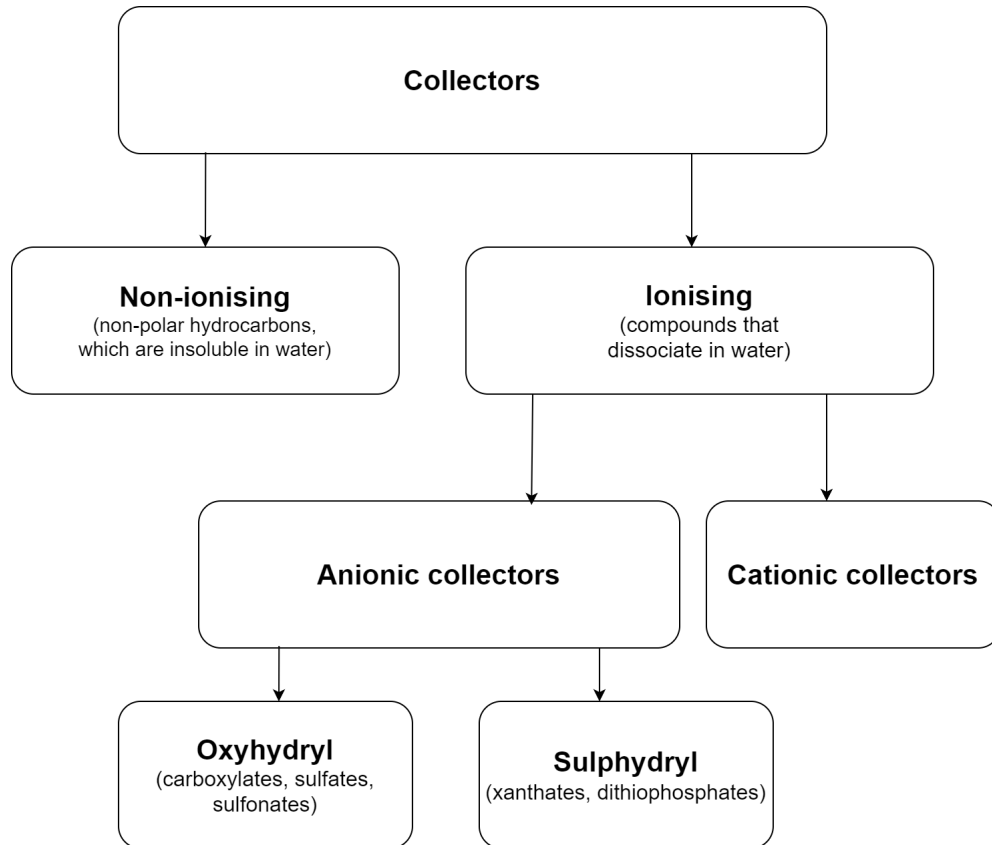


Fig. 6: Classification of froth flotation collectors [30]

Frothers comprise a polar constituent, which interacts with water molecules, and a non-polar constituent, which interacts with air bubbles. The frother reagents are concentrated in the air-water interface and create a condition for stable froth formation [30]. Based on their behaviour at different pH levels, frothers can be divided into two groups, neutral and acidic. The latter exhibits a good performance only in an acid environment, whereas neutral frothers can be used in the overall range of pH. A well-known example of a neutral collector is Methyl isobutyl carbinol (MIBC) [30].

Generally, auxiliary reagents represent supplementary chemicals, which allow selective recovery, favouring the desired mineral. They include depressant which prevents gangue minerals from collector adsorption, and activator which promotes the adsorption of reagents on the desired mineral. In addition, pH regulators belong in this group, as they can either act as depressants or activators depending on the pH of the pulp [25].

2.4. Hallimond tube

Flotation can be carried out on large or small scale. On a small scale, flotation of a single particle can be achieved in a Hallimond tube that is designed to test the flotation of one mineral of interest [31]. In Hallimond tube tests, the pure mineral is used since the small ore sample may have no single particle of the investigated mineral. Such small-scale flotation device provides a quick and robust way to investigate the flotation of a single mineral. The schematic diagram of the Hallimond tube is shown in Figure 7 [32]. The pulp with pure mineral sample is placed in the tube. Rising air bubbles supplied from the bottom transfer the hydrophobic particles to the surface, causing separation.

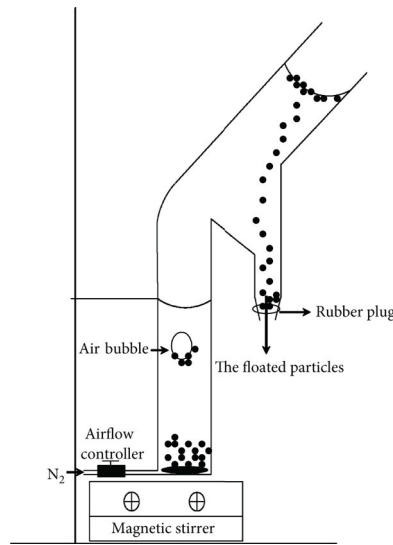


Fig. 7: A schematic diagram of Hallimond tube

2.5. Scheelite flotation

Scheelite is a semi-soluble salt-type mineral that is composed of Ca^{2+} cations, and WO_4^{2-} anions [33]. The zeta potential of the scheelite surface was reported to be negatively charged over the whole pH range, possibly due to excess ions of WO_4^{2-} on the surface [34]. Active Ca^{2+} cations and the negative zeta potential on the scheelite surface enable the use of both cationic and anionic collectors for scheelite flotation.

2.5.1. Collectors

Cationic collectors are able to collect scheelite effectively through electrostatic attraction since the mineral has a negative zeta potential. Amines are an example of cationic collectors and are commonly used for collecting silicates, oxides, and various other minerals. Even though amines are able to collect scheelite, they are often not applicable in the industry for scheelite flotation, as silicates are usually one of the main gangue minerals in scheelite ore [5]. In addition, selectivity between and scheelite is challenging, as they tend to exhibit response. A recent study reported that dodecyl amine (DDA) potentially has better absorption on scheelite than calcite, through the electrostatic bond between NH_3^+ cations, and WO_4^{2-} [35]. However, the mentioned mechanism in the actual scheelite ore has not been tested yet.

Anionic collectors include various reagents that are designed to form a chemical bond to active cations on the mineral surface, such as scheelite [8]. The most widespread anionic collectors are carboxylates, known as fatty acids. Fatty acids are commonly used for various flotation schemes in the industry, due to their low cost, and abundance. More importantly, fatty acids, namely sodium oleate can readily collect scheelite. The oleate group in fatty acid, $RCOO^-$, is adsorbed to the cationic surface of scheelite, hence creating a hydrophobic layer, as illustrated in Figure 8. However, with the use of sodium oleate, it is challenging to separate scheelite and other calcium-bearing minerals as they exhibit the same adsorption mechanisms [8].

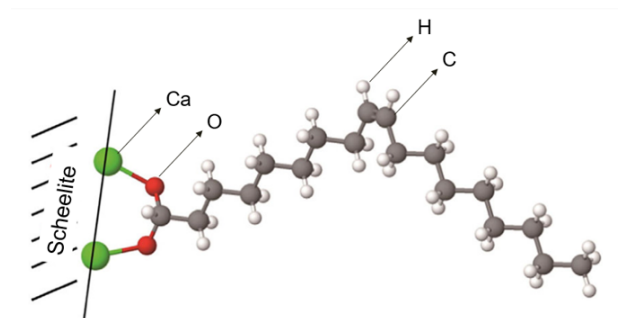


Fig. 8: A schematic diagram of sodium oleate adsorption on scheelite surface

Hydroxamates are the anionic form of hydroxamic acids, which are adsorbed to the cationic mineral surface, enabling flotation. Hydroxamic acid usage has been investigated in various studies over the years. Benzo hydroxamic acid (BHA) and cyclohexyl hydroxamic acid (CHA) were specifically employed for scheelite flotation studies and the latter was reported to be the more effective one out of the two [36]. However, the performance of hydroxamic acids is deemed not sufficient compared to fatty acids. Therefore, an addition of Pb^{2+} ions in BHA was investigated in several studies to improve its performance and the selectivity of scheelite from other similar salt minerals. Theoretically, BHA tends to form ionic bonding with lead ions more readily than calcium ions. The study suggests that lead ions could adsorb to the scheelite surface, promoting selective flotation of scheelite [37]. BHA mixed with lead nitrate was applied in a mine located in China and improved scheelite recovery and selectivity were reported [38]. However, the necessary lead nitrate dosage was quite high, with a molar ratio of lead nitrate to BHA being 2:1. Moreover, since lead nitrate is an extremely toxic reagent, the aforementioned practice in high dosage is not desirable considering the environmental issues it entails.

Other anionic collectors, such as sulphates, phosphonates, and sulphonates, were previously tested in a limited capacity. However, the selectivity between scheelite and other calcium-bearing minerals was reported to be poor in the studies regarding scheelite flotation [39].

2.5.2. Associated gangue minerals

Semi-soluble salt minerals, including calcite, fluorite, and apatite, contain similar surface compositions and often exhibit similar responses to the flotation process. In scheelite flotation, the main challenge is the effective separation of scheelite from calcite, since calcite is one of the main gangue minerals often found in scheelite ore [5].

Hornblende is a complex of inosilicate minerals and it refers to the calcium-amphibole group of amphibole minerals. Amphiboles are commonly found in metamorphic and igneous rock zones. Generally, silicates are the main gangue minerals in scheelite ore and [40] such calcium-bearing amphiboles behave in a similar manner as scheelite and complicate selective flotation [8].

Talc is a hydrated magnesium silicate, that is often found to be associated with other minerals, including silicates, carbonates, sulphides, and scheelite. Talc is a naturally hydrophobic mineral, with a general chemical formula of $Mg_3Si_4O_{10}(OH)_2$.

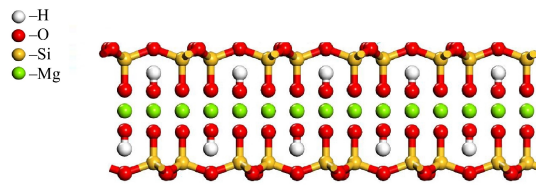


Fig. 9: An illustration of talc molecular structure

In an environment with sodium oleate as a collector, both scheelite and talc exhibit high floatability [41]. Consequently, the talc gangue phase often becomes an obstacle in metallurgical processes, leaving MgO trace in the process product [42]. An addition of depressant is necessary to depress talc, as the mineral is able to float even in a collectorless environment. For this purpose, various reagents, such as sodium silicate, guar gum, and carboxy methyl cellulose (CMC), were investigated in numerous publications. The use of sodium silicate as talc depressant in industrial scheelite flotation exhibits limited selectivity [42]. Moreover, ion influence on talc recovery has been reported. As illustrated in Figure 9, charged magnesium hydroxo complexes in talc molecular structure become liberated during the dissolution of talc. As the study suggests, they subsequently react with dissolved ions in the bulk solution, enabling the adsorption of certain reagents [43].

2.5.3. Depressants

Sodium silicate is the main depressant reagent applied in the industry for scheelite flotation, often coupled with fatty acids as a collector. Sodium silicate is widespread due to its low cost and accessibility. Both the ratio SiO_2 to Na_2O and pH seem to influence the adsorption of sodium silicate [44][45]. In pH range of 7-11, silica monomers $SiO(OH)_3^-$, and $Si(OH)_4$ are the dominant monomers present in aqueous solutions. Several adsorption mechanisms of sodium silicate are proposed in the case of calcium-bearing minerals. First, $SiO(OH)_3^-$ ions could get adsorbed into a Ca^{2+} cationic surface on the mineral, blocking fatty acid collectors from possible adsorption [46]. The second suggested assumption is that the presence of colloidal silica is a reason for the depressing effect of sodium silicate [39]. However, the drawbacks of sodium silicate usage are its high dosage and poor selectivity between scheelite and calcium-bearing gangue minerals.

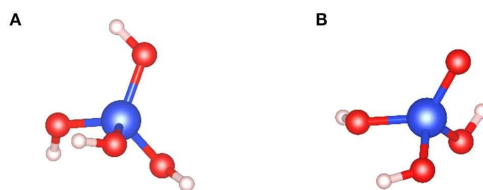


Fig. 10: An illustration of silica monomers: (A) acidic, $Si(OH)_4$ (B) basic, $SiO(OH)_3^-$ [5]

Therefore, the use of acidified sodium silicate has drawn attention for potential application. In earlier studies, the depressing effect of both alkaline and acidic sodium silicate was investigated, in which the latter showed a stronger depressing effect on the gangue minerals. This is possibly due to the high concentration of silica monomer species when sodium silica is mixed with acid [44]. However, the preparation of acidified sodium silicate is inconsistent in publications as the ratio of sodium silica to acid varies and further implementation has not developed as of now [7]. Moreover, a recent study suggested that the reason behind the observed improvement in acidified sodium silicate's depressing effect on calcite is the formation of colloidal silica when the ratio of sodium silicate to acid is 3:1 [47].

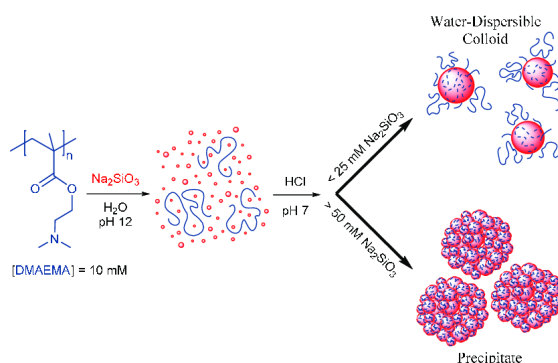


Fig. 11: An illustration of colloidal silica formation in acidified sodium silicate [48]

Colloidal silica is a possible reason for the depressing effect of sodium silicate on the calcium-bearing gangue minerals [47]. A colloid refers to a substance that is evenly dispersed throughout the mixture. Colloidal silica refers to amorphous silica nanoparticles, which have a wide range of applications in the industry, such as fillers, surface modifiers, flocculants, and coating. The advantages of these nano-sized particles with high surface area are fully utilized when they are well-dispersed. Typically, colloidal silica is stable at a pH of 10-11. However, due to their natural aggregation behaviour, they can become unstable forming a colloidal gel, which is a formation of an aggregate network of silica throughout the suspension volume [49]. Therefore, different types of surface-modified colloidal silica are developed and examined in several studies to achieve stability. The aluminate-modified surface of colloidal silica resulted in more negative zeta potential, which implies less coagulation and more stability [49]. Alternatively, silane-modified colloidal silica is examined in gelation tests, and it showed more stability compared to the untreated colloidal silica [50]. A potential use of colloidal silica as a calcite depressant was tested recently [10].

Quebracho is a wood-derived compound, which belongs to a group of tannin acids. Quebracho is a well-known reagent in the industry as an excellent depressant for calcium-bearing

minerals [51]. The speculated adsorption mechanism of quebracho is the interaction between OH^- groups of quebracho and the cationic surface of the mineral [5]. There could be also a depression effect on both scheelite and calcite, as the minerals contain Ca^{2+} surface cations. A study reported that with quebracho alone, the zeta potential of the scheelite surface could be more negative than calcite, favouring a scheelite depression [52]. Moreover, another study suggested that quebracho at a high dosage could bind to a scheelite surface in the presence of excess calcium ions, displacing fatty acid collector [53].

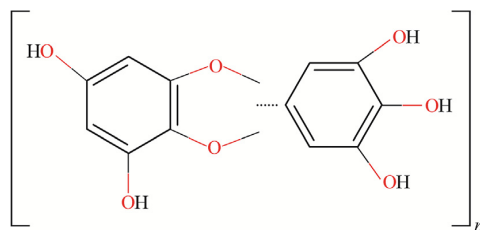


Fig. 12: An illustration of quebracho chemical structure

2.6. Mineral liberation analyser

MLA is a Scanning electron microscope (SEM)-based automated measurement tool for quantitative analysis of mineralogy. The development of current MLA technology started way back in 1997, introducing a novel way to combine Back-scattered electron (BSE) image analysis and x-ray acquisition. BSE signals produce grey-scale images, where the grain boundaries are identified. Consequently, the sample is subjected to x-rays to determine a mineral identity [54]. Depending on the application and complexity, there are several MLA measurement modes available [55].

	Name	Description
1	Standard BSE liberation analysis (BSE)	distinguishes minerals through BSE grey-scale images
2	Extended BSE liberation analysis (XBSE)	identifies minerals through BSE imaging and X-ray analysis
3	Grain-based x-ray mapping (GXMAP)	identifies minerals through BSE imaging and X-ray mapping
4	Sparse phase liberation analysis (SPL)	performs XBSE analysis on particles, that contain mineral phases of interest
5	X-ray modal analysis (XMOD)	provides modal mineralogy information, collecting X-ray spectrum from each grid point

Tab. 1: A list of MLA measurement modes

2.7. Particle-based kinetic flotation model

Modelling froth flotation is a complicated task to accomplish, as the process consists of micro-processes. In the simplest form, froth flotation can be modelled equivalent to a chemical reaction between particles and bubbles [56]. Based on this assumption, the kinetic model of the flotation process can be formulated as below [57].

$$\frac{dC}{dt} = -kC^n C_b^m \quad (\text{Eq. 2.8})$$

C stands for concentration of particles, C_b for concentration of bubbles, k for flotation rate constant, t for time, n and m represent reaction order of particles and bubbles, respectively.

The classical first-order kinetic flotation model, as shown in Equation 2.9 [58], is commonly used in practice. To fit the model, a series of experiments on the investigated mineral needs to be performed to obtain the recovery values at different time intervals.

$$R_t = R_{max}(1 - e^{-kt}) \quad (\text{Eq. 2.9})$$

k stands for flotation rate constant, t for time, R_t for recovery of the given mineral at time t , and R_{max} represents maximum recovery of the given mineral at $t = \infty$.

Recovery of the given mineral in the concentrate product can be calculated as below [59].

$$R = \frac{C * c}{F * f} \quad (\text{Eq. 2.10})$$

C stands for the mass of the concentrate, F for the mass of the feed, and c and f represent the grade of the investigated mineral in the concentrate and feed, respectively.

The flotation rate constant, k , is often used as a measure of the flotation efficiency per unit of time, whereas maximum recovery, R_{max} , is a measure for the maximum floatable fraction. As some process conditions could influence only one of them, modified flotation rate constant, k_m is utilized to get a comprehensive view of the particle's overall floatability. The modified flotation rate constant can be formulated as below [60].

$$k_m = k * R_{max} \quad (\text{Eq. 2.11})$$

k_m stands for modified flotation rate constant, k for flotation rate constant, and R_{max} represents maximum recovery of the given mineral at $t = \infty$.

Improving the selectivity of the targeted mineral against gangue mineral is the main challenge for froth flotation. A measure of selectivity is the selectivity index, which can be formulated in various ways depending on how it is defined. First, SI can be calculated from the total recovery ratio, to compare the observed recovery of two minerals [60].

$$SI_{A/B} = \frac{R_A}{R_B} \quad (\text{Eq. 2.12})$$

$SI_{A/B}$ stands for the selectivity index of mineral A compared to mineral B, R_A , and R_B represent the total recovery of minerals A and B, respectively.

Moreover, the selectivity index, SI can be calculated from the modified flotation rate values, to compare the floatability of two minerals in the given process condition. The modified flotation rate constant takes into consideration both how high the flotation rate is and how much of the mineral is recovered [60].

$$SI_{A/B} = \frac{k_{m,A}}{k_{m,B}} \quad (\text{Eq. 2.13})$$

$SI_{A/B}$ stands for the selectivity index of mineral A compared to mineral B, $k_{m,A}$, and $k_{m,B}$ represent the modified flotation rate of mineral A and B, respectively.

Recently, a novel Particle-based separation model (PSM), which estimates the recovery probability of individual particles, was proposed [15]. Using MLA, particle data sets are obtained from process products and it is used to train the predictive model. The training involves a Least absolute shrinkage and selection operator (LASSO)-regularized logistic regression, which computes the response parameters accounting for the influence of each particle parameter on the process. Irrelevant particle properties are removed from the computation scheme. The intercept of the trained model needs to be adjusted for particle balance. The model validation is done using the data set from a feed sample. Subsequently, the validated trained model can be used to predict the probabilities of each particle in a new feed sample either to different concentrate fractions or to the tailing. The overall workflow is illustrated

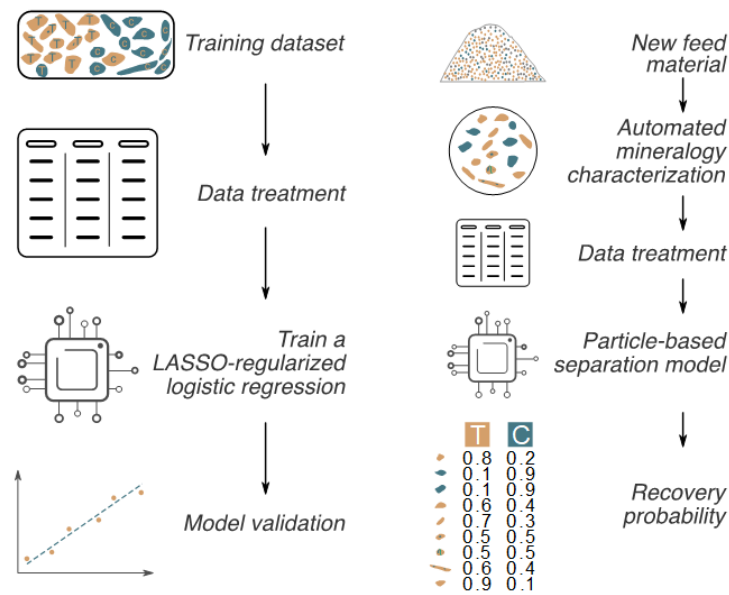


Fig. 13: An illustration of the particle-based model creation workflow [15]

in Figure 13.

The cumulative recovery probability is calculated through the cumulative summation of predicted recovery probability in different concentrate products. These values can be fitted into kinetic flotation models, such as the first-order kinetic model, as illustrated in Figure 14. The model provides information about flotation kinetic at the single-particle level. Obtained recovery probability in the model could be deemed essentially equivalent to bulk recovery, as the latter only describes a large number of particles [15].

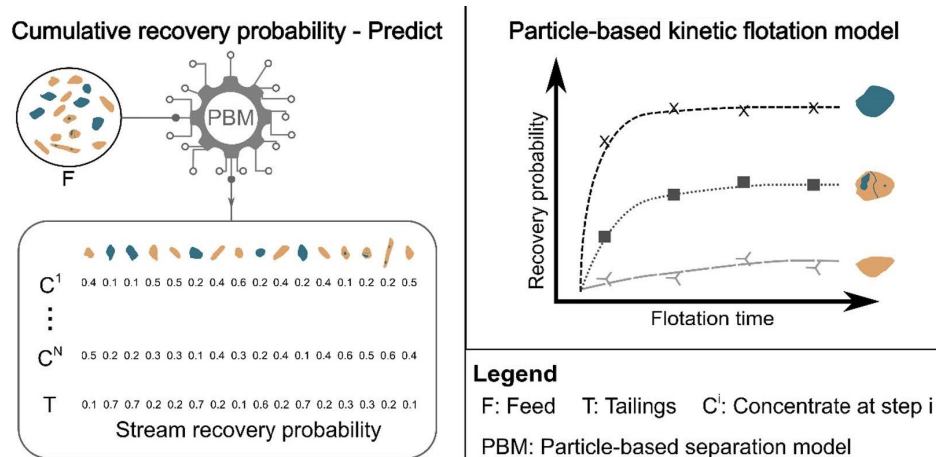


Fig. 14: An illustration of particle-based kinetic flotation model [15]

2.8. Design of experiments

Design of experiments (DoE) is a statistical method to determine the relationship between key input and output variables. Since experiments could require a significant amount of resources and time, DoE is a practical approach for conducting experimental research.

When dealing with DoE, there are certain terminologies to know, such as factor, level, and response. Factor is any controlled input variable, that affects the experiment, and response is an output variable from the experiments, which is to be optimized. Levels are the controlled values for the given factor. The correlation between these terms is illustrated in the schematic diagram below, known as "Black Box" [61].

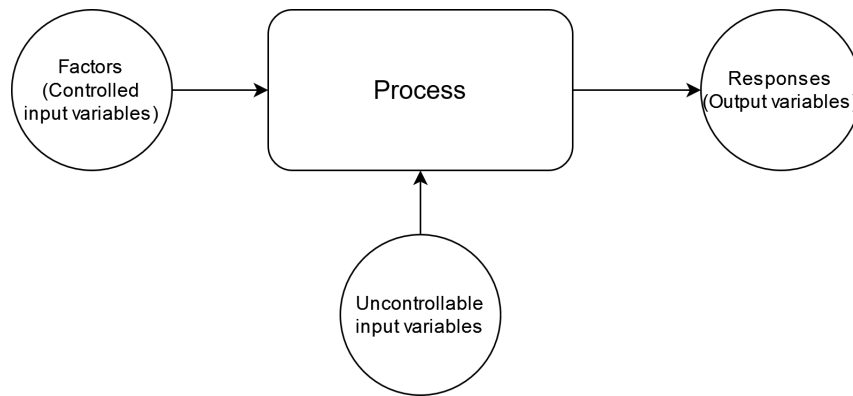


Fig. 15: A schematic diagram of A "Black Box" process

Different designs are available depending on the number of factors to be considered. The simplest DoE would be a one-factor factorial design, where only one factor is studied. A number of levels must be more than one, and repeated experiments are necessary for each level.

The most common DOE approach is a two-way factorial design, where two factors are considered. A representative two-factor two-level factorial design is illustrated in the figure below.

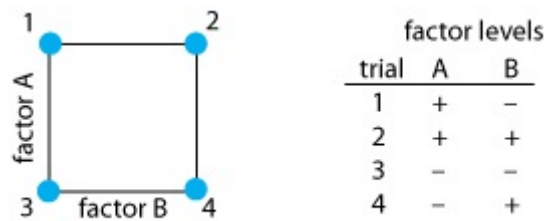


Fig. 16: An illustration of two-factor two-level factorial design

In this design, both factors A and B affect the response, therefore their interactions should be investigated. Since one repetition cannot provide sufficient information about their interaction, repetitions are carried out. The number of effective repetitions needed for the given number of levels is formulated below [61].

$$n = \frac{l * m}{l + m - 1} \quad (\text{Eq. 2.14})$$

n stands for the number of experiments, l and m represent the levels of factors A and B,

respectively.

In certain applications, three or more factors can be investigated by DoE. The number of experiments necessary for the full factorial designs can be calculated from the number of factors, and number of levels, as shown below.

$$n = (x)^k \quad (\text{Eq. 2.15})$$

n stands for number of experiments, x for number of levels, and k represents number of factors.

For multi-factor full factorial designs, the number of experiments increases exponentially. Therefore, the concept of fractional factorial design is developed, where the required number of experiments is reduced [61]. The number of experiments required for fractional factorial design is calculated as below.

$$n = (x)^{k-p} \quad (\text{Eq. 2.16})$$

n stands for number of experiments, x for number of levels, k for number of factors, and p represents size of fraction.

In some cases, the centre point is included in the DOE to ensure the linearity of the response function. An example of a three-factor two-level full factorial DoE with a centre point is provided below [62].

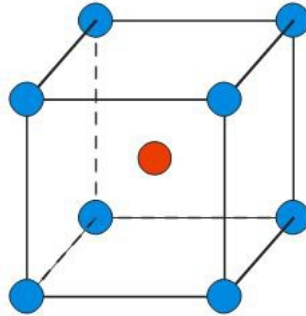


Fig. 17: A graphical illustration of three-factor full factorial design with centre point

2.8.1. Pareto plot & Magnitude of effect

The Pareto plot is a statistical approach to quantify and compare the effect of the investigated factors by calculating the magnitude of the effect. This approach is often used in quantifying the influence of factors observed in the design of experiments [63].

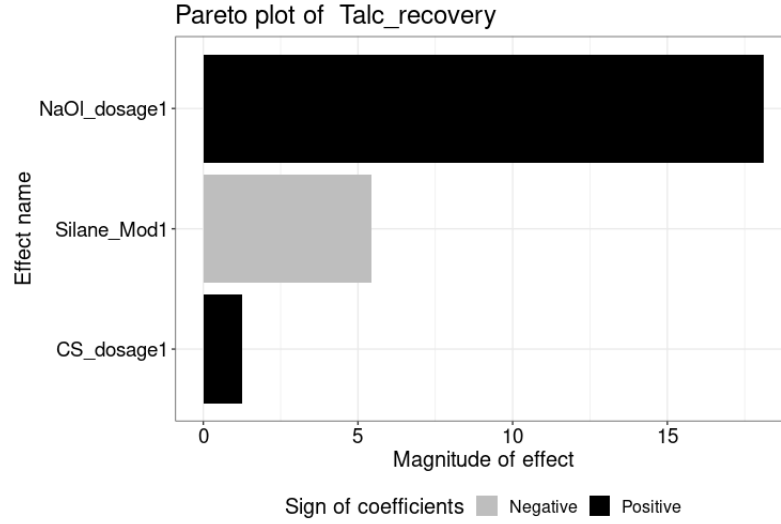


Fig. 18: An example of Pareto plot showing the magnitude of effect for each factor

The magnitude of effect is determined from the difference between the mean values of the factor at levels, as formulated below.

$$\theta = \frac{\mu_{max} - \mu_{min}}{2} \quad (\text{Eq. 2.17})$$

θ stands for magnitude of effect, μ_{max} and, μ_{min} represent the mean values at maximum and minimum levels, respectively.

2.9. Dynamic image analysis

Dynamic image analysis employs a photo-optical-based system, where a high-frame-rate camera is used to capture images of particles in the system. Particle size and shape characteristics can be extracted through image analysis, and it provides information needed for process optimization and monitoring [64]. It is a common alternative for particle size distribution determination, as the accuracy of conventional sieve analysis can suffer significantly from measurement errors, especially for finer particles. Moreover, dynamic image analysis allows the possibility to do the measurement inside a process vessel for monitoring, unlike offline sieve analysis [65].

The laser diffraction method is another widespread alternative for particle characterization. Particle size distribution is determined based on the different angles of light diffraction caused by the different sizes of particles. Coarser particles diffract the light at smaller angles. However, the laser-based system assumes the particle shape as an ideal sphere, thus not suitable for a system that contains irregularly shaped particles. In addition, it is able to only measure the properties of particle collectives instead of particle discrete information [65].

Hence, the photo-optical-based system coupled with dynamic image analysis has the potential to provide the most promising results regarding particle information. Nevertheless, the complication lies in the automated analysis of captured images [64].

2.10. SOPAT system

Smart online particle analysis technology (SOPAT) system is one of the recent advancements in photo-optical-based technology for particle characterization. An inline probe, as shown in Figure 19, is used to capture well-illuminated images and subsequent image analysis is necessary to obtain the particle information. The advantage of inline measurements is that the information can be acquired with less delay between acquisition and result, compared to the offline measurements through sampling. Although the inline probe is placed in the process vessel, it disrupts the process only slightly [64].



Fig. 19: An image of the inline probe of SOPAT system

SOPAT system is employed in various applications, including the determination of size distributions of particles and bubbles [64]. In Figure 20, segmentation of particles is shown, where the particle size and shape information is obtained.

For scheelite froth flotation, particle [49] and bubble size distributions [13] reportedly influence the process behaviour significantly. Therefore, to understand the process that is heavily influenced by particle and bubble properties, such an optical-based system can be used for the investigation of particle bubble coagulates and their size distributions [64].

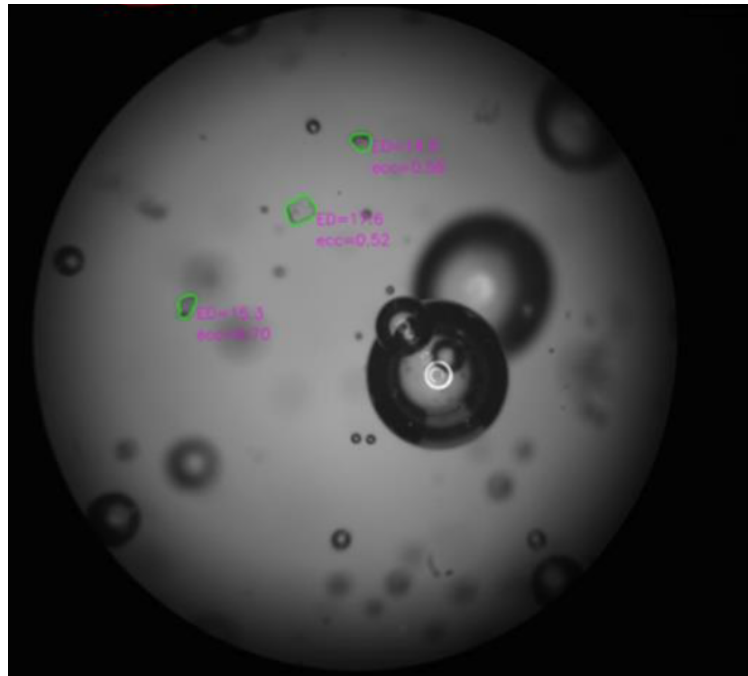


Fig. 20: An example image produced from a photo-optical-based system for the determination of particle size and shape information [64]

3. Experiment

3.1. Micro-flotation tests

3.1.1. Experiment plan

To better understand the effect of colloidal silica on gangue minerals, microflotation experiments are carried out. Calcite and scheelite microflotation experiments have already been completed in previous research works.

In the scope of this study, hornblende (representative silicate gangue mineral) and talc microflotation experiments are performed. pH of the suspension is fixed at 8 as well as the previous microflotation experiments for comparability. As shown in Table 3, four types of colloidal silica, which differ by their modification and specific surface area, are tested. Various process parameters and effects are investigated. All the tests are performed in two-level full factorial DoE. R Shiny platform is used for the analysis of microflotation results [66]. The parameters to be studied and their levels are listed in Table 2. Dosage levels are set based on the previous practice ranges for pure microflotation tests. NaOl dosage ranges between 0 and 0.001 mol/l , and CS dosage ranges between 10 and 100 mg/l . CS modification effect is studied through experiments either with non-functionalized CS, which is represented by the value of 0, or with aluminate/silane-modified CS, which is given the value of 1. The value of 0 in the calcite supernatant factor represents tests without calcite supernatant, where colloidal silica is directly in the microflotation. In contrast, the value of 1 corresponds to the tests with calcite supernatant, where colloidal silica is added during calcite supernatant preparation. Quebracho dosage ranges between 10 and 100 mg/l , and aluminate-modified CSs with SSA of 500 and 1100 m^2/g are tested. Three repetitions are performed for each level.

Parameter/effect	Min level	Max level	Unit
Sodium oleate dosage	0	$1 * 10^{-3}$	(mol/l)
CS modification	0	1	0 - non-functionalized 1 - modified
CS dosage	10	100	(mg/l)
Calcite supernatant	0	1	0 - no supernatant 1 - with supernatant
Quebracho dosage	0	50	(mg/l)
CS SSA	500	1100	(m^2/g)

Tab. 2: A list of controlled parameters during microflotation

Calcite supernatant is used in the microflotation, to mimic the environment, where the calcium species can be dissolved from calcite. To account for the possible effects of calcium species, most experiments are performed in this manner using calcite supernatant. As colloidal silica could facilitate the dissolution of calcium species from calcite, the colloidal silica is added during the calcite supernatant preparation. A prepared supernatant is then used for the microflotation. A detailed procedure is described in section 3.1.4.

Moreover, to validate the possible absorption of calcium species on the mineral surface, quebracho is added for certain tests, as it is an excellent depressant for calcium-bearing minerals.

3.1.2. Sample preparation

Talc, hornblende, and calcite rock minerals are provided by Helmholtz Institute Freiberg for Resource Technology (HIF). Soap stones, which largely consist of talc, are crushed by hammer and granulated manually using porcelain mortar and pestle. The ground material is sieved to obtain +63-100 μm size fraction. From this, 1 g samples are prepared for the talc microflotation experiment.

Hornblende lump samples are milled for 2 minutes in Vibratory Disc Mill RS 200 at 700 rpm. The +63-80 μm size fraction is used to prepare 1 g hornblende samples.

Pure calcite rocks (Brilon, Germany) are milled in Vibratory Disc Mill RS 200 for 10 min at 700 rpm and +63-106 μm fraction is obtained by dry sieving. 1 g samples are prepared for calcite supernatant preparation.



(a) Talc



(b) Hornblende



(c) Calcite

Fig. 21: Materials used for sample preparation

3.1.3. Re-agent preparation

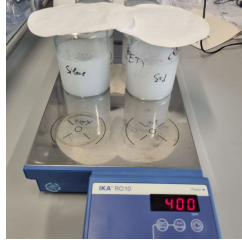
5 % solution of Sodium oleate (NaOl) is used as a collector. Either 0.1 M NaOH or HCl is used for pH conditioning. 10 % solution of quebracho extract is prepared and tested in the microflotation. KCl solution with a concentration of 0.01 M is used throughout the experiment. 10 % solutions of four types of colloidal silica are prepared and used. These colloidal silica solutions and their specifications are listed below.

Colloidal silica	Specific surface area (m^2/g)	Modification	Abbreviation
Levasil CS15-150P	500	-	CS15
Levasil CS15-450P	500	Aluminate	CS15Al
Levasil CC15-151P	500	Silane	CS15S
Levasil WT110P	1100	Aluminate	WT110

Tab. 3: A list of CS solutions and their specifications

3.1.4. Supernatant preparation

1 g calcite sample is introduced into a 0.01 M KCl solution. Colloidal silica is added to the solution and stirred at 400 rpm for 1 hour in a closed beaker. The suspension is then filtered to extract the calcite supernatant.



(a) 1g calcite in CS-containing KCl solution stirred for 1 hour

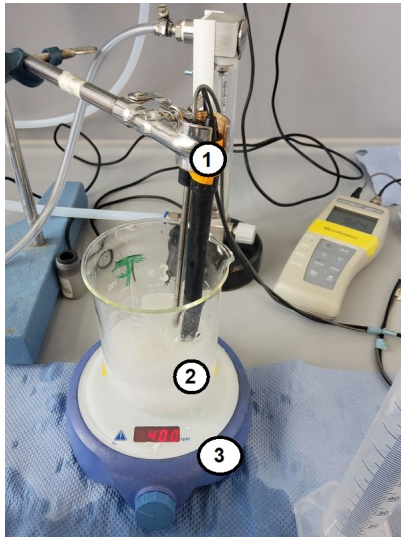


(b) Filtration to extract the calcite supernatant

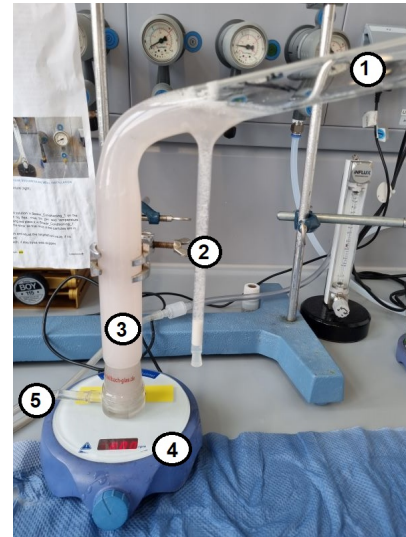
Fig. 22: Supernatant preparation

3.1.5. Experimental set-up

The flotation pulp for micro-flotation is formed by adding 1 g pure mineral sample either into a prepared 160 ml calcite supernatant or a 160 ml KCl solution. The pulp is mixed by the magnetic stirrer at 400 rpm. The pH is adjusted using HCl and NaOH solutions and conditioned for 2 min. Sodium oleate is added into the pulp, and conditioned for 3 min. Subsequently, either quebracho or colloidal silica is added and conditioned for 3 min. The pulp is then transferred to the Hallimond tube and further agitated at 800 rpm for 2 min. After this, the airflow rate is set to 20 cm³/min, and micro-flotation continues for 2 min. The collected concentrate and tailing products are filtered, and dried in an oven for 1 hour at 60 °C. The experimental setup and overall microflotation scheme are shown in the figures below.



(a) Preparation for microflotation
(1- pH meter probe
2- prepared pulp
3- magnetic stirrer)



(b) Experimental set-up for microflotation
(1- Hallimond tube, 2- floated product
3- non-floated product
4- magnetic stirrer, 5- air supply)

Fig. 23: Microflotation experiment

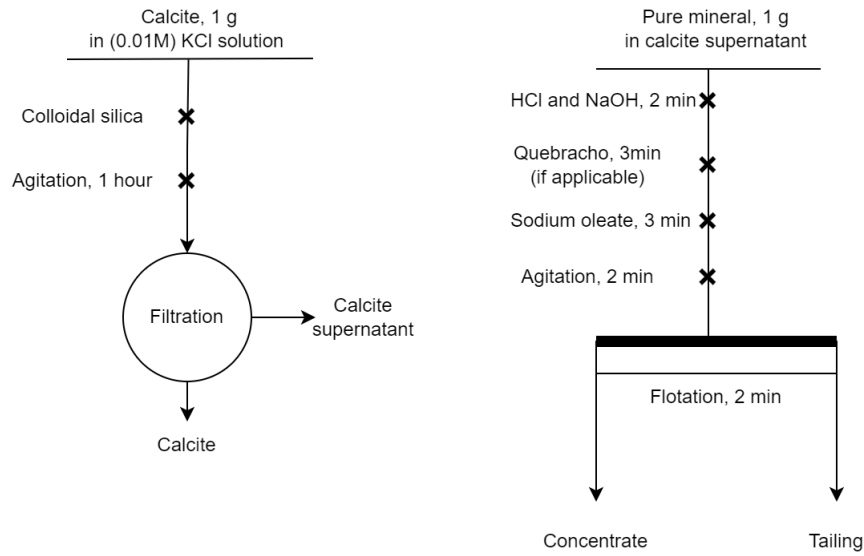


Fig. 24: An illustration of calcite supernatant preparation and microflotation scheme

3.2. MLA measurement

3.2.1. Sample preparation

The samples for MLA analysis are obtained from batch flotation experiments performed at HIF. The feed sample is from a low-grade tungsten ore deposit in Mittersill, Austria. To activate the surface for a flotation experiment, 500 g scheelite ore sample is ground in a laboratory rod mill for 3 min in the presence of 300 g distilled water. The sample is introduced, and pulp is created in the 1.5 l cell of the bottom-driven flotation machine, Magotteaux, as seen in Figure 25.



Fig. 25: An image of Magotteaux flotation machine

The rotational speed of the agitator is set at 450 rpm and after adjusting pH, the pulp is conditioned for 3 min. 0.1 M NaOH and HCl are used as pH conditioning reagents. After pH conditioning, reagents are added, and the conditioning time is 3 min each. After adding the reagents, 5 l/min air is supplied from the bottom of the cell. Subsequently, Concentrate 1 (C1), Concentrate 2 (C2), and Concentrate 3 (C3) are collected at 1 min, 3 min, and 7 min intervals, respectively. The rest of the sample in the cell is considered a tailing. A detailed scheme is illustrated in Figure 26.

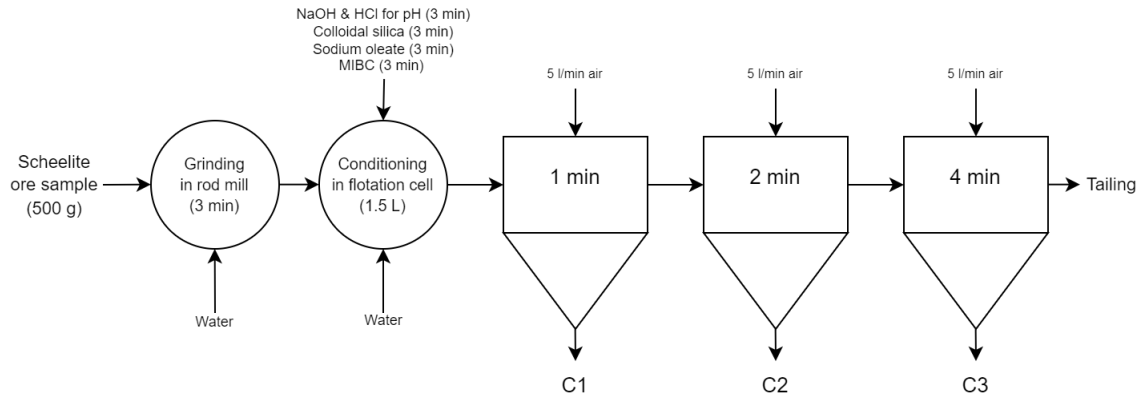


Fig. 26: An illustration for batch flotation scheme of scheelite ore

For each colloidal silica type, a DoE is performed for three process parameters with two repetitions. The frother dosage is fixed at 35 g/t . As shown in Figure 27, pH is varied between 8 and 10, and NaOI dosage is between 100 g/t and 400 g/t . Colloidal silica dosage is tested between 50 g/t and 550 g/t and different colloidal silica types, as listed in Table 3, are investigated in the scope of this thesis work.

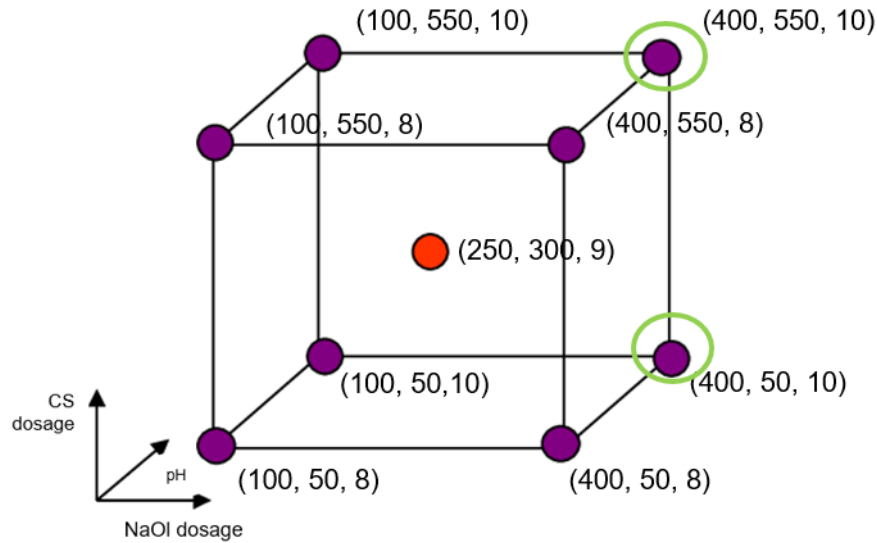


Fig. 27: A graphical illustration of DoE for the scheelite batch flotation

Due to the limited time frame of this work and the availability of MLA equipment, the samples fixed at pH 10, and collector dosage of 400 g/t are chosen for MLA measurement. The main purpose of these measurements is to investigate CS modification, SSA, and dosage effect in scheelite batch flotation. These chosen samples performed at either maximum or minimum CS dosage in the DoE scheme, which are 50 g/t and 550 g/t , as shown in Table 4.

Parameters	Minimum value	Maximum value	Central value
pH	8	10	9
NaOl dosage	100 g/t	400 g/t	250 g/t
CS dosage	50 g/t	550 g/t	300 g/t

Tab. 4: A list of DoE parameters for scheelite batch flotation experiments

Two samples from identical experiments are mixed and divided using a riffle splitter and 1-2 g samples are obtained. Each sample is mixed with graphite and embedded in an epoxy resin, as shown in Figure 28.

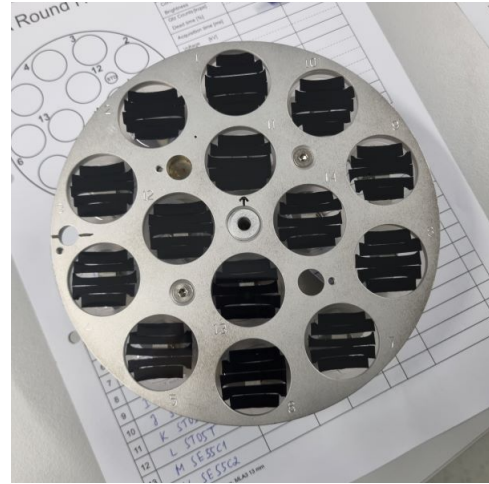


Fig. 28: Epoxy samples for MLA measurement

Using the LEICA EM coater, samples are coated with a carbon layer with a thickness of approximately 8 nm. In total, 36 samples were prepared for MLA measurement.



(a) Carbon coating device



(b) An image of carbon-coated epoxy samples

Fig. 29: Carbon coating

The samples are analysed using FEI Quanta 650 MLA equipped with energy dispersive spectroscopy (EDS) detectors and the MLA-Suite software. The measurement mode is GXMAP and the probe current is set at 10 nA. The MLA measurement parameters are listed in the table below.

Parameters	Value	Unit
Voltage	25	kV
Specimen current	10	nA
Pixel size	1	$\mu\text{m}/\text{pixel}$
Epoxy range	20-250	
Calibration material	Copper	
Step size	8	μm

Tab. 5: A list of MLA measurement parameters

3.2.2. MLA image processing and data handling

After the measurements, BSE and x-ray images of the sample are processed in MLA image processing software from FEI. The first step is classification, where the mineral list contains spectrum references for minerals to be identified. The mineral list was able to identify 83 different minerals and around 200,000 particles characterized per sample, as shown in Figure 30.

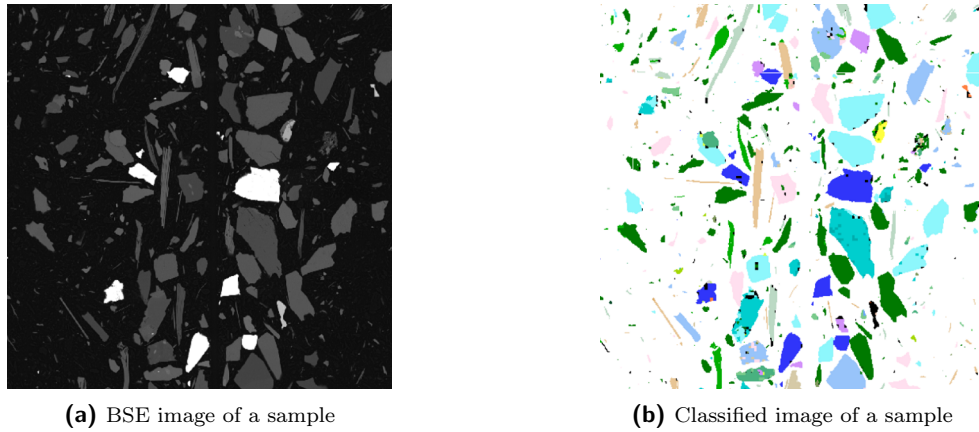


Fig. 30: An example of BSE and classified images

Some agglomerated and touching particles are present in the images (as shown below). Thus, they are removed or separated manually to ensure the quality of the data. The same amount of effort was made for the manual image processing of each sample.

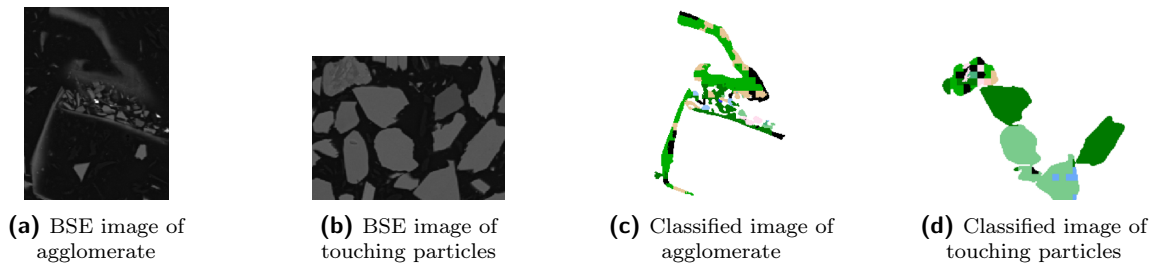


Fig. 31: An example image of agglomerates and touching particles

Following the characterization, the collected particle data sets are ready to be processed. Due to the huge amount of data to be processed, the use of a programming environment is required. For this reason, the R Studio program is utilized for handling large particle data sets.

3.3. Measurements with SOPAT system

3.3.1. Sample & reagent preparation

500 g sample of scheelite ore sample (Mittersill, Austria) is prepared for each measurement. Solutions of NaOl and MIBC are prepared for the function of collector and frother, respectively. Solutions of different types of CS, as listed in Table 3, are prepared for usage as a depressant. 0.1 M NaOH and HCl are prepared for pH adjustment.

3.3.2. Experiment plan

To investigate the effect of colloidal silica on particle-bubble hetero-coagulates, 16 experiments are planned at different process conditions, as listed in Table 6. Various colloidal silica modifications, dosage, and specific surface area of CS are tested, and pH is adjusted to either 8 or 10.

Number	pH	CS Modification	CS SSA (m^2/g)	CS dosage (g/t)
1	8	-	500	50
2	8	-	500	550
3	10	-	500	50
4	10	-	500	550
5	8	Silane	500	50
6	8	Silane	500	550
7	10	Silane	500	50
8	10	Silane	500	550
9	8	Aluminate	500	50
10	8	Aluminate	500	550
11	10	Aluminate	500	50
12	10	Aluminate	500	550
13	8	Aluminate	1100	50
14	8	Aluminate	1100	550
15	10	Aluminate	1100	50
16	10	Aluminate	1100	550

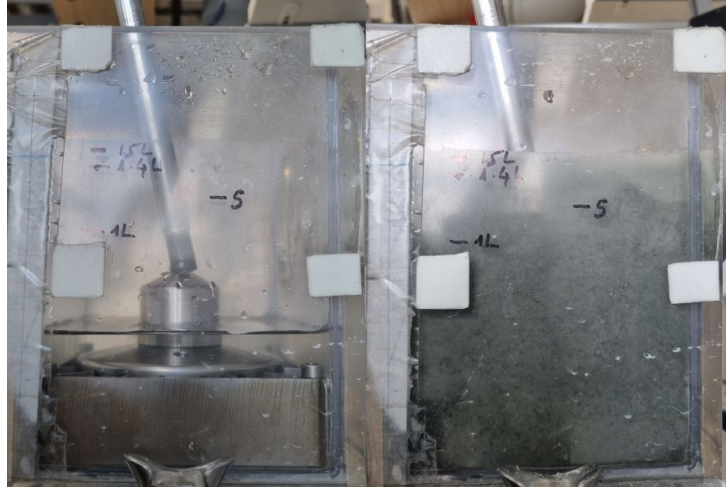
Tab. 6: A list of experiment parameters for SOPAT measurement

3.3.3. Measurement set-up

The batch flotation experiment is carried out in a bottom-driven flotation cell, Magotteaux. The cell size is 1.5 l and the solid concentration is at around 33%. An inline endoscope, called Pa probe, is mounted on top of the cell, as shown in Figure 32a. The probe is placed roughly at the centre of the suspension in the cell and inclined at around 60 degrees, as seen in Figure 32b. To capture more bubble-particle coagulates, the centre position is selected over the positions near the corner.



(a) Inline probe in batch flotation cell



(b) The location of the inline probe in the cell

Fig. 32: An image showing SOPAT measurement set-up

The rotational speed of the rotor is set at 450 *rpm* and after adjustment pH and the addition of reagents, constant air supply at a rate of 5 *l/min* is introduced. The image capturing starts when the air is introduced to the system. The probe control parameters are adjusted in pretests to find out the optimal settings for high-quality images. A reference image captured before bubble generation is shown in Figure 33. As seen in the figure, extremely dark or white-coloured particles can be distinguished from the background. After deciding on the setting of the probe, SOPAT measurement parameters are kept constant throughout the planned experiments, as shown below.

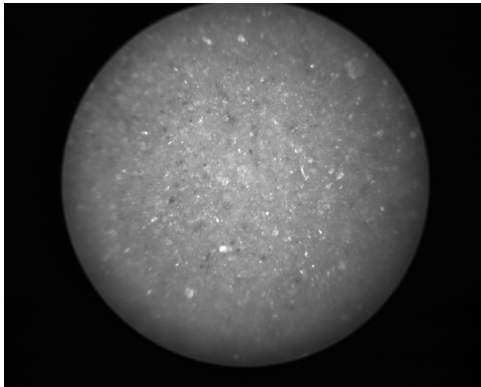


Fig. 33: A reference image from SOPAT

Parameters	Value	Unit
Exposure time	10000	μs
Focus position	255	μm
Frame rate	20	fps
Strobe intensity	30	%
Conversion factor	1.74	$\mu\text{m}/\text{pixel}$
Gain	10	%

Tab. 7: A list of SOPAT measurement parameters

4. Results

4.1. Hornblende microflotation

4.1.1. CS modification and dosage effect

Figure 34 shows the magnitude of effect of these three parameters on hornblende recovery. The coloured bars in the graph represent three different colloidal silica types, non-functionalized CS, aluminate-modified CS, and silane-modified CS. As the first column indicates, the calculated NaOH dosage effect on hornblende recovery is roughly 10-12% across all CS modifications. The second column shows that there is a slight positive effect ($<2\%$) of both aluminate and silane modifications on hornblende recovery. In contrast, CS dosage has a slight negative effect ($<3\%$) and in the case of non-functionalized CS, the magnitude of the dosage effect is greater compared to the modifications, as shown in the last column.

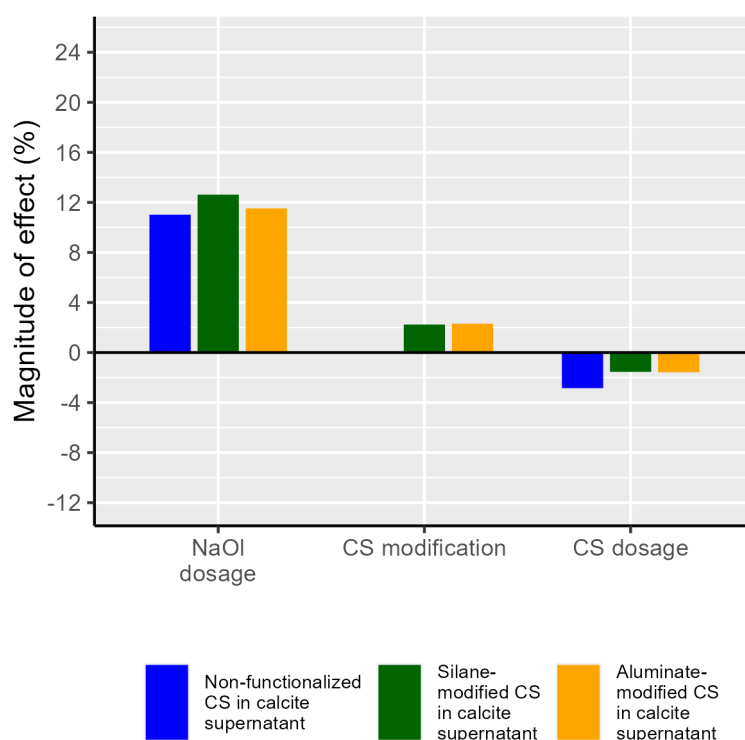


Fig. 34: A diagram showing the magnitude of CS modification and dosage effects on hornblende recovery

4.1.2. Calcite supernatant effect

In this batch of tests, the calcite supernatant effect is investigated in addition. Figure 35 shows the magnitude of effect of these parameters on hornblende recovery.

The last column in the figure indicates the effect of calcite supernatant on hornblende recovery. It appears that calcite supernatant has a slight positive effect ($<4\%$) on hornblende recovery. The calcite supernatant effect is slightly higher when aluminate-modified CS is used and lowest when silane-modified CS is used. The CS dosage effect is shifted more to the negative side, reaching roughly -5% for non-functionalized CS.

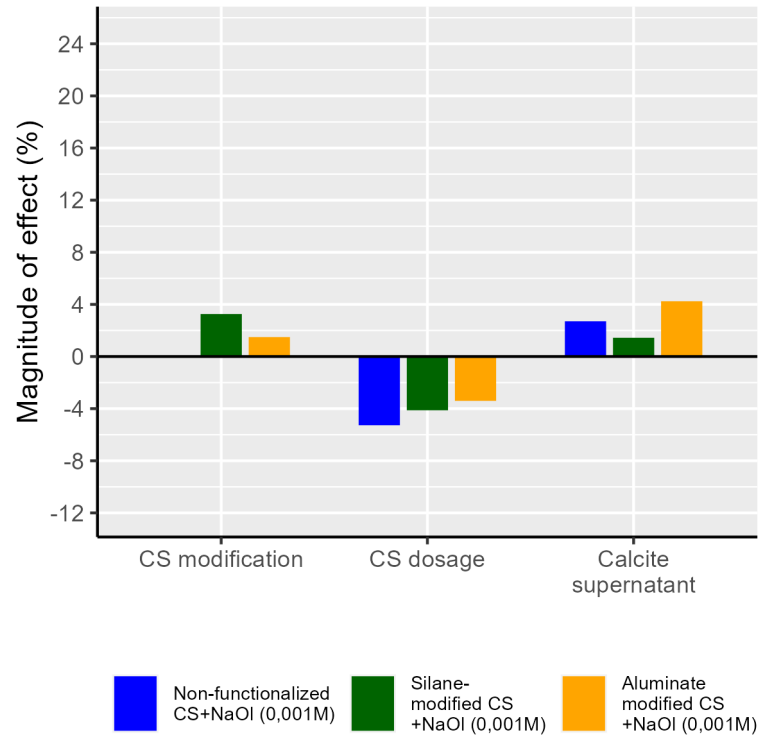


Fig. 35: A diagram showing the magnitude of CS modification, dosage, and calcite supernatant effects on hornblende recovery

4.1.3. Quebracho effect

In this batch of tests, the quebracho dosage effect is investigated in addition. Figure 36 shows the magnitude of effect of these parameters on hornblende recovery.

The last column in the figure indicates the effect of quebracho dosage on hornblende recovery. Quebracho exhibited a slight negative effect, relatively more pronounced in aluminate and silane modifications of CS. The magnitude effect is roughly -4% across all CS types. However, CS modification and dosage effect are relatively lower (<2%) in the presence of quebracho. Moreover, a slight decrease in the effect of NaOH dosage is observed in the test with quebracho.

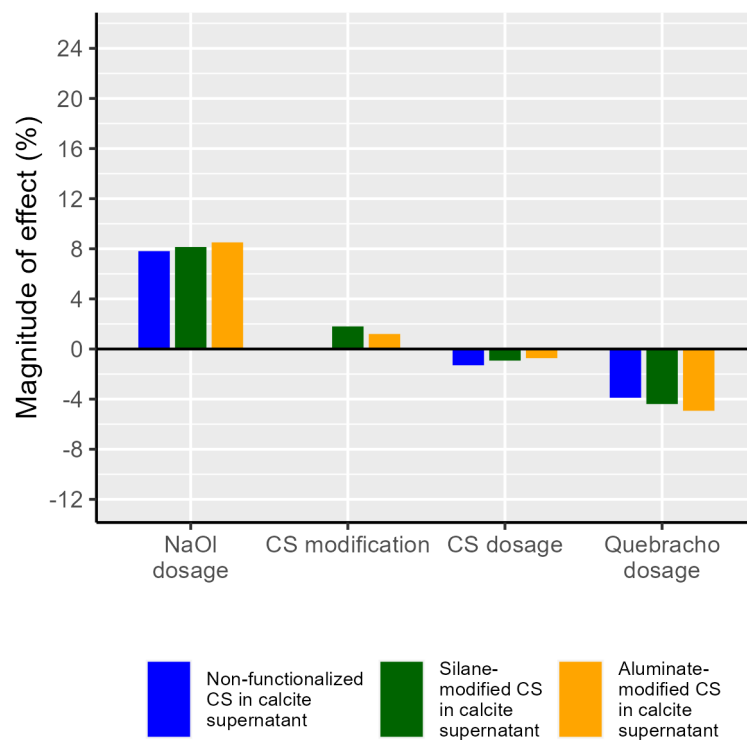


Fig. 36: An illustration showing the magnitude of CS modification, dosage, and quebracho dosage effects on hornblende recovery

4.1.4. CS SSA effect

In this batch of tests, the CS SSA effect is investigated in addition. Figure 37 shows the magnitude of effect of these parameters on hornblende recovery.

The last column in the figure indicates the effect of CS SSA on hornblende recovery, in the case of aluminate-modified CS. The specific surface area of aluminate-modified CS exhibited roughly no effect on hornblende recovery in the case of microflotation. Whereas the effects of NaOH and Quebracho dosage remain at the same level, the CS dosage effect decreased and seems to have no direct influence on the hornblende recovery for higher SSA of aluminate-modified CS.

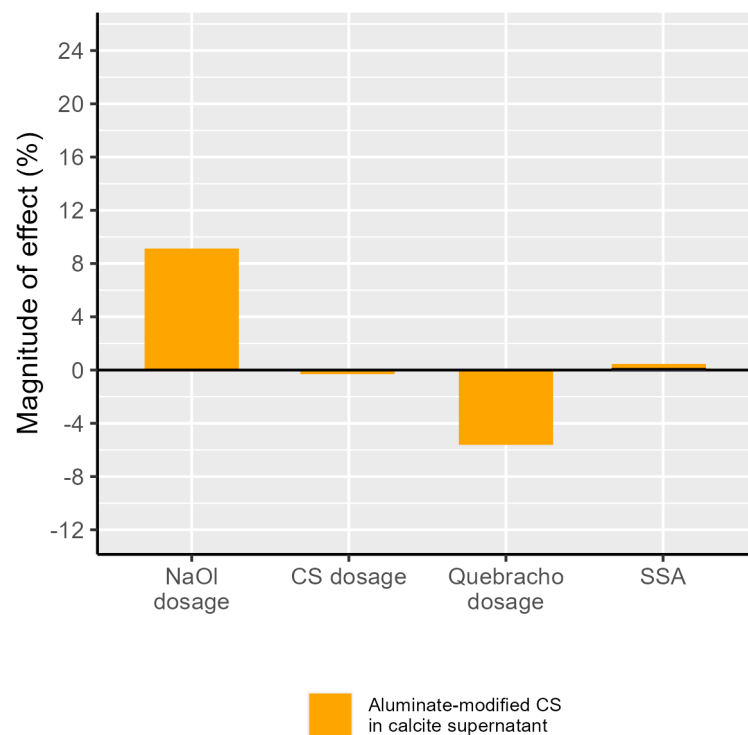
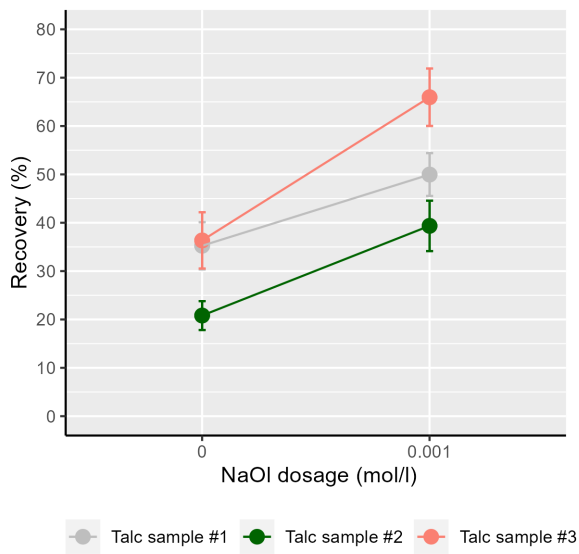


Fig. 37: An illustration showing the magnitude of CS modification, dosage, SSA, and quebracho dosage effects on hornblende recovery

4.2. Talc microflotation

4.2.1. Talc sample tests

Figure 38a and Figure 38b show the responses of different talc samples and their mineralogical composition, respectively. According to the X-ray powder diffraction (XRD) results, both talc samples #1 and #3 contain more than 93% talc, whereas sample #2 contains 53.5% talc. Associated minerals in those talc samples were kaolinite, and clinochlore, which are both silicate minerals. In Figure 38a, the talc recovery of the three samples is illustrated as a function of NaOl dosage. At the same NaOl dosage of 0.001 mol/l, the highest recovery at roughly 65% is observed in sample #3, while the values for samples #2 and #3 are lower at 50% and 40%, respectively. Three repetitions are performed for each point and the standard error values are calculated as represented in the error bars.



(a) Talc responses

Talc sample	Appearance	Mineralogical composition
Sample #1		98% Talc 2% Chlorite
Sample #2		53.5% Talc 46.5% Clinochlore (Chlorite)
Sample #3		93% Talc 7% Kaolinite

(b) XRD analysis result

Fig. 38: Talc samples

Talc can be associated with different minerals naturally and its effect has become an additional interest of this study, as the talc rock samples present different contaminant minerals in their composition. As the talc samples exhibited slightly different responses, subsequent experiments are carried out separately for these three samples, which will be referred to as samples #1, #2, and #3.

4.2.2. CS modification and dosage effect

Figure 39 shows the result of microflotation experiments carried out in three talc samples. On the x-axis, three process parameters are aligned, whereas the y-axis represents the magnitude of the effect of each factor. The coloured bars in the graph represent three different colloidal silica types, non-functionalized CS, aluminate-modified CS, and silane-modified CS.

The magnitude effect of NaOl dosage on talc recovery is illustrated in the first column. Across all types of CS, the value for sample #3 is relatively higher than the others, reaching 18-22%, whereas, for samples #1 and #2, the value is around 8-12%. Secondly, the CS modification effect can be shown in the next column. CS modification resulted in a small negative effect in sample #3, whereas for samples #1 and #2, a small positive effect is observed. In the last column, the CS dosage effect is illustrated and a slight positive effect ($<4\%$) on talc recovery is present in all samples.

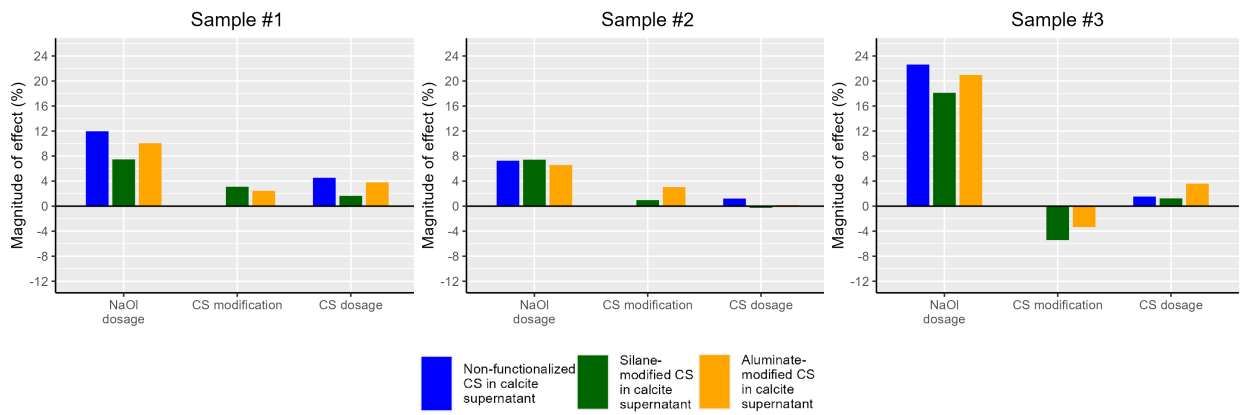


Fig. 39: A diagram showing the magnitude of CS modification and dosage effects on talc recovery

4.2.3. Calcite supernatant effect

Figure 40 shows three factors and their corresponding magnitude of effect on talc recovery. The last column represents the effect of calcite supernatant, and the magnitude is positive for all samples. The effect is more prominent in samples #1 and #3, ranging between 6% and 14%. Across all three samples, the magnitude of the calcite supernatant effect appears to be slightly higher when non-functionalized CS is used and the lowest for silane-modified CS. An interaction between calcite supernatant and colloidal silica is possible, as the magnitude of effect for both CS modification and dosage is shifted slightly in this DoE.

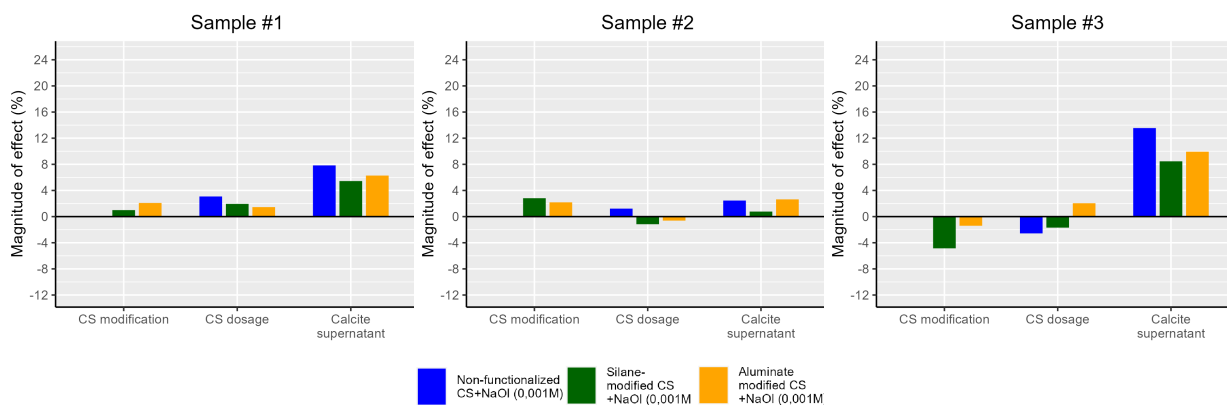


Fig. 40: A diagram showing the magnitude of CS modification, dosage, and calcite supernatant effects on talc recovery

4.2.4. Quebracho effect

Figure 41 shows the four factors and their corresponding magnitude of effect on talc recovery. The fourth column represents the effect of quebracho dosage and the magnitude of the quebracho effect is negative for all talc samples. The effect is greater in samples #1 and #3, ranging between -6% and -10%, whereas for sample #2, the effect of quebracho is between -4% and -2%.

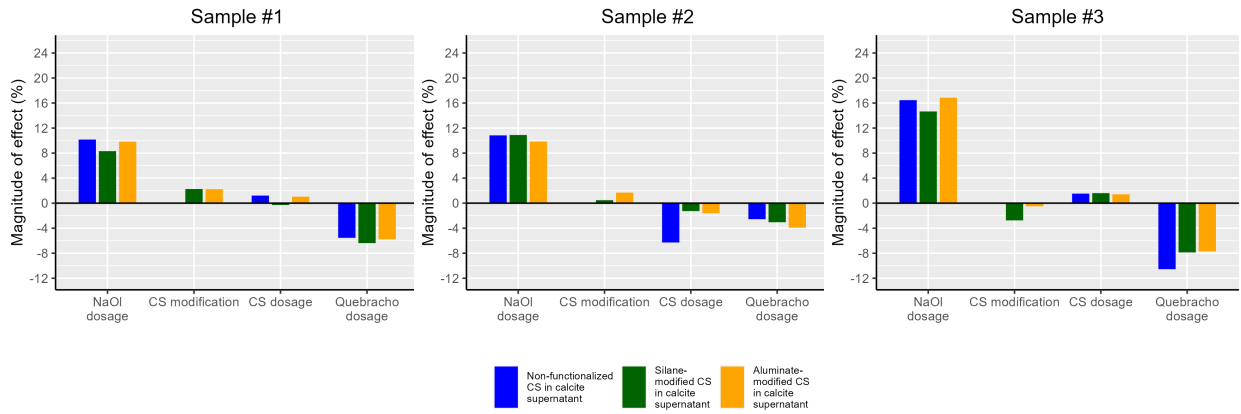


Fig. 41: An illustration showing the magnitude of CS modification, dosage, and quebracho dosage effects on hornblende recovery

4.2.5. CS SSA effect

In this batch of experiments, the CS specific surface area effect on talc recovery is investigated in the case of aluminate-modified CS. Figure 42 illustrates the four factors, including CS specific surface area and their magnitude of effect on talc recovery. CS SSA appears to have no significant effect, having a magnitude of 0-2% across three samples.

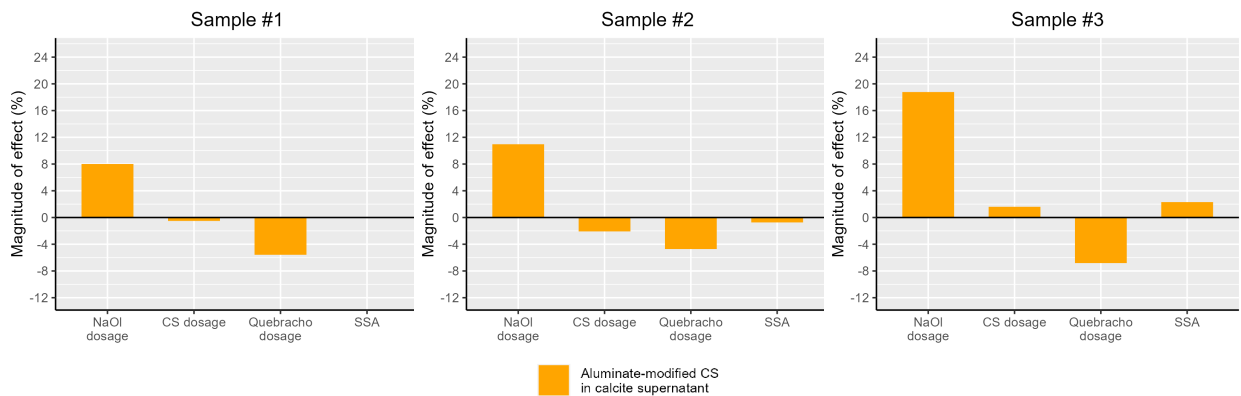


Fig. 42: An illustration showing the magnitude of CS modification, dosage, SSA, and quebracho dosage effects on talc recovery

4.3. Mineral liberation analysis

In batch flotation experiments two batches of samples were taken from two different ore deposit locations and time frames. Therefore, several distinct differences are observed in the composition of feed samples for different colloidal silica tests. Figure A.1 shows the weight distribution of the most common minerals present in the batch flotation feed samples, derived from MLA data.

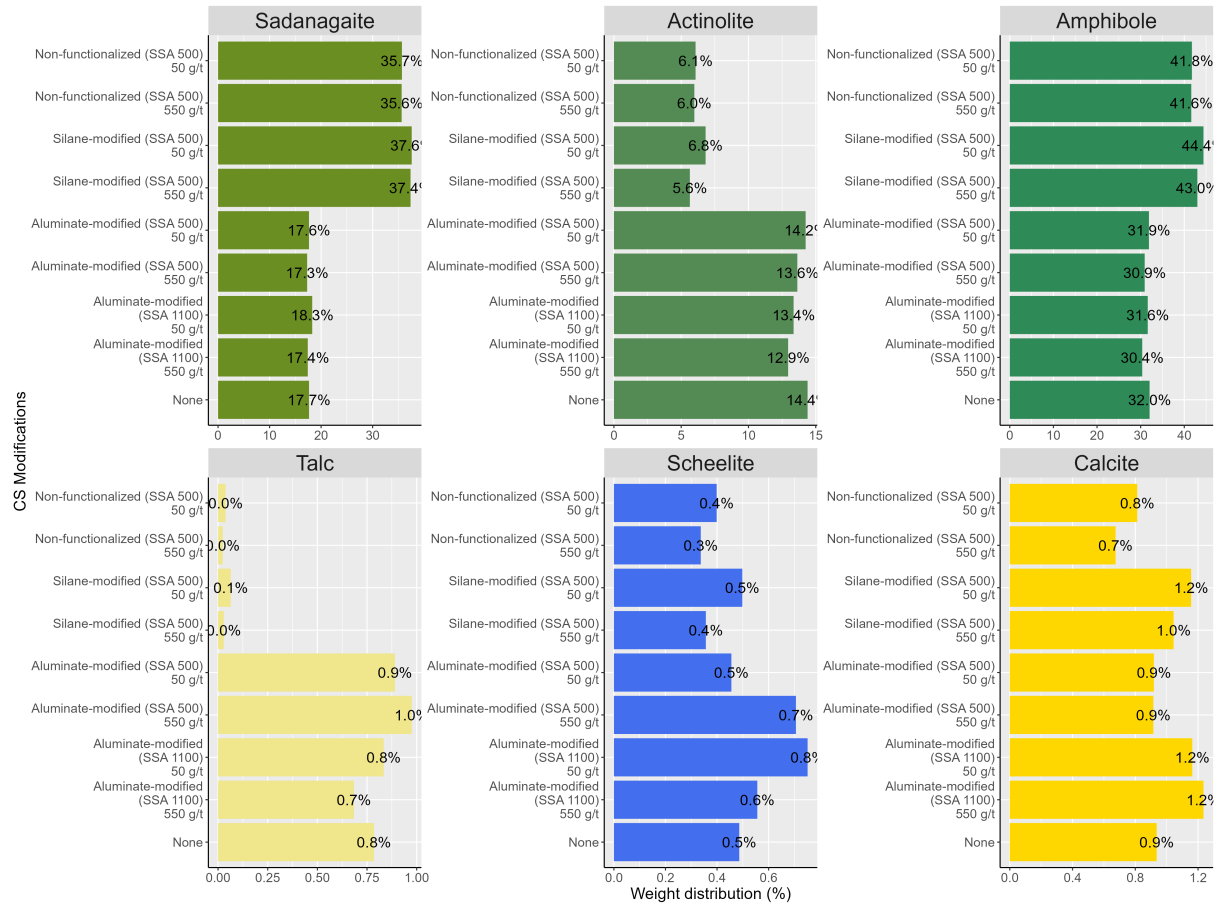


Fig. 43: Mineralogical compositions of the batch flotation feed samples based on MLA

Generally, feed samples for non-functionalized and silane-modified colloidal silica experiments have similar mineralogical composition, whereas aluminate-modified CS and no colloidal silica have the same composition. The first difference is the content of calcium-amphiboles in the two batches of feed samples. As illustrated in Figure 43, samples for non-functionalized and silane-modified colloidal silica experiments have around 35-37% sadanagaite and 5-7% actinolite in their composition, whereas the other batch contains 17-18% sadanagaite and 12-14% actinolite. Moreover, talc content in the feed samples for non-functionalized and silane-modified colloidal silica experiments is extremely low (<0.1%), whereas feed samples for aluminate-modified CS and no colloidal silica experiments contain 0.7%-1%. Therefore, for the CS effect on talc, only the tests in the latter are comparable. Despite these differences, the mineralogical composition of all samples is similar, containing 0.4%-0.8% scheelite, and 0.7%-1.2% calcite. Sadanagaite and actinolite have similar compositions and can be grouped into a calcium-amphibole group. The content of this amphibole group is 30-40% in the feed samples across all tests.

83 different minerals that are identified in MLA are classified into 11 mineral groups, as listed in Table 8. The groups include the main minerals investigated in this study, such as scheelite, calcite, talc, and apatite. The most common gangue silicate minerals, sadanagaite, and actinolite, belong to a calcium-amphibole group, also known as hornblende. The rest of the silicate minerals are classified into chlorite, micas, and other silicates mineral group. Other SSSM group includes fluorite, dolomite, magnesite, ankerite, and so on. The remaining minerals are classified into mineral groups of sulphides and oxides.

Group number	Mineral group	Minerals included
Group 1	Scheelite	Scheelite
Group 2	Calcite	Calcite
Group 3	Talc	Talc
Group 4	Amphibole (Hornblende)	Sadanagaite, Actinolite
Group 5	Chlorite	Clinocllore, Chamosite
Group 6	Micas	Muscovite, Biotite, Phlogopite
Group 7	Other silicates	Quartz, Albite, Plagioclase, Kaolinite, K-Feldspar, Illite, Epidote, Zircon, Serpentine, Zoisite, Anorthite, Diopside, Hedenbergite, Titanite
Group 8	Apatite	Apatite
Group 9	Other semi-soluble salt-type minerals (Other SSSM)	Fluorite, Ankerite, Dolomite, Magnesite, Siderite, Xenotime, Monazite
Group 10	Sulphides	Pyrite, Chalcopryrite, Pyrrhotite, Arsenopyrite, Molybdenite, Galena, Gypsum, Barite, Covellite, Bornite, Sphalerite, Chalcocite, Tennantite, Tetrahedrite, Cobaltite, Freibergite
Group 11	Oxides	Anhydrite, Hematite, Rutile, Chromite, Ilmenite, Franklinite, Cassiterite, Goethite, Spinel, Gahnite, Jarosite, Gibbsite

Tab. 8: A list of mineral groupings

Based on MLA data, the weight distribution of the mineral groups in the feed and product samples from different batch flotation experiments are illustrated in Figure 44. In this diagram, columns represent tests with four different CSs, and two rows show minimum and maximum CS dosage levels, 50 g/t and 550 g/t. Silicates, including amphiboles and other silicates, are the main gangue minerals in the feed and product classes, roughly weighing more than 75% in the first concentrate across all tests. Calcite and talc (only in talc-containing samples) are the following gangue minerals in the concentrate products, whereas oxides and sulphides appear to be the smallest fractions in the product samples. For the further particle-based model, the quality of these MLA samples is important, as they should represent the whole product class produced from the experiment. Compositions of feed samples appear consistent across various tests, as well as the compositions of representative MLA samples for concentrates and tailing. On the right side of the diagram, the benchmark test without CS is shown. Compared to this benchmark test, slight variations of calcite and scheelite composition in the concentrate products are observed in CS tests, specifically more pronounced at 550 g/t dosage of aluminate-modified CS. A deeper look into the grade and recovery comparison of the main minerals is introduced later in section 4.4.2.

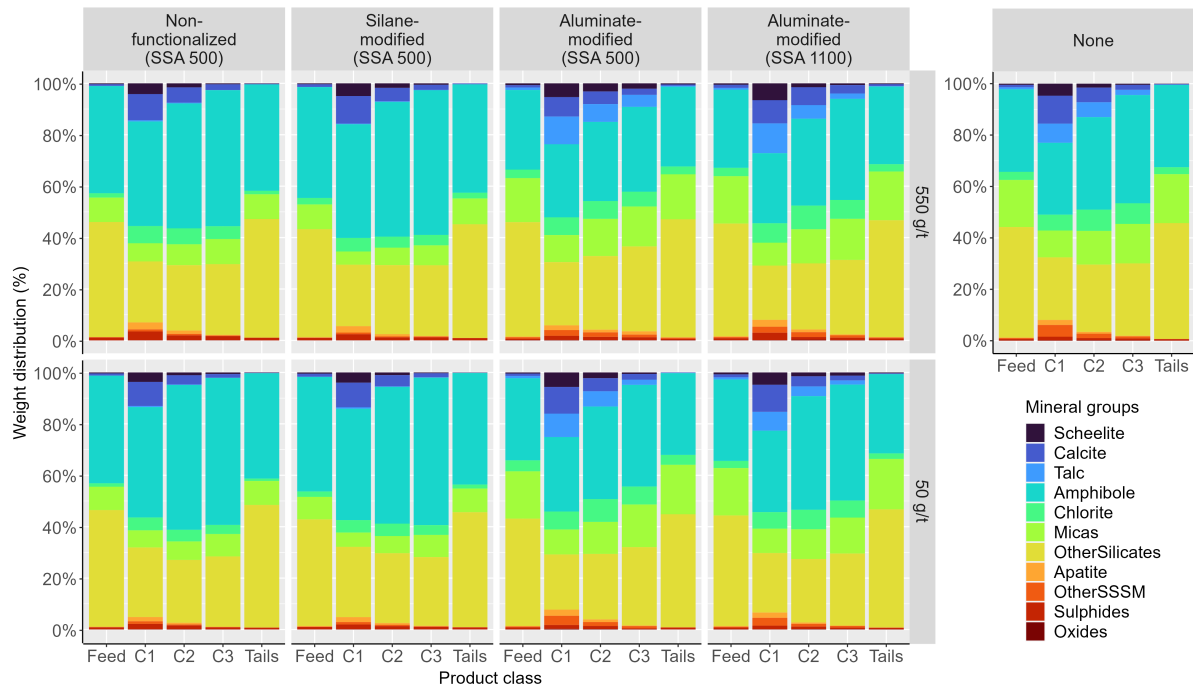


Fig. 44: Modal mineralogy of the product classes based on MLA data

Figure 45 shows the particle size distribution of the MLA samples of feed and products from various colloidal silica tests carried out using different CS modifications, dosages, and a benchmark test. Based on MLA, particle size distributions of the feed samples appear consistent, with 80% of the sample having a particle size of roughly less than 100-130 μm , as indicated by a red line. Concentrate products are finer than the feed, whereas the tailing appears coarser. This validates the credibility of the MLA data sets used for this work with respect to particle size distribution.

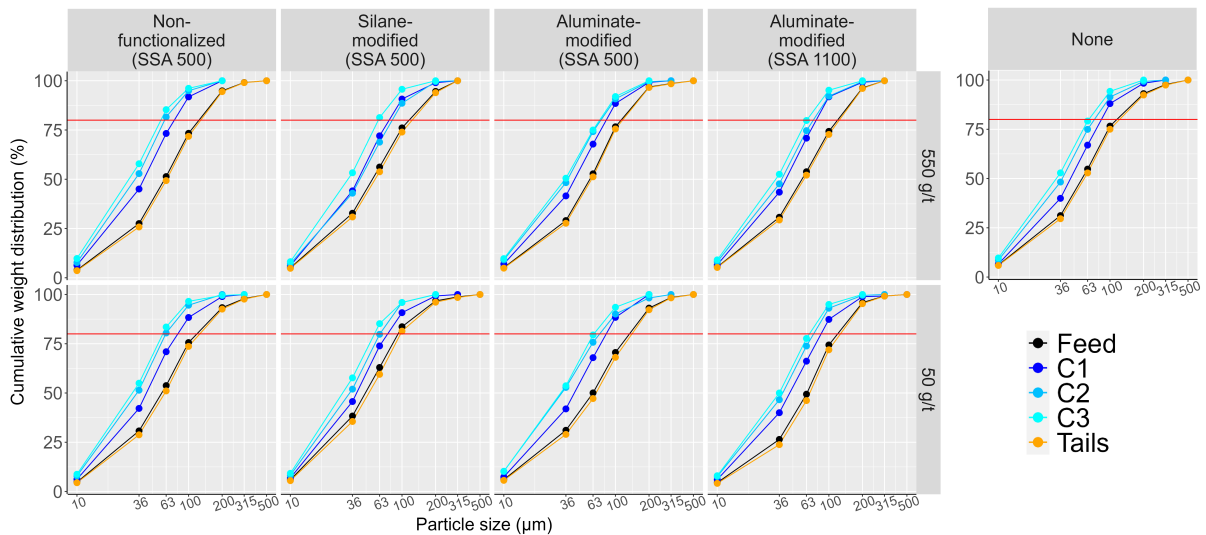


Fig. 45: PSD of the test samples based on MLA data

4.4. Particle-based kinetic flotation model

4.4.1. Validation of the first-order kinetic model fitting

The particle-based flotation model is trained from the particle properties retrieved from MLA data, including size, shape, and composition. Subsequently, the kinetic model is fitted to the predicted recovery probability. Fitting of the kinetic model curve from discrete values of recovery could be a source of uncertainty on the flotation kinetic parameters, including maximum recovery, and flotation rate constant. Cumulative recovery probability values of individual particles at cumulative times of 1, 3, and 7 *min* were predicted based on a particle-based separation model, and a first-order kinetic model was used for the kinetic model fitting. In Figure 46, the total recovery probability of scheelite and calcite particles are plotted against maximum recovery, R_{max} , which is calculated from the fitted kinetic model. Total recovery probability refers to the cumulative probability of a particle to get recovered in the concentrate, which is the cumulative recovery probability of C3 in this case. Across all tests, total recovery probability and maximum recovery of individual scheelite and calcite particles appear to match. No significant overestimation or underestimation of R_{max} is observed in the first-order kinetic model. This gives credibility to the kinetic model parameters for their further use as a measure of the flotation kinetics of individual particles.

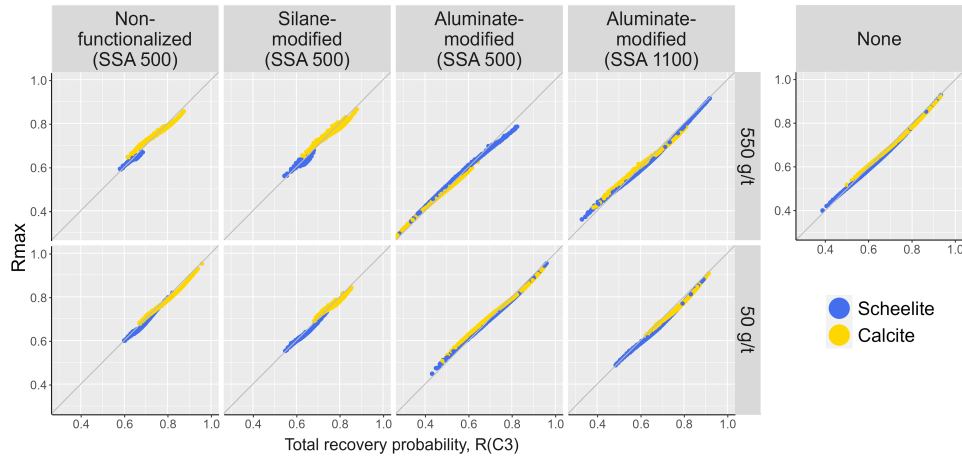


Fig. 46: Total recovery probability vs R_{max} of scheelite and calcite particles

4.4.2. Comparison of grade and recovery curves & Validation of particle-based flotation model

Figure 47 shows the observed grade and recovery curves of the main mineral groups based on MLA data and the predicted grade and recovery curves from the particle-based flotation model. In comparison, the predicted recovery of the main mineral groups generally matches with the observed recovery in MLA data. A slight shift in recovery values can be observed in certain mineral groups. However, the difference is rather small in our case, as both recovery and grade curves tend to match, especially when comparing different tests with each other. Moreover, from the grade-recovery curves, possible minerals with true flotation can be identified by their downward direction and they are scheelite, calcite, talc, and apatite. On the other hand, the gangue minerals floated by entrainment have upward curves and they include amphibole, micas, other silicates, and so on. From this observation, calcite, talc, and apatite can be assumed that they have true flotation mechanisms.

Grade and recovery curves are based on the bulk recovery values and give an overview of which CS affects the given mineral recovery and grade more than the others. As seen in both observed and predicted grade and recovery curves, high dosages of aluminate-modified CSs with SSA of 500 and 1100 m^2/g seem to result in less recovery of calcite, compared to other tests. Nevertheless, with a particle-based flotation model more detailed investigation of these CS effects on the main minerals or mineral groups can be carried out on a single particle level. In addition, the flotation kinetics of individual particles with respect to their composition, size, and shape, can be estimated. Results from the particle-based kinetic model are presented in the following sections.

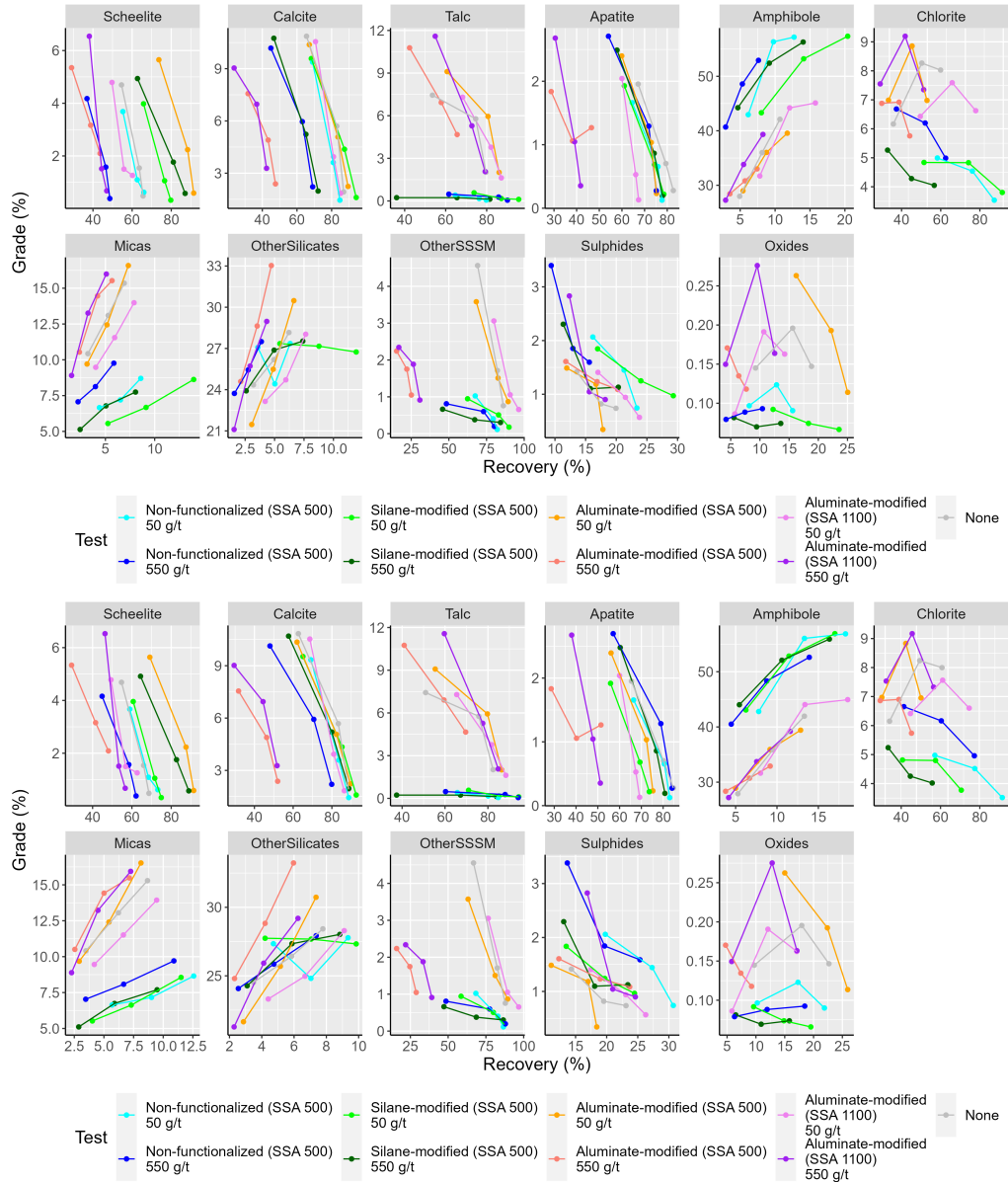


Fig. 47: Grade and recovery curves of the main minerals in various CS tests

4.4.3. Recovery, R of the fully-liberated particles

For the evaluation, only fully liberated particles and their response are plotted as box plots in the following diagrams. 5th, and 95th percentiles of particles represent the minimum and maximum values as whiskers. The lower quartile, median, and upper quartile in the box plot indicate the 25th, 50, and 75th percentiles of the particles. Figure 48 shows the maximum recovery of the main minerals at different process conditions. Different CS modifications are represented as columns of box plots and two different dosage levels are shown.

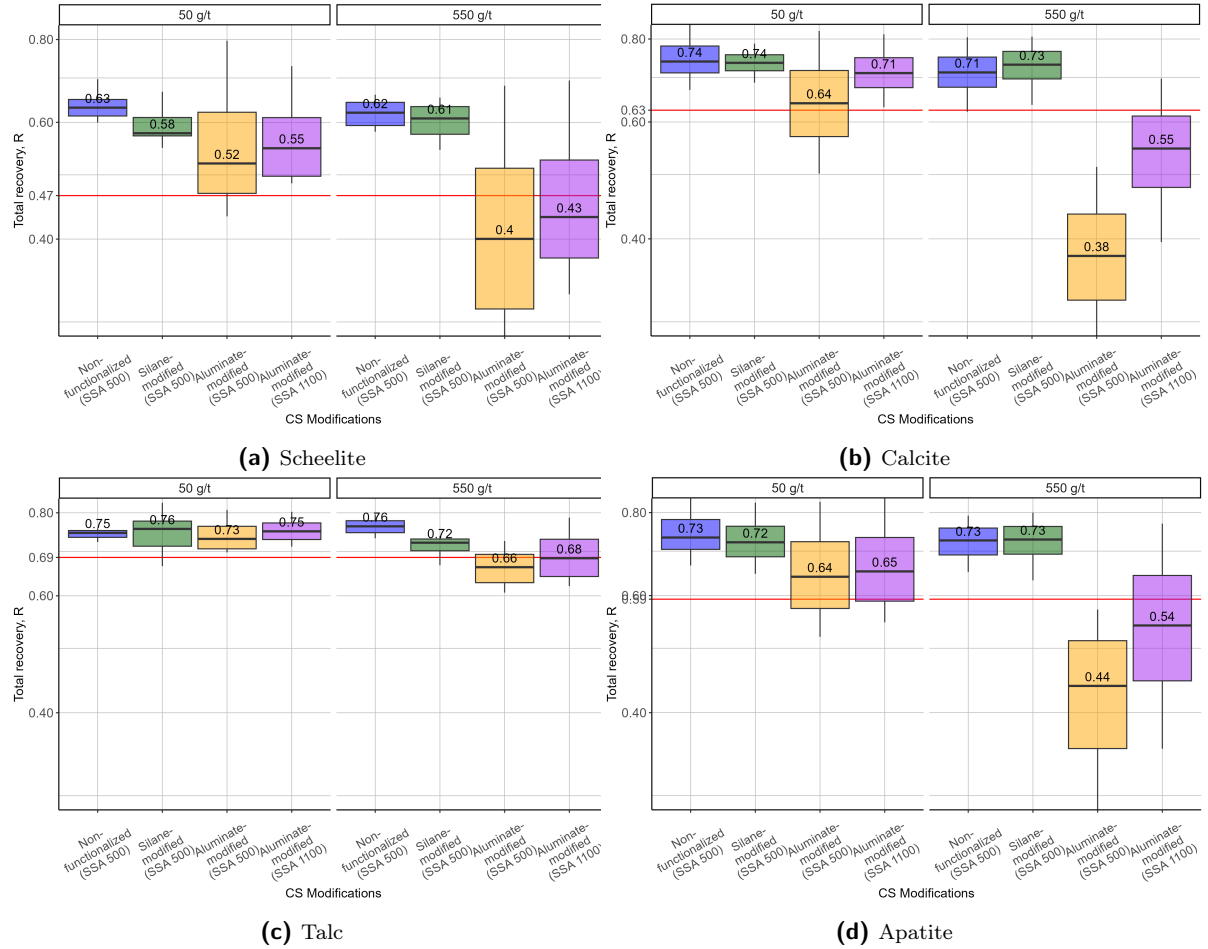


Fig. 48: Total recovery (R) of the main minerals in different process conditions
 * red line represents the median value for the test without colloidal silica

- Effect of non-functionalized colloidal silica

The first column of the box plots in Figure 48 represents the R values of each mineral in non-functionalized CS tests. For all the main minerals, the presence of non-functionalized CS appears to increase the median R value, compared to the test without colloidal silica, which is indicated by a red line. This effect is observed for both dosage levels.

- Effect of colloidal silica modifications

The first three columns of box plots in Figure 48 represent the CSs with different modifications and the same specific surface area of $500 \text{ m}^2/\text{g}$. The medians of R of scheelite, calcite, and apatite, are the lowest when aluminate-modified CS is used, compared to the non-functionalized CS. R medians for non-functionalized and silane-modified colloidal silica appear roughly the same for all the minerals. In the case of talc, low dosages of both aluminate and silane modification seem to have little to no effect on the median R .

- Effect of colloidal silica dosage

CS dosage of non-functionalized and silane-modified CSs seems to have low or no effect on the median R of particles for the main minerals. On the other hand, a high dosage of aluminate-modified CS resulted in a significant decrease in the median R , especially for scheelite, calcite, and apatite.

- Effect of colloidal silica SSA

Aluminate-modified CS with a higher specific surface area of $1100 \text{ m}^2/\text{g}$ is plotted in the last column of Figure 48. Compared to the same modification with SSA of $500 \text{ m}^2/\text{g}$, median R values for scheelite, calcite, and apatite particles are significantly higher at a high dosage of 550 g/t . However, at a low dosage of 50 g/t , median R values for these minerals are roughly as same as the modification with a specific surface area of $500 \text{ m}^2/\text{g}$.

4.4.4. Modified flotation rate constant, k_m of the fully-liberated particles

The flotation kinetics of the particles is measured in maximum recovery, R_{max} , flotation rate constant, k , and modified flotation rate constant, k_m , which is a product of the previous two parameters. For the evaluation, only fully liberated particles and their response are plotted as box plots in the following diagrams. 5th, and 95th percentiles of particles represent the maximum and minimum values as whiskers. The lower quartile, median, and upper quartile in the box plot indicate the 25th, 50, and 75th percentiles of the particles.

Figure 49 displays the modified flotation rate, k_m , of the main minerals in different CS tests. To quantify the floatability of each particle, modified flotation rate constant, k_m was calculated from the product of R_{max} and, k values. Box plots of the k_m for the main minerals are shown in the diagram.

- Effect of non-functionalized colloidal silica

The first column of the box plots in Figure 49 represents the k_m values of each mineral in non-functionalized CS tests. At a low dosage of 50 g/t , the modified flotation rate increases for the main minerals, compared to the test without colloidal silica, which is indicated by a red line. At high dosage 550 g/t , the median values of k_m for calcite and talc drop to the value from the test without colloidal silica, whereas for scheelite and apatite, the median value of k_m stays higher.

- Effect of colloidal silica modifications

The first three columns of box plots in Figure 49 represent the CS modifications for the same specific surface area of $500 \text{ m}^2/\text{g}$. The medians of modified flotation rate constant of scheelite, calcite, talc, and apatite, are the lowest when aluminate-modified CS is used, compared to non-functionalized CS. The responses to both non-functionalized and silane-modified colloidal silica are generally similar, the median k_m staying higher than aluminate-modified CS for the main minerals and at both dosage levels.

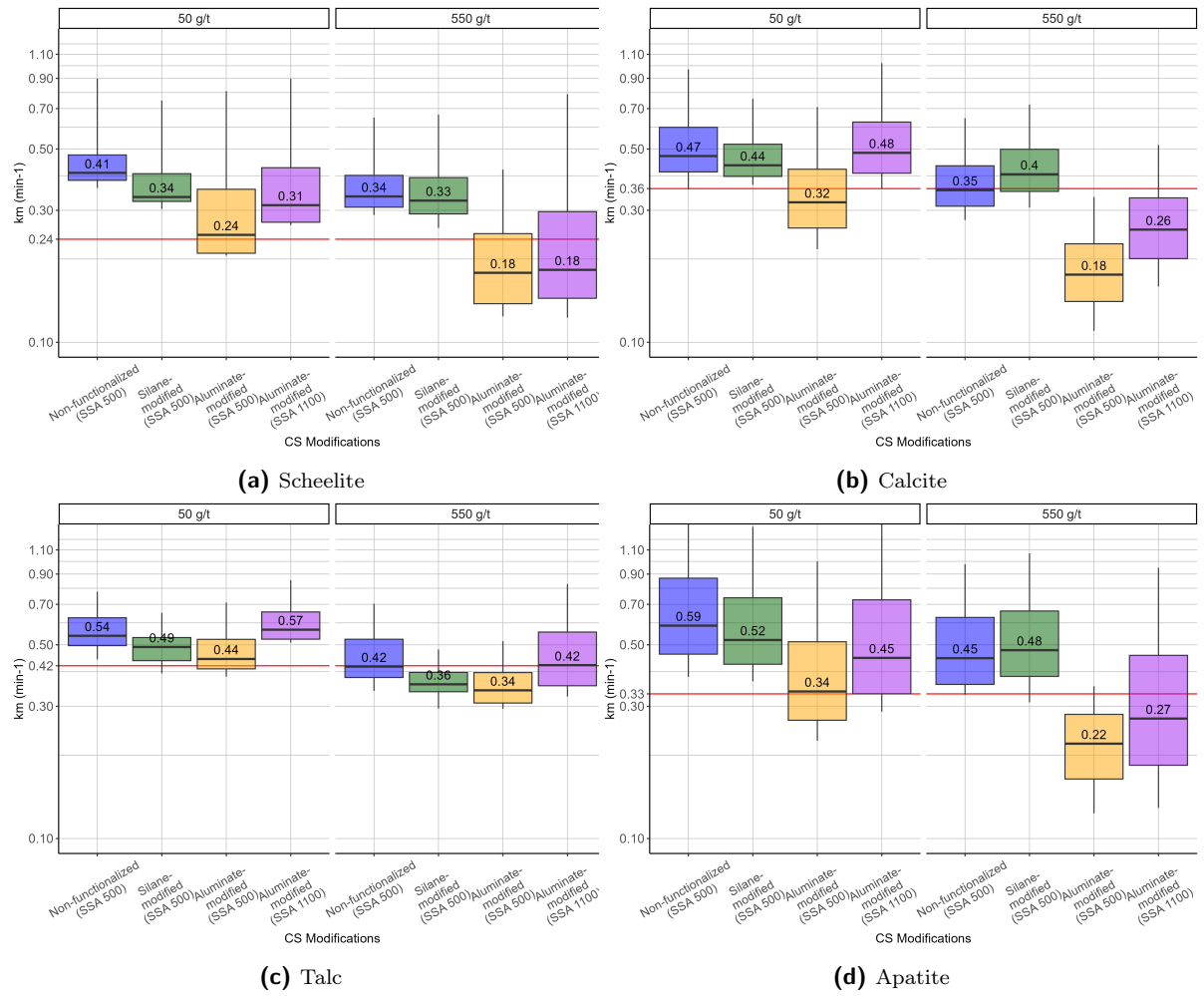


Fig. 49: Modified flotation rate (k_m) of the main minerals in different process conditions
 * red line represents the median value for the test without colloidal silica

- Effect of colloidal silica dosage

Silane-modified CS dosage seems to not affect the median k_m , whereas the dosage effect is seen as more significant in non-functionalized and aluminate-modified CS for the main minerals.

- Effect of colloidal silica SSA

Aluminate-modified CS with a higher specific surface area of $1100 \text{ m}^2/\text{g}$ is plotted in the last column of Figure 49. Compared to the same modification with SSA of $500 \text{ m}^2/\text{g}$, median k_m values of scheelite, calcite, talc, and apatite are significantly higher at a low dosage of 50 g/t . At a high dosage of 550 g/t , the same trend is observed except for scheelite.

4.4.5. Recovery of the silicate gangue mineral particles

Figure 50 shows the total recovery probability of the gangue mineral groups at different process conditions. Different CS types are represented as columns of box plots and two different dosage levels are shown.

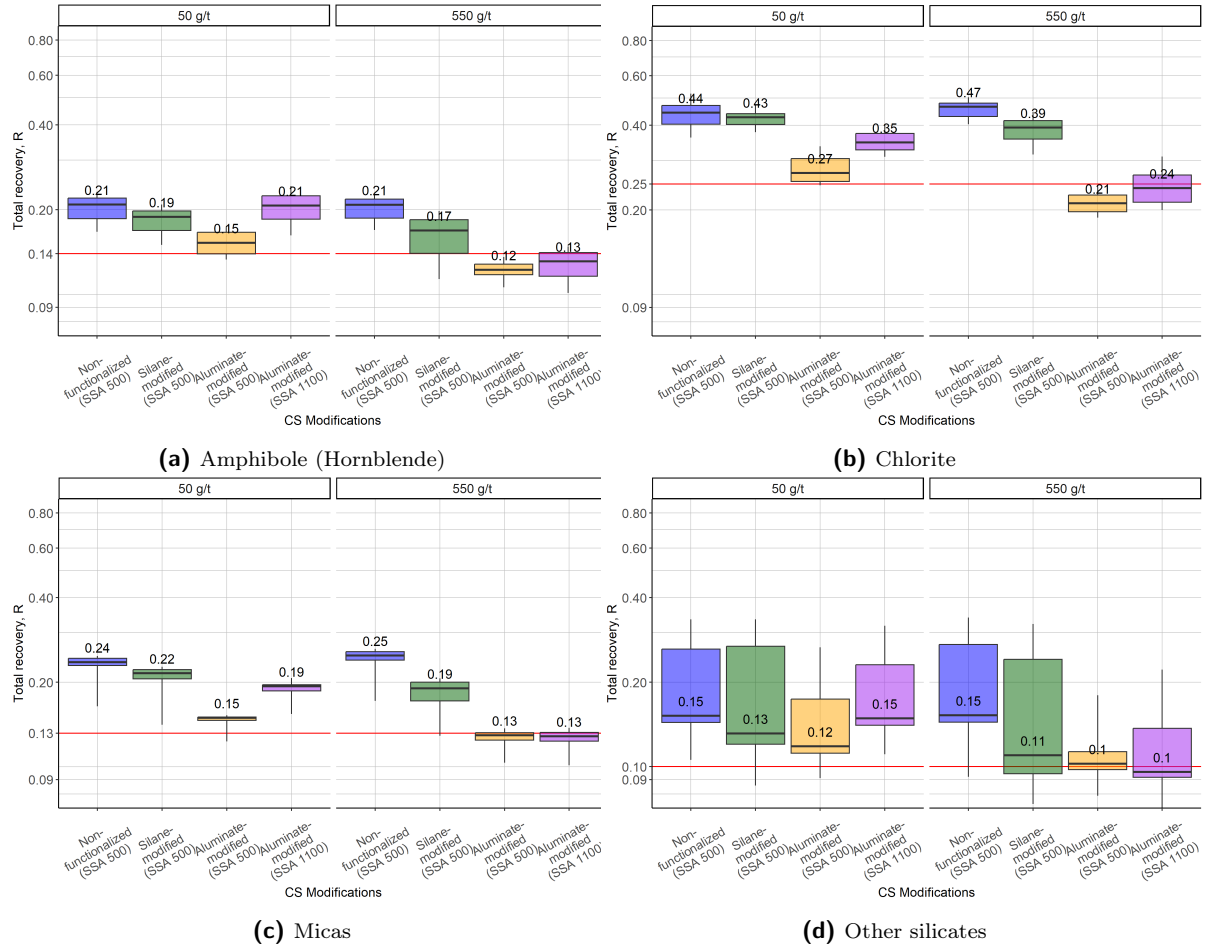


Fig. 50: Total recovery (R) of the gangue minerals in different process conditions
 * red line represents the median value for the test without colloidal silica

- Effect of non-functionalized colloidal silica

The first column of the box plots in Figure 50 represents the median total recovery, R values of each mineral in non-functionalized CS tests. For the gangue minerals, including amphibole, chlorite, and other silicates, the presence of non-functionalized CS appears to increase the median of overall recovery probability, compared to the test without colloidal silica. This stays true for both dosage levels.

- Effect of colloidal silica modifications

The first three columns of box plots in Figure 50 represent the CS modifications for the same specific surface area of $500 \text{ m}^2/\text{g}$. The medians of total recovery for amphibole and chlorite, are the lowest when aluminate-modified CS is used, compared to the non-functionalized CS. The total recovery medians for non-functionalized and silane-modified colloidal silica appear roughly the same for amphibole and chlorite particles.

- Effect of colloidal silica dosage

CS dosages of non-functionalized, aluminate, and silane-modified CS seem to have low or no effect on the median total recovery for the gangue minerals, including amphibole, chlorite, micas, and other silicates. The exception is aluminated-modified CS (SSA 1100), which appears to decrease the total recovery at a higher dosage.

- Effect of colloidal silica SSA

Aluminate-modified CS with a higher specific surface area of $1100 \text{ m}^2/\text{g}$ is plotted in the last column of Figure 50. Compared to the same modification with SSA of $500 \text{ m}^2/\text{g}$, median total recovery values of amphibole, chlorite, and other silicate groups are higher at a low dosage of 50 g/t . However, at a low dosage of 550 g/t , the median total recovery values of amphibole, and other silicates are roughly as same as the modification with a specific surface area of $500 \text{ m}^2/\text{g}$.

4.4.6. Effect of aspect ratio and solidity on the recovery and flotation kinetics of main minerals

With the particle-based model, it is possible to investigate the effect of particle properties, including particle shape and size. Figures A.3 and A.4 show the recovery and flotation kinetics of main minerals with respect to particle shape parameters, aspect ratio, and solidity. As seen in the diagram, for calcite, scheelite, and amphibole group, particle shape parameters seem to have no significant effect on the recovery or kinetics.

4.4.7. Effect of particle size on the recovery and flotation kinetics of main minerals

In Figure 51 the recovery and flotation kinetics of the main minerals concerning particle size in various CS tests. R_{max} of scheelite goes above calcite at a high dosage of aluminate-modified CS (SSA 500), as opposed to the trend seen in other CS modifications. At a high dosage of aluminate-modified CS (SSA 1100), the gap between R_{max} curves of scheelite and calcite closes as the particle size increases and R_{max} of scheelite places above calcite at the coarser size. Moreover, the modified flotation rate constant of calcite generally overlaps scheelite, however, in the case of a high dosage of aluminate-modified CS (SSA 1100), the gap between k_m curves of calcite and scheelite widens, as the particle size increases, implying more selectivity.

In a particle-based model, median values of flotation kinetic parameters could be heavily influenced by the high number of finer particles. As for scheelite and calcite, lower particle size appears to result in a lower modified flotation rate constant and lower maximum recovery of the particle, as seen in Figure 51. Therefore, previously presented box plots of flotation kinetic parameters could be impacted by these lower values of fine particles. Finer particles mean a higher number of particles per weight, and this can influence the median value significantly since the weight of each particle is not taken into account for median values. Thus, the weight distribution of each particle size class and corresponding flotation kinetic parameters in each size class are investigated further.

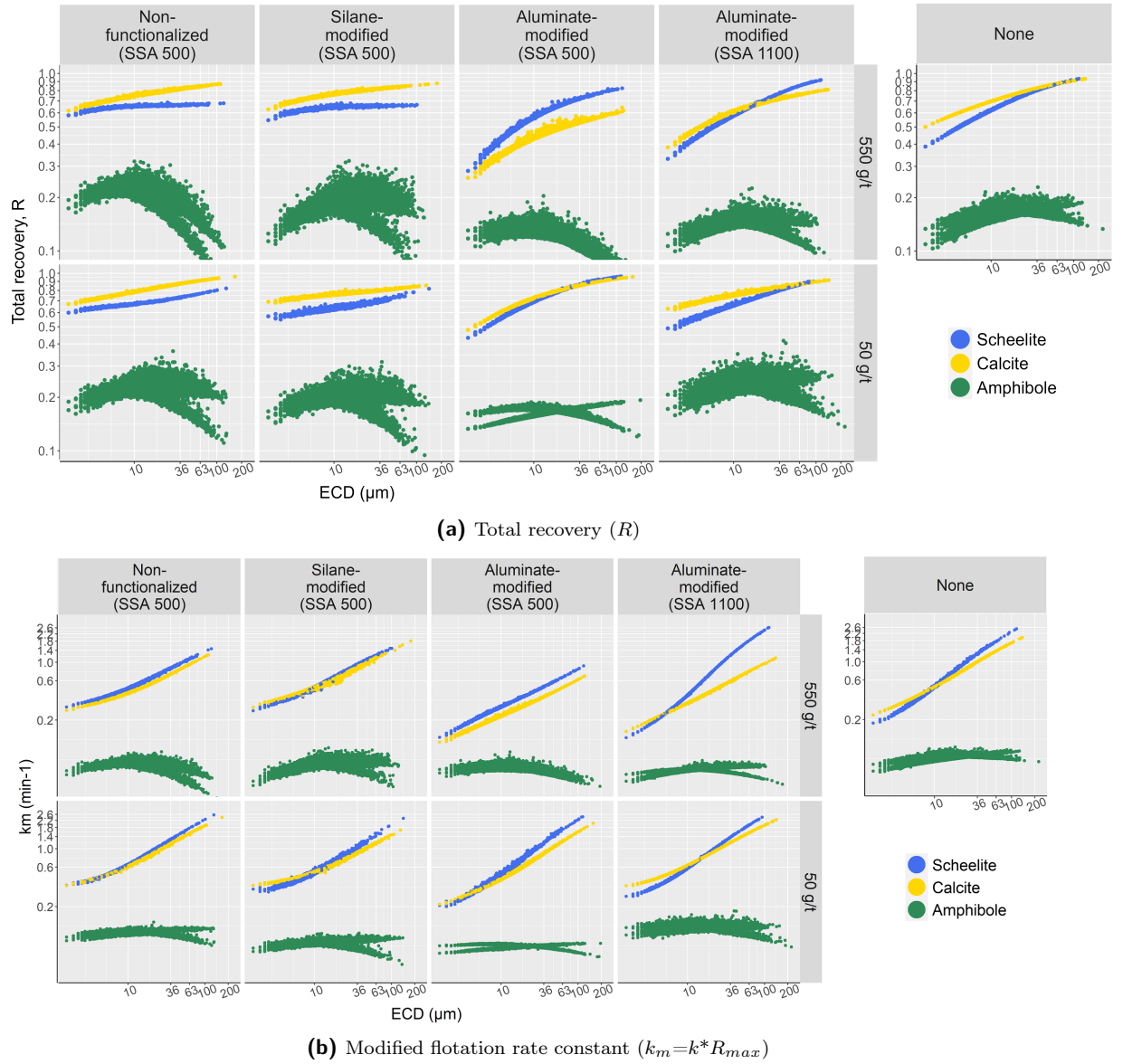


Fig. 51: Flotation kinetic of the main minerals with respect to particle size

Figure 52 shows the weight distribution of different particle size classes for scheelite and calcite. 25%-35% of the calcite particles are finer particles with particle sizes less than 36 μm across all tests. Similarly, the weight percentage of such fine particles of scheelite is 30-35%. On the other hand, coarse particles of calcite with the size of 100-200 μm takes up to 15-25%. Particle distributions of scheelite and calcite appear evenly distributed along different size ranges and they seem to have a different response to the process, as previously seen in Figure 51.

Moreover, finer particles tend to behave differently than the coarser particles, as their settling velocity is lower, which makes them more susceptible to entrainment. Therefore, classifying the particles in different size classes and evaluating the median flotation kinetic parameters in each size class is more suitable. Flotation kinetics of scheelite and calcite can be evaluated in five different size classes, including 0-10 μm, 10-36 μm, 36-63 μm, 63-100 μm, and 100-200 μm.

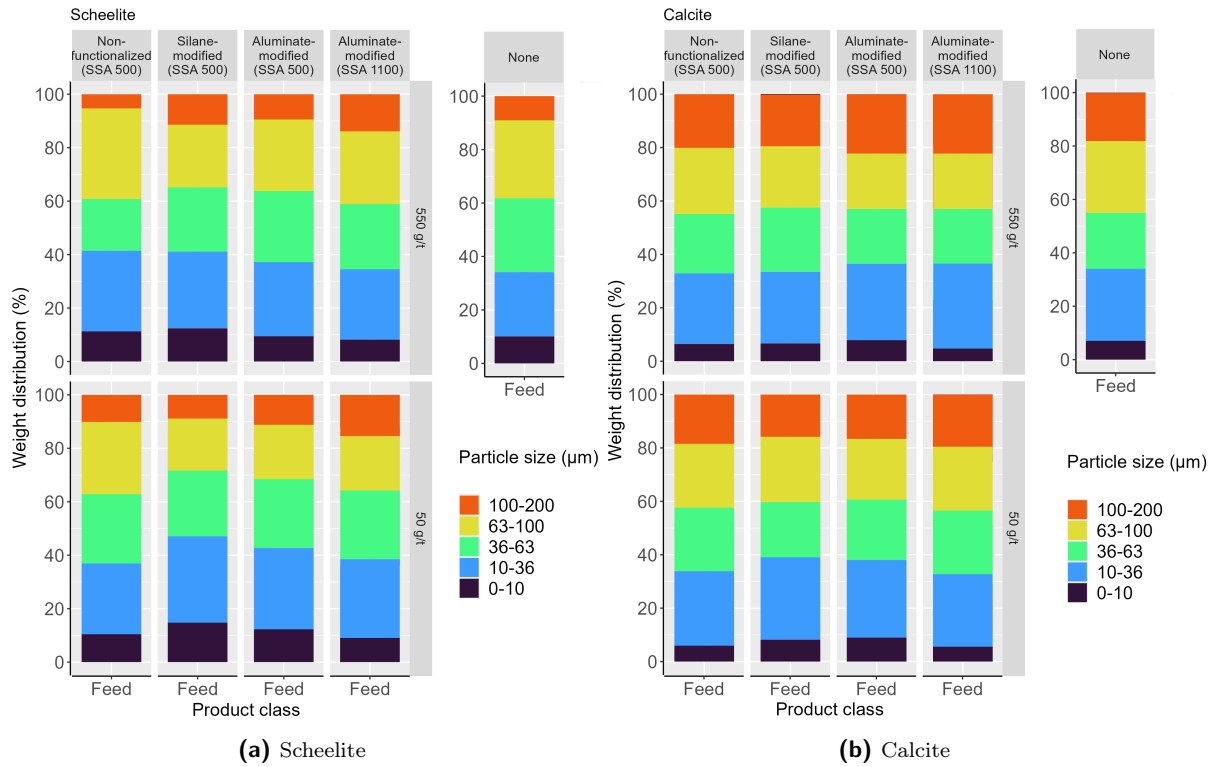
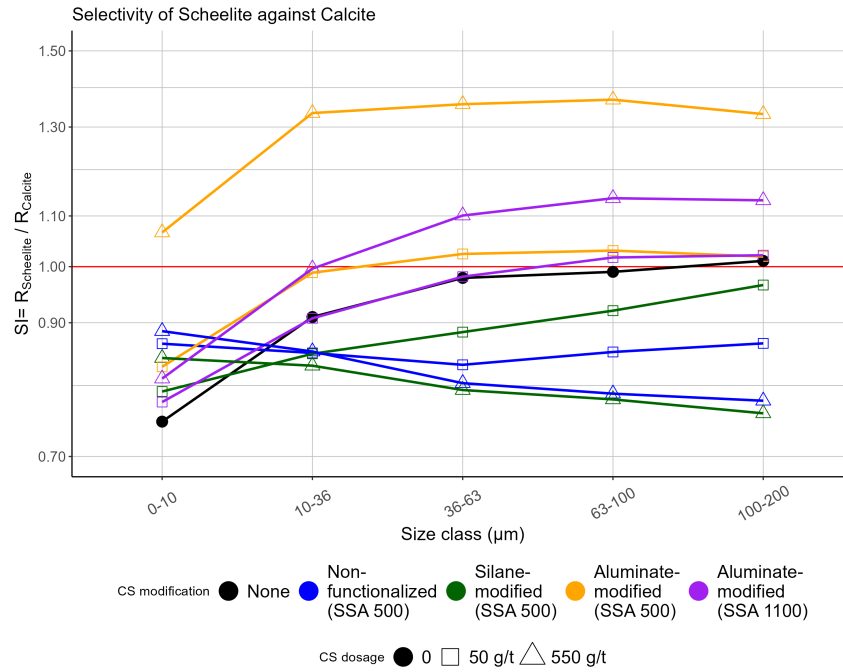


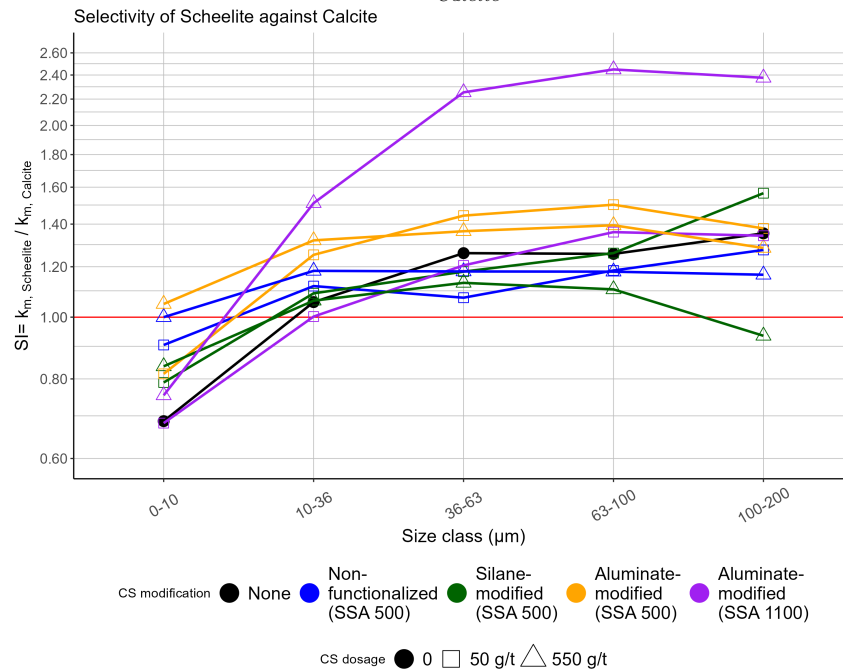
Fig. 52: Weight distribution of scheelite and calcite in different particle size classes

Figure 53a shows the selectivity index of scheelite against calcite evaluated for five different particle size classes under various CS modifications, dosage, and SSA. The selectivity index is calculated from the ratio of scheelite to calcite total recovery, R . A high dosage of both aluminate-modified CSs with SSA of 500 and 1100 m^2/g appears to improve the selectivity of scheelite against calcite in all size classes, compared to the test without CS, indicated by a black line. On the other hand, a low concentration of both aluminate-modified CSs seems to slightly improve the selectivity in each size class as well. However, non-functionalized and silane-modified CSs seem to lower the selectivity index for size classes higher than 10 μm . For tests with aluminate-modified CSs and benchmark tests without CS, a sharp increase in selectivity index is observed between size classes 0-10 μm , and 10-36 μm .

Figure 53b shows the selectivity index of scheelite against calcite evaluated for different particle size classes, this time calculated from modified flotation rate constants. With respect to flotation kinetics, aluminate-modified CSs with SSA of 500 and 1100 m^2/g appear to improve the selectivity index, compared to the test without CS. As we compare different size classes, a distinct difference in selectivity index is observed in the smallest size fraction of 0-10 μm . For fine particles of scheelite and calcite with a size of less than 10 μm , the selectivity index seems to be much lower in both with and without CS tests, compared to coarser fractions. Starting from 10-36 μm size fraction, the selectivity index is significantly higher than the previous finer fraction. Specifically at a high dosage of aluminate-modified CS (SSA 1100), a sharp increase in the selectivity index is observed compared to other modifications. For the next three size fractions, including 36-63 μm , 63-100 μm , and 100-200 μm , the selectivity index is roughly at the same level. The biggest increase in selectivity index with respect to particle size is observed at a high dosage of aluminate-modified CS (SSA 1100).



(a) Based on total recovery
 $(SI = \frac{R_{Scheelite}}{R_{Calcite}})$



(b) Based on modified flotation rate constant
 $(SI = \frac{k_{m,Scheelite}}{k_{m,Calcite}})$

Fig. 53: Selectivity index of scheelite against calcite in different size classes

Figure 54 shows the weight distribution of different particle size classes for the amphibole group and talc. For amphibole group, 0-10 μm fraction takes up to 5%, whereas 10-36 μm fraction is 30-35% of the total amphibole weight in the sample. Each bigger size fraction, including 36-63 μm , 63-100 μm , and 100-200 μm , takes up to 15-25% of the amphibole weight across all tests. For talc, similar size distribution is observed in feed samples for non-functionalized, and aluminate-modified CS tests. However, for non-functionalized and silane-modified CS tests, no 100-200 μm talc fraction is found, and 63-100 μm fraction of talc appears to be higher in the feed.

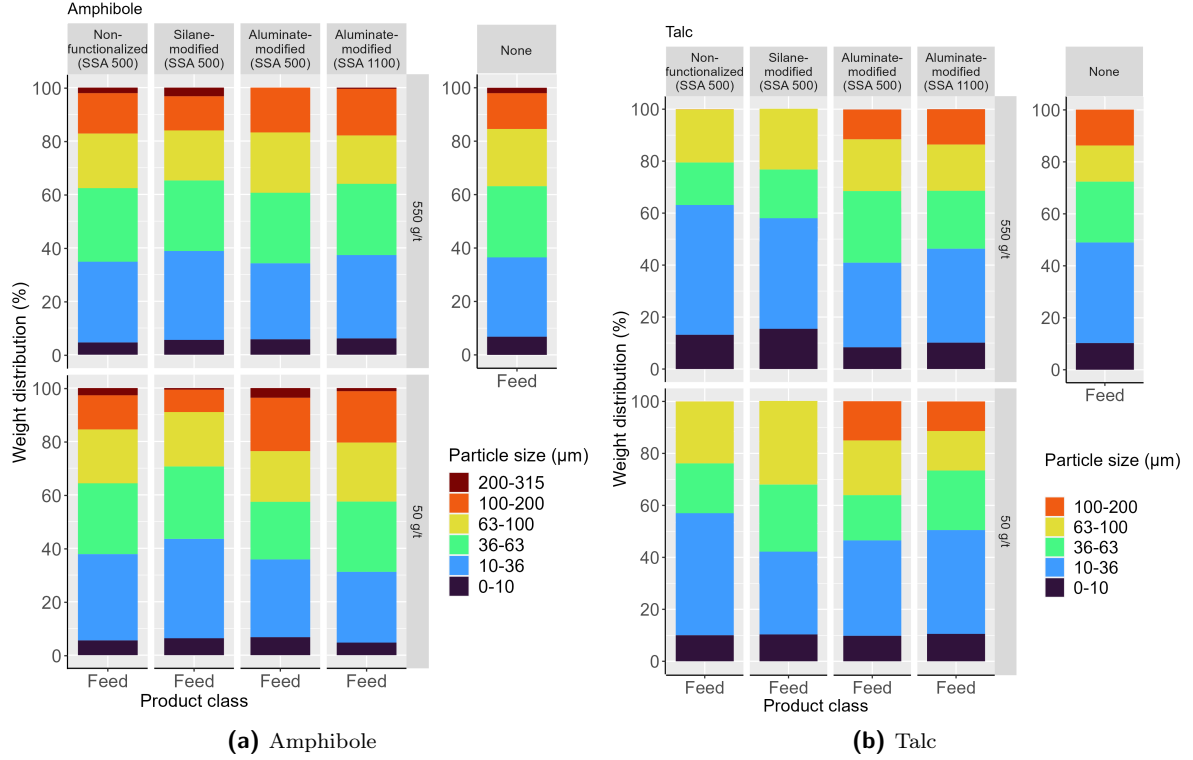
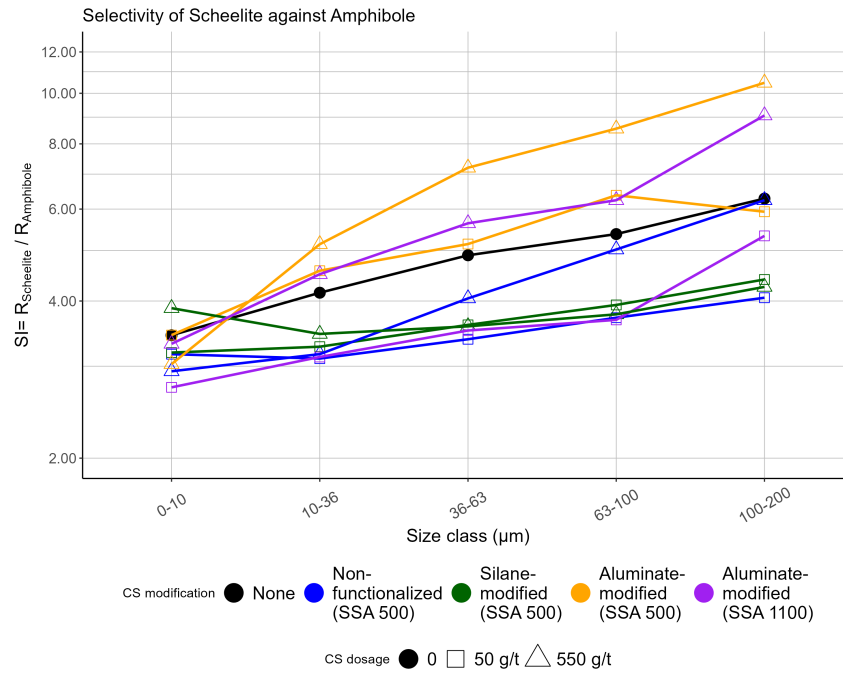


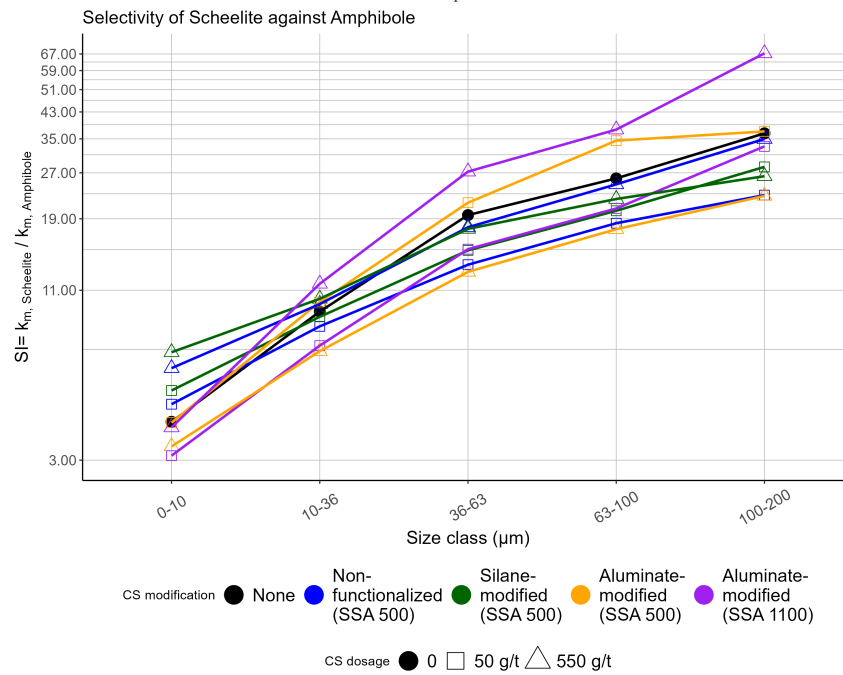
Fig. 54: Weight distribution of hornblende and talc in different particle size classes

In Figure 55a, the selectivity index of scheelite against the amphibole group with respect to particle size is plotted for various CS tests. High dosages of both aluminate-modified CSs with SSA of 500, and 1100 m^2/g appear to have higher selectivity index values than benchmark test without CS, specifically for the particle size classes greater than 10 μm . On the other hand, non-functionalized and silane-modified CS seem to decrease the selectivity index of scheelite recovery against amphibole at both dosages. Overall, a high dosage of aluminate-modified CS (SSA 500) seems to bring the highest selectivity of scheelite against amphibole for size classes bigger than 10 μm , which takes up more than 95% of the total amphibole weight in the sample.

On the other hand, Figure 55b shows the selectivity index of scheelite against amphibole, calculated from the modified flotation kinetics. A high dosage of aluminate-modified CS (SSA 1100) appears to have the highest selectivity of scheelite against amphibole, for particles bigger than 10 μm , whereas the selectivity index for a high dosage of aluminate-modified CS (SSA 500) appears to be the lowest in this case.



(a) Based on total recovery
 $(SI = \frac{R_{Scheelite}}{R_{Amphibole}})$

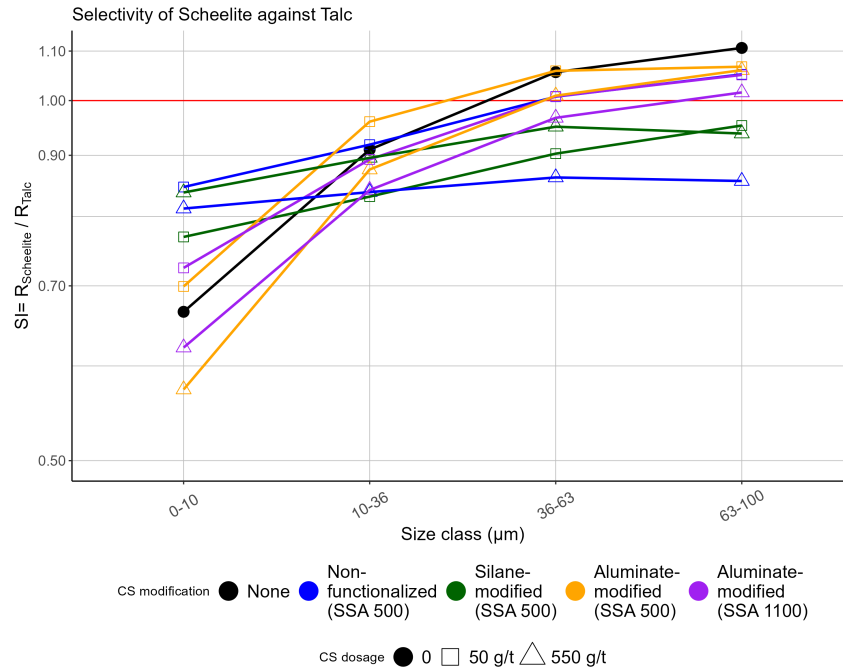


(b) Based on modified flotation rate constant
 $(SI = \frac{k_{m, Scheelite}}{k_{m, Amphibole}})$

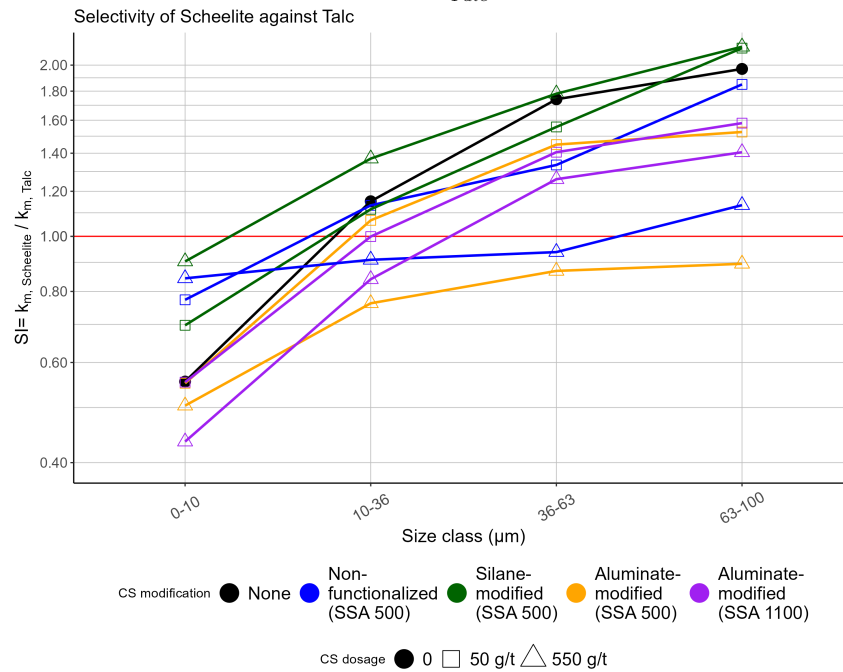
Fig. 55: Selectivity index of scheelite against amphibole in different size classes

As shown in Figure 56a, the selectivity index of scheelite against talc in different particle size classes is plotted for various CS tests, calculated from the total recovery values. Both aluminate-modified CSs with SSA of 500, and 1100 m^2/g generally seem to have no significant effect on the selectivity index of scheelite against talc, but a slight decrease in the selectivity for tests with high concentration of aluminate-modified CS. Taking the fractions with particle size bigger than 10 μm into consideration, the higher SSA of aluminate-modified CS seems to have a slightly negative or no effect on the selectivity of scheelite against talc. Generally, non-functionalized and silane-modified CSs seem to decrease the selectivity index for particle size ranges higher than 10 μm .

On the other hand, Figure 56b shows the selectivity index of scheelite against talc, calculated from the modified flotation kinetics. In all particle size classes, both dosage levels of aluminate-modified CSs seem to decrease the selectivity, whereas a high dosage of silane-modified CS seems to slightly increase the selectivity index.



(a) Based on total recovery
 $(SI = \frac{R_{Scheelite}}{R_{Talc}})$



(b) Based on modified flotation rate constant
 $(SI = \frac{k_{m,Scheelite}}{k_{m,Talc}})$

Fig. 56: Selectivity index of scheelite against talc in different size classes

4.4.8. Overall selectivity index, SI of scheelite against calcite

In Figure 57, the selectivity index is calculated from the ratio of total scheelite recovery to calcite. Considering all particles of scheelite and calcite, a high dosage of aluminate-modified CS (SSA 500) appears to result in the highest median value of selectivity index, followed by non-functionalized CS, as seen in Figure 57a. Similarly, when 0-10 μm fraction is excluded, a **maximum dosage of aluminate-modified CS (SSA 500)** brings the highest value of selectivity index of scheelite against calcite with respect to their recovery. However, aluminate-modified CS (SSA 1100) seems to have the second-best selectivity index of scheelite against calcite, as shown in Figure 57b.

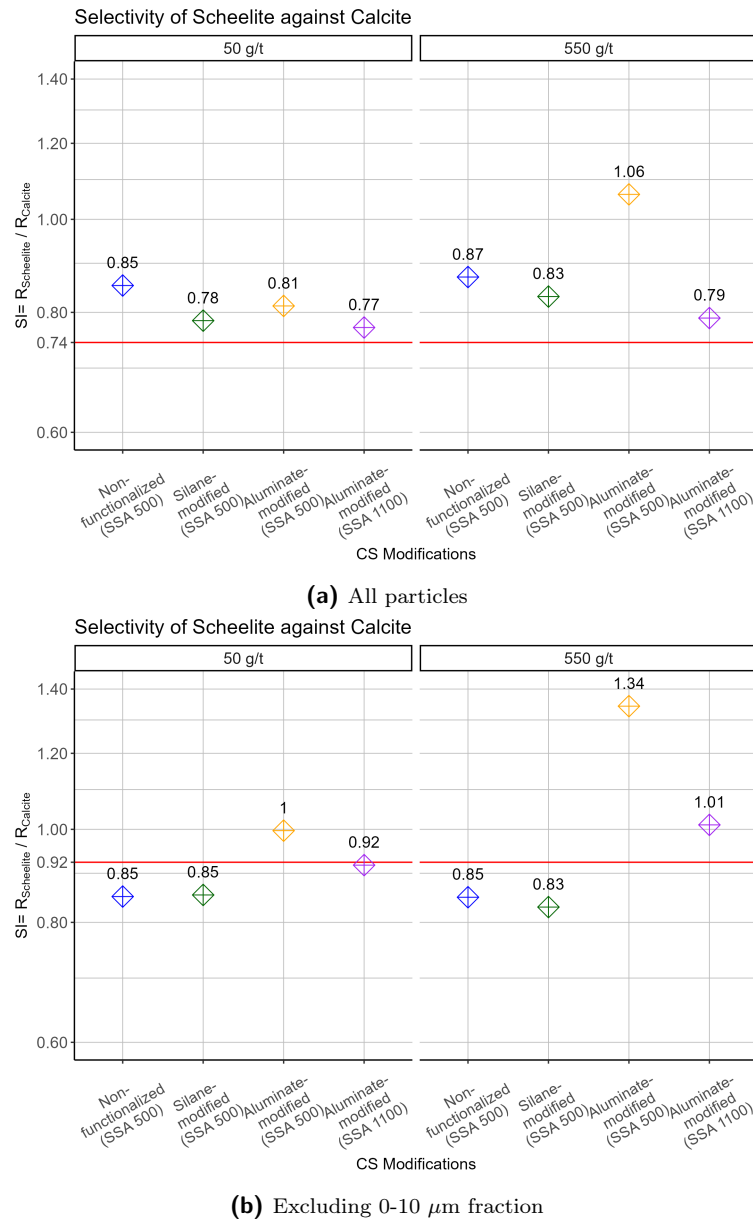


Fig. 57: Overall selectivity index of scheelite against calcite, ($SI = \frac{R_{Scheelite}}{R_{Calcite}}$), in different process conditions

In Figure 58, the selectivity index is calculated from the ratio of scheelite modified flotation rate constant to calcite. The median values of the selectivity index are plotted in the diagram.

Figure 58a shows the overall selectivity index of scheelite against calcite for all particles in various CS tests. Figure 58b shows the median selectivity index of scheelite against calcite for all the particles excluding 0-10 μm fractions. Consideration of all particles indicated that a high dosage of aluminate-modified CS (SSA 500) has the highest selectivity index, as seen in Figure 58a. However, excluding 0-10 μm fraction, a high dosage of aluminate-modified CS (SSA 1100) has the highest selectivity. As these two cases indicate different results on which CS is performing better, weight consideration can be taken into account. More representative media value of selectivity index is evaluated excluding 0-10 μm fraction, which is up to 10% of the total weight of scheelite and calcite, as shown in Figure 52. Therefore, **a high dosage of aluminate-modified CS (SSA 1100)** has the highest selectivity of scheelite against calcite with respect to flotation kinetics, followed by aluminate-modified CS (SSA 500).

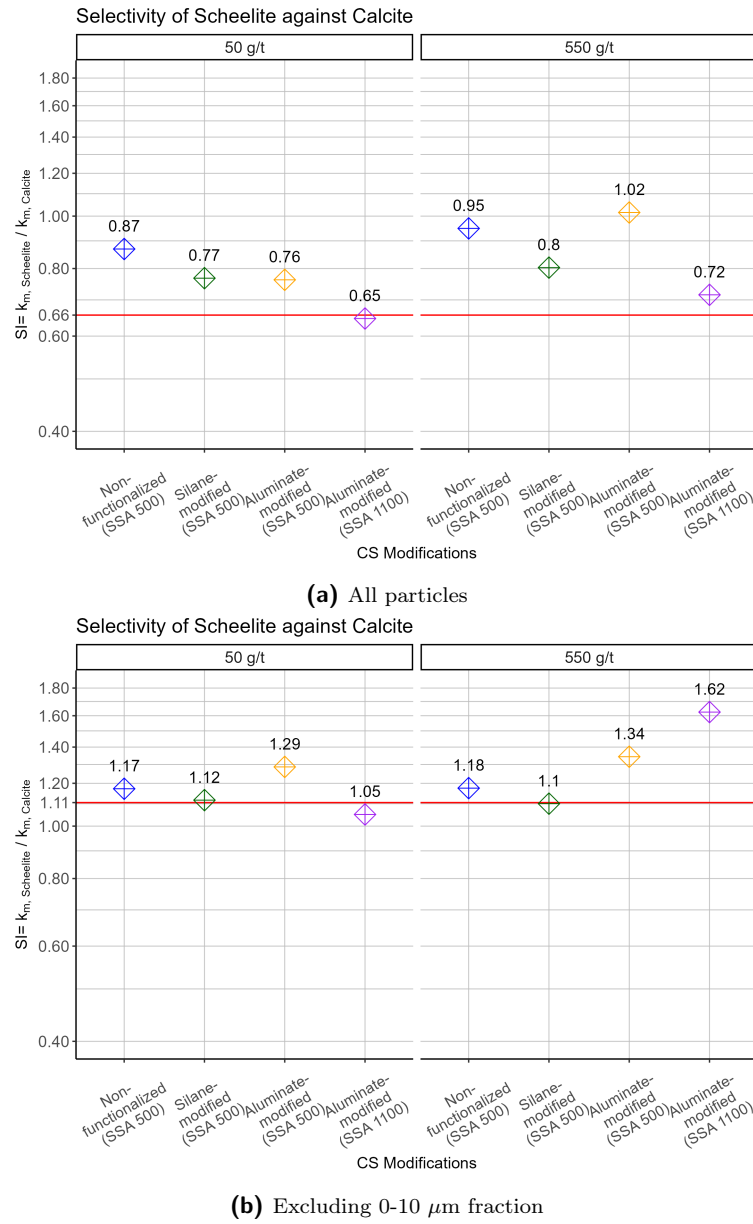


Fig. 58: Overall selectivity index of scheelite against calcite, ($SI = \frac{k_{m,Scheelite}}{k_{m,Calcite}}$), in different process conditions

4.4.9. Overall selectivity index, *SI* of scheelite against amphibole

In Figure 59, the selectivity index is calculated from the ratio of total scheelite recovery to amphibole. Considering all particles of scheelite and amphibole, a high dosage of silane-modified CS appears to result in the highest median value of selectivity index, followed by aluminate-modified CS (SSA 500), as seen in Figure 59a. However, when the 0-10 μm fraction is excluded, a maximum dosage of aluminate-modified CS (SSA 500) has the highest median value of the selectivity index. At the same dosage level, aluminate-modified CS (SSA 1100) seems to have the second-best selectivity index of scheelite against amphibole, as shown in Figure 59b. For particles higher than 10 μm , high dosages of both aluminate-modified CSs seem to improve the selectivity of scheelite against amphibole, compared to the benchmark test without CS, indicated by a red line. However, for non-functionalized, and silane-modified CSs no improvement is observed.

As previously shown in Figure 54, 0-10 μm fraction takes up to only 5% of the total amphibole in the feed. Therefore, excluding this fraction for median value evaluation appears to bring a more representative value for this mineral group. Based on this assumption, **a high dosage of aluminate-modified CS (SSA 500)** brings the highest selectivity of scheelite against the amphibole group with respect to their recovery, followed by aluminate-modified CS (SSA 1100).

In Figure 60, the selectivity index is calculated from the ratio of scheelite modified flotation rate constant to amphibole. The median values of the selectivity index are plotted in the diagram. Figure 60a shows the overall selectivity index of scheelite against amphibole for all particles in various CS tests. Figure 60b shows the median selectivity index of scheelite against amphibole for all the particles excluding 0-10 μm fractions.

Consideration of all the particles indicated that high dosages of non-functionalized, and silane-modified CSs have the highest selectivity index, as seen in Figure 60a. As previously mentioned, 5% of the total weight of amphibole is in 0-10 μm fraction. Therefore, 0-10 μm fraction excluded median values provide a more representative measure here as well. Excluding 0-10 μm fraction, **a high dosage of aluminate-modified CS (SSA 1100)** has the highest selectivity of scheelite against the amphibole group with respect to flotation kinetics, followed by silane-modified CSs.

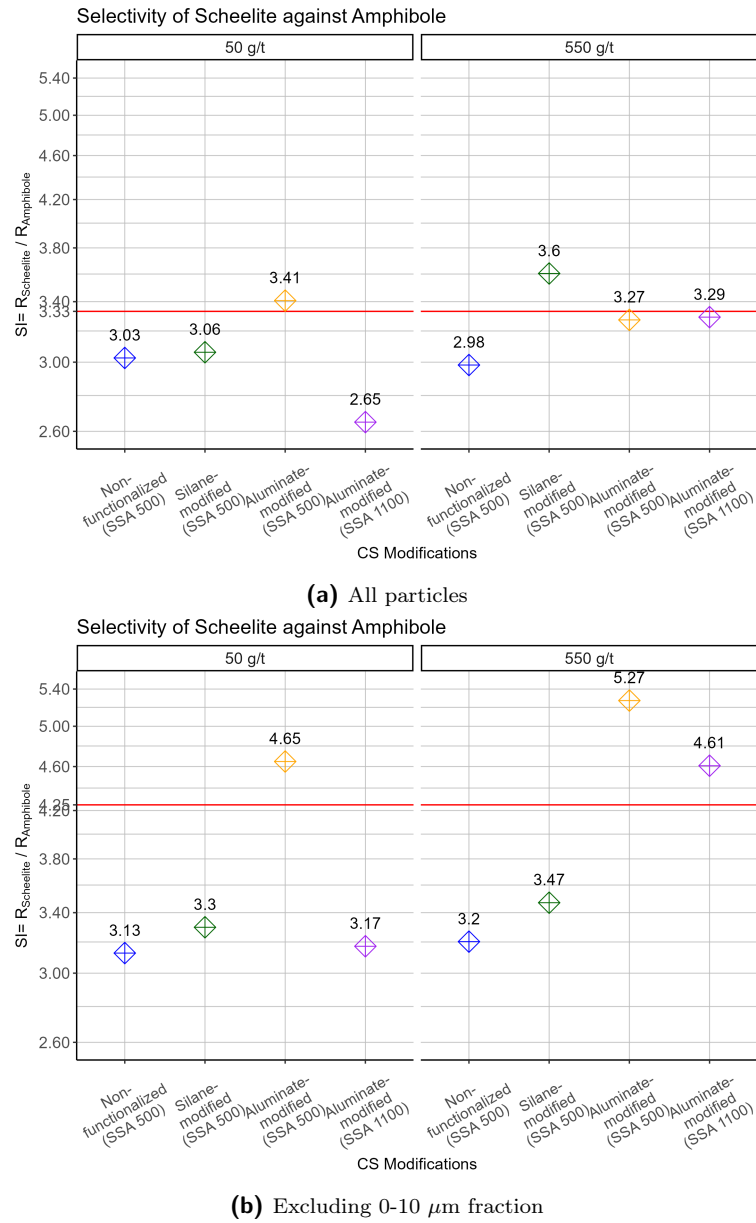
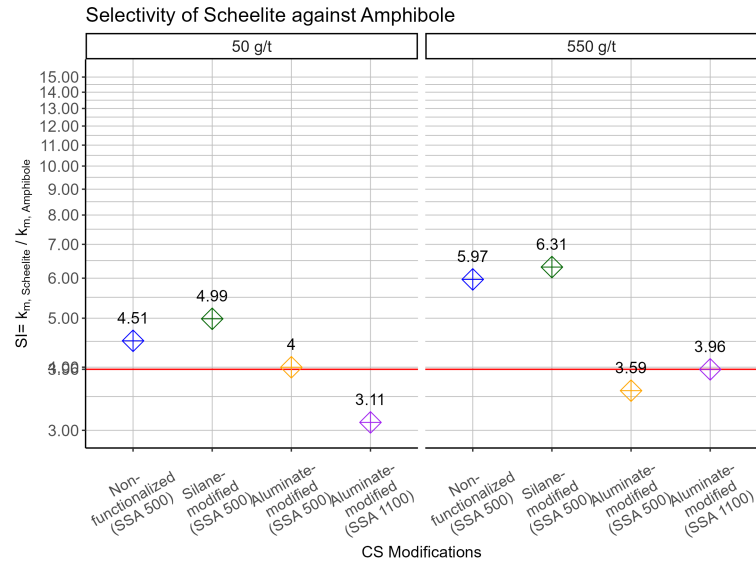


Fig. 59: Overall selectivity index of scheelite against amphibole, ($SI = \frac{R_{Scheelite}}{R_{Amphibole}}$), in different process conditions



(a) All particles

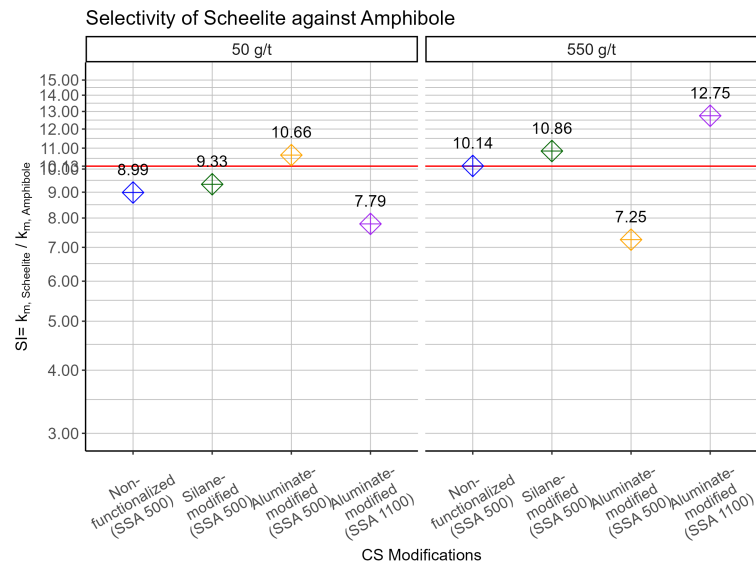
(b) Excluding 0-10 μm fraction

Fig. 60: Overall selectivity index of scheelite against amphibole, ($SI = \frac{k_{m,Scheelite}}{k_{m,Amphibole}}$), in different process conditions

4.4.10. Overall selectivity index, SI of scheelite against talc

In Figure 61, the selectivity index is calculated from the ratio of total scheelite recovery to talc. Considering all particles of scheelite and talc, non-functionalized, and silane-modified CSs appear to result in the highest median value of selectivity index, as seen in Figure 61a. When the selectivity index median is evaluated excluding 0-10 μm fraction, no significant effect of CS on the selectivity index of scheelite against talc is observed for all types compared to the benchmark test without CS. Out of the CS modifications, silane and aluminate-modified CSs (SSA 500) have the highest median value of the selectivity index. 0-10 μm fraction of talc takes up to around 10% of the total talc mass, as previously shown in Figure 54. The SSA effect of aluminate-modified CS appears to be not significant for the selectivity index of scheelite against talc.

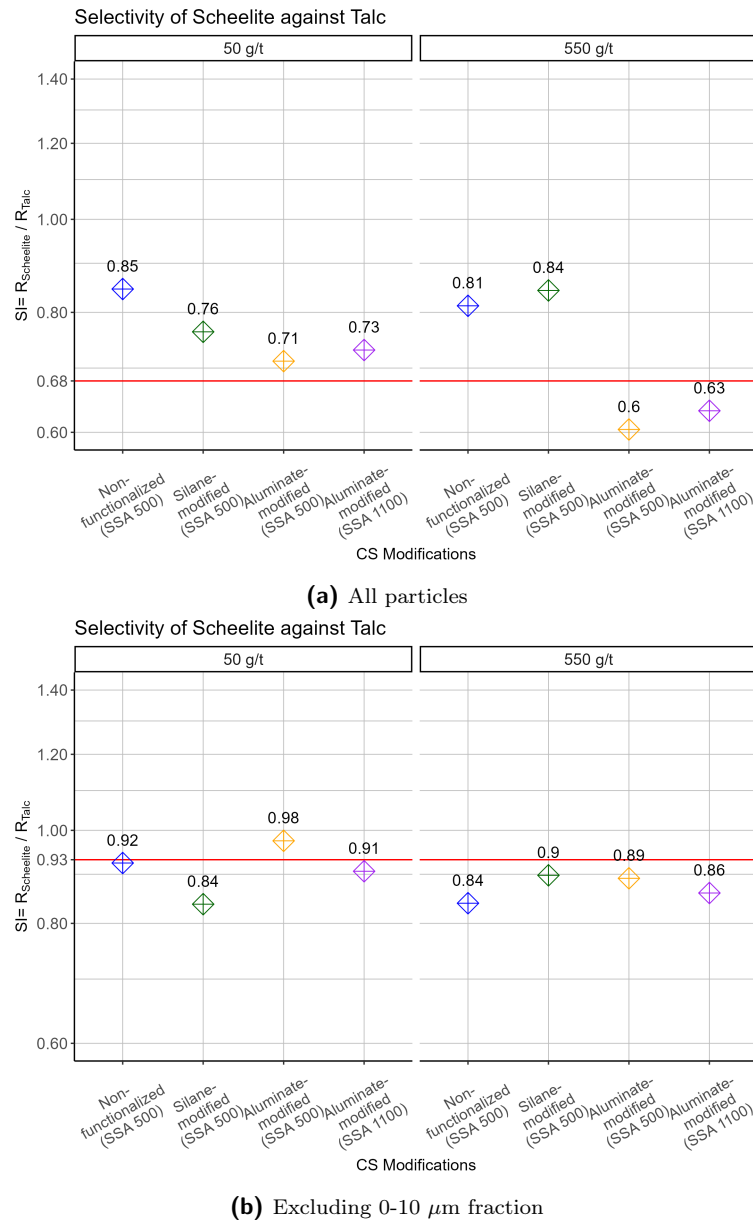


Fig. 61: Overall selectivity index of scheelite against talc, ($SI = \frac{R_{Scheelite}}{R_{Talc}}$), in different process conditions

In Figure 62, the selectivity index is calculated from the ratio of scheelite modified flotation rate constant to talc. The median values of the selectivity index are plotted in the diagram. Figure 62a shows the overall selectivity index of scheelite against talc for all particles in various CS tests. Figure 62b shows the median selectivity index of scheelite against talc for all the particles excluding 0-10 μm fractions. Taking all particles into account, a high dosage of silane-modified CS has the highest selectivity index, as seen in Figure 62a. As shown in Figure 62b, more representative median values can be evaluated excluding 0-10 μm fraction, which is up to 10% of the total weight of scheelite and talc. excluding 0-10 μm fraction, a high dosage of silane-modified CS has the highest selectivity of scheelite against talc with respect to flotation kinetics. Aluminate-modified CSs seem to not improve the selectivity, compared to benchmark tests without CS. Not including 0-10 μm fraction, higher SSA of aluminate-modified CS seems to increase the selectivity slightly with respect to flotation kinetics.

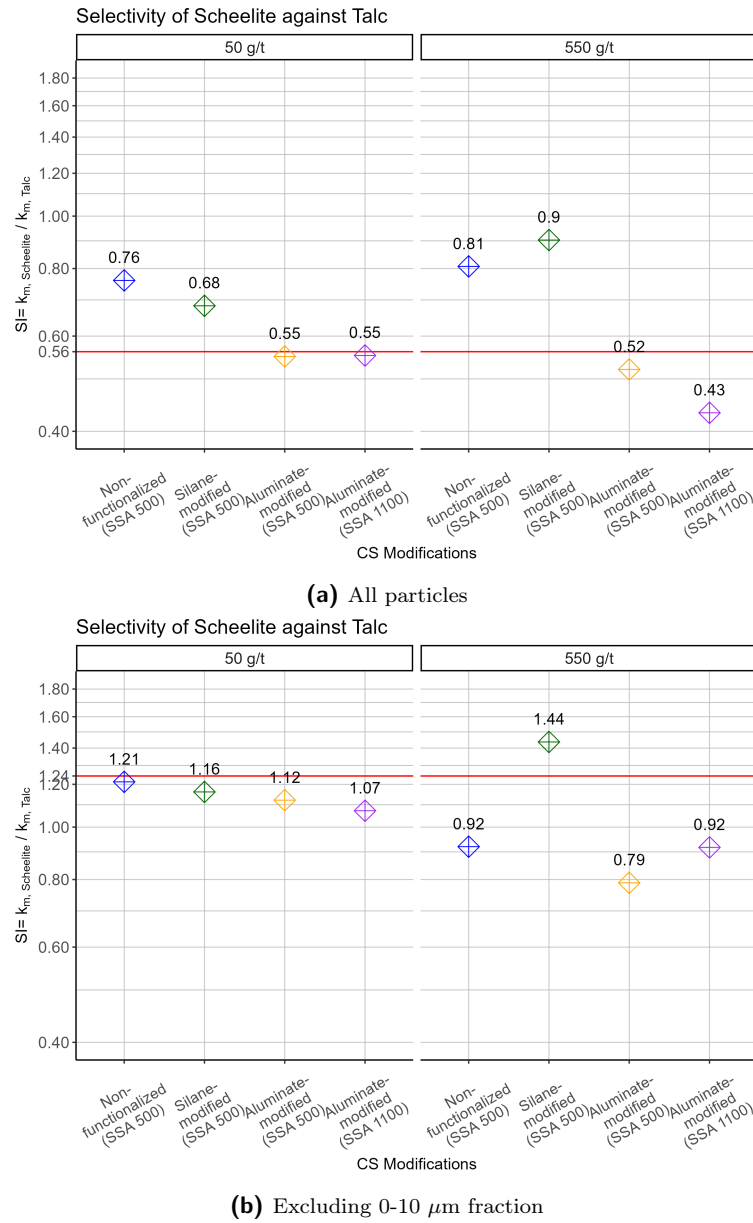


Fig. 62: Overall selectivity index of scheelite against talc, ($SI = \frac{k_{m,Scheelite}}{k_{m,Talc}}$), in different process conditions

4.4.11. Recovery, R of scheelite-bearing unliberated particles

In addition, recovery of unliberated scheelite particles can be plotted with respect to their particle size and associated gangue mineral or mineral group, as shown in Figure 63. Overall, the silicates, including micas, amphibole, and chlorite, seem to reduce the recovery of scheelite the most, whereas scheelite particles associated with calcite, talc, apatite, or any semi-soluble salt-type mineral appear to have higher total recovery.

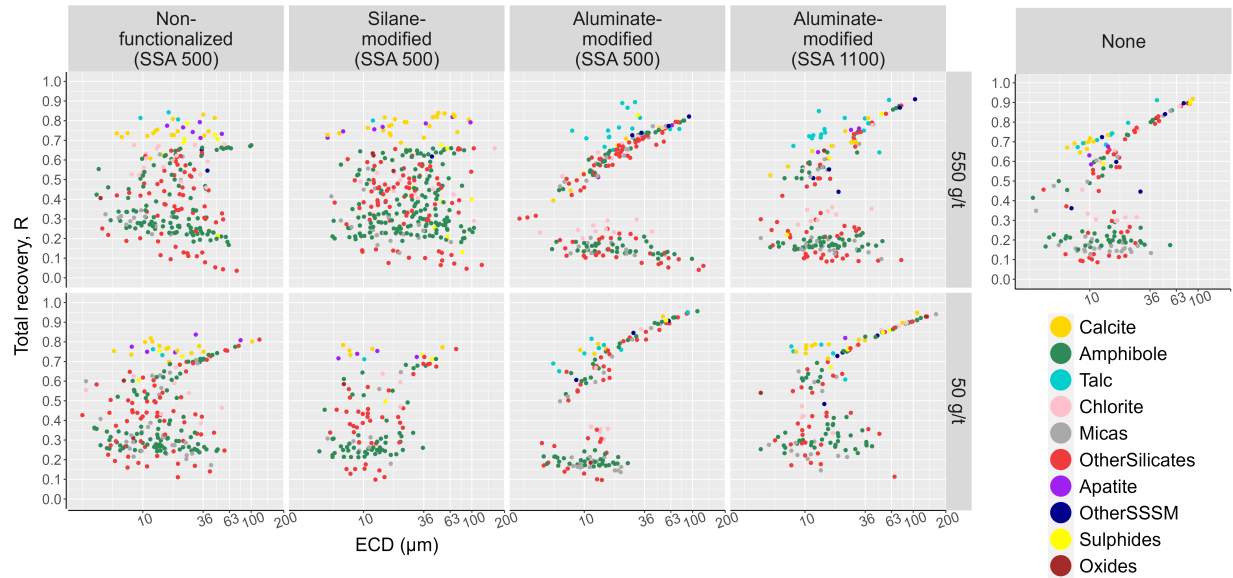


Fig. 63: Total recovery, R of scheelite-bearing unliberated particles

4.5. Qualitative analysis on the captured images from SOPAT

A trigger initiates the capture of multiple frames. With 10 triggers each capturing 150 frames, a total of 1500 images are produced from each experiment. Captured images are 2476×1980 pixels and the conversion factor is $1.74 \mu\text{m}$ per pixel, which depends on the focus position. Each captured image from the measurement covers a field of view with a diameter of about $3300 \mu\text{m}$.

Figure 64 shows the representative images from the batch flotation tests carried out at different pH values, using different CS modifications, SSA, and dosages. The following observations are made from the representative images at different conditions.

- Effect of pH & CS modifications

Images in the first three columns in Figure 64 represent the CS modifications for the same specific surface area of $500 \text{ m}^2/\text{g}$. Based on the qualitative analysis of all the captured images, no significant effect on the bubble size and coagulates was observed at both dosage and pH levels.

- Effect of colloidal silica dosage

The first row in Figure 64 represents the tests at a high dosage of CS, whereas the second row is at a low dosage. At lower dosages of CS, a relatively high number of small-sized bubbles with size $50\text{-}200 \mu\text{m}$ are observed, more pronounced at pH 8.

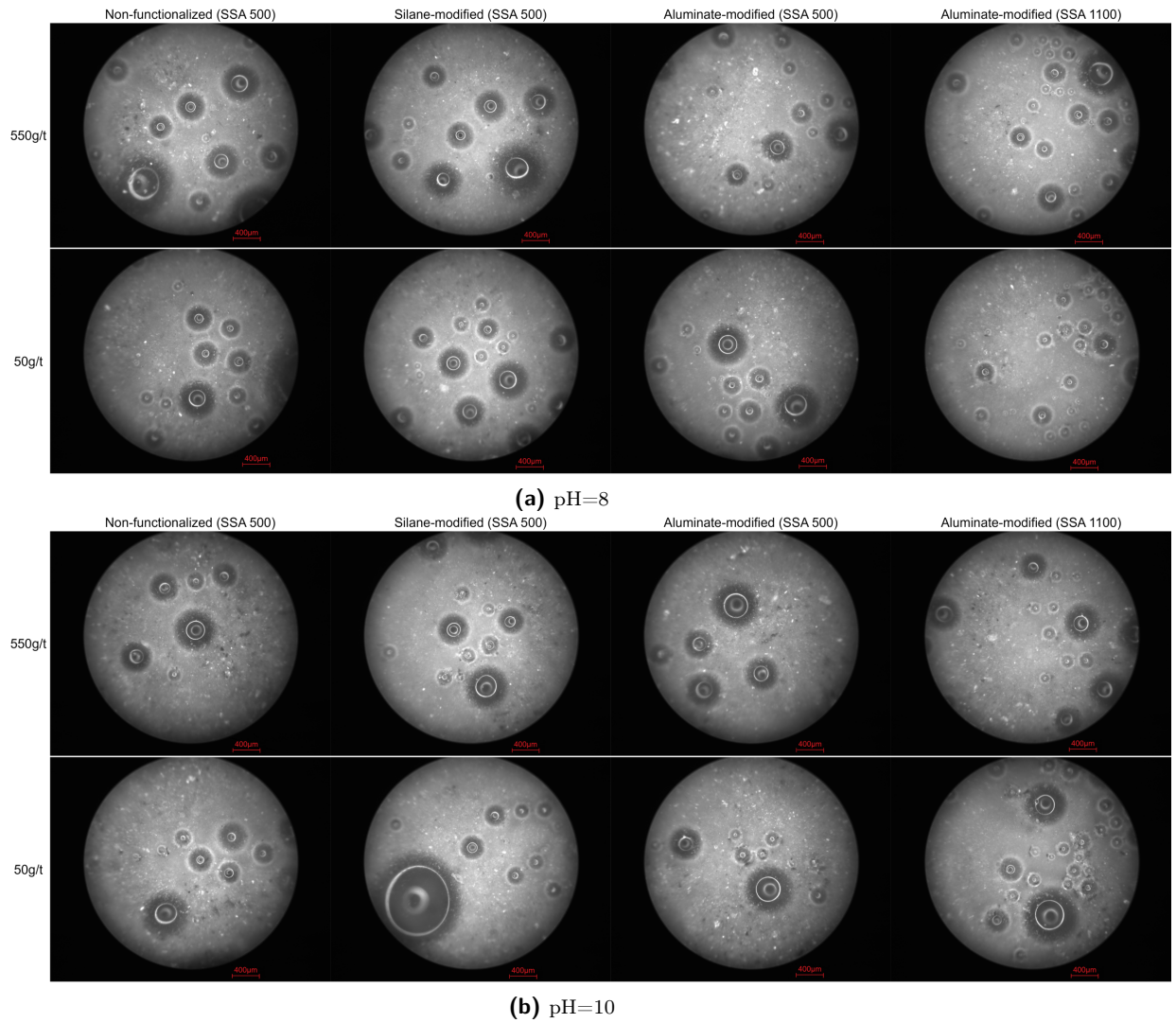


Fig. 64: Bubble-particle coagulates at different pH, CS modifications, and dosages

- Effect of colloidal silica SSA

Aluminate-modified CS with a higher specific surface area of $1100 \text{ m}^2/\text{g}$ is shown in the last column of Figure 64. Compared to the same modification with SSA of $500 \text{ m}^2/\text{g}$, a higher number of small-sized bubbles is observed. At a low dosage of 50 g/t of aluminate-modified CS with a higher specific surface area of $1100 \text{ m}^2/\text{g}$, clusters of particle-loaded bubbles are observed.

5. Discussion

5.1. Evaluation of microflotation results

Microflotation experiments for talc and hornblende were carried out to investigate the possible effect of dissolved calcium species on the main gangue minerals when CS is used. CS was already added in the calcite supernatant, under the assumption that there can be an interaction between the dissolved calcium species and CS dosage, modification, or SSA. Based on the microflotation results, the following key findings can be drawn:

5.1.1. Effect of CS modification & dosage & SSA in hornblende microflotation

As the hornblende microflotation result presented in Figure 34 suggests, both CS modifications could result in a slight increase in the recovery, whereas higher CS dosage seems to result in a slight decrease in recovery. However, these observed effects are comparatively small at <2%. Such surface modifications are said to improve the stability of CS nanoparticles, as they tend to become unstable, forming a colloidal gel. Previous studies reported that aluminate modification shifts the zeta potential to a negative direction [49], whereas silane-modified CS showed more stability, forming no visible colloidal gel in gelation tests [50]. However, in the case of hornblende microflotation tests, the observed effects of CS modification were not significant.

As presented in Figures 42 and 37, the higher specific surface area of aluminate-modified CS did not have a significant effect on hornblende recovery. Overall, in hornblende microflotation, the interaction between dissolved calcium species and CS modification, or dosage, or SSA seems to be not significant.

5.1.2. Effect of CS modification & dosage & SSA in talc microflotation

As presented in Figure 39, the CS modification effect was slightly contradicting in the microflotation of talc sample #1 and sample #3, despite their talc content being more than 90%. In sample #1, which contains 2% of chlorite, both aluminate- and silane-modified CS resulted in higher talc recovery in microflotation. On the other hand, in sample #3, the CS modification effect shifted to the negative side, more pronounced in silane modification. This could be due to the sample's mineralogical content, containing 7% kaolinite. Associated minerals seem to slightly influence the CS modification effect on talc. Considering the purity of the samples, results from sample #1 could be considered more representative, as it contains 98% talc.

Under this assumption, the result implies that CS modifications could increase the talc recovery in the microflotation scale. As for CS dosage, a higher dosage results in a slight increase in talc recovery. Nevertheless, compared to NaOl dosage, the effects of CS modification and dosage on talc recovery are rather small, staying under 4% in microflotation. As presented in Figures 42, the higher specific surface area of aluminate-modified CS did not have a significant effect.

From these results and assumptions, the following deductions can be made. The effect of CS modification and dosage is observed to be small, despite the reports that such surface modifications change zeta potential and affect the stability of CS nanoparticles [49]. It should be noted that all these experiments are carried out in supernatant. For this study, we wanted to see if there is an interaction between dissolved calcium species and CS modifications. Results from these experiments imply that, in microflotation dissolved calcium species' effect on talc

recovery is not significantly affected by CS modification, dosage, or SSA. However, a slight positive effect for both modifications and higher dosage can be present.

5.1.3. Effect of calcite supernatant in hornblende and talc microflotation

The main goal of the hornblende and talc microflotation experimental study was to investigate the dissolved calcium species' effect on the recovery of these gangue minerals. To mimic the environment with dissolved calcium species, calcite supernatant was prepared and used through the experiments.

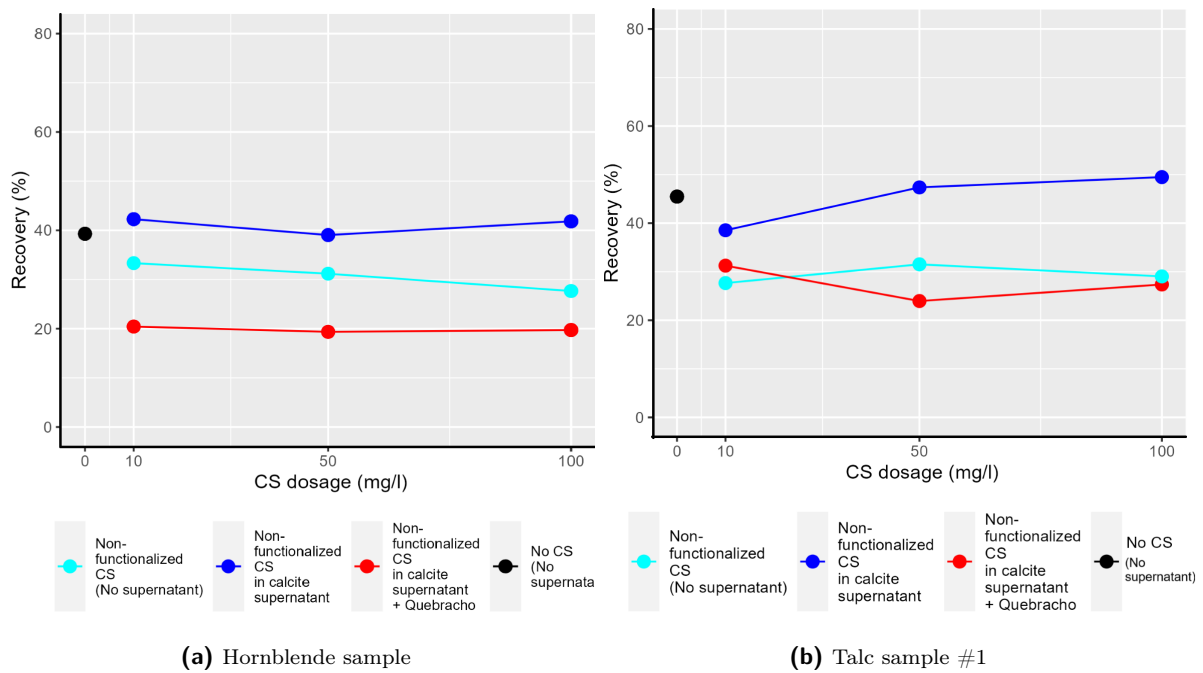


Fig. 65: Effect of calcite supernatant in hornblende and talc microflotation

As shown in Figure 65, microflotation tests with non-functionalized colloidal silica in calcite supernatant resulted in higher recovery, compared to the test with the same CS, but without calcite supernatant. This effect is observed more significant in talc microflotation than in hornblende. The fact that with calcite supernatant we see an increase in recovery can imply one of these two things:

- **Scenario 1: Dissolved calcium species are formed**
The implication from this scenario is that dissolved calcium species could be affecting the flotation behaviour of gangue minerals, such as hornblende, and talc. Hornblende and talc are silica-containing complex minerals. A previous study suggested that silica surfaces could be activated through calcium species absorption and get subsequently collected by fatty acid collector [4]. Similarly, microflotation results can imply that calcium ions derived from calcite supernatant could be affecting the microflotation when CS is used, as the usage of calcite supernatant resulted in higher recovery in both hornblende and talc microflotation tests.
- **Scenario 2: No calcite is dissolved, and microflotation tests are carried out with no dissolved calcium species**

As previously presented in Figures 35 and 40, calcite supernatant effect is the lowest for silane-modified CS in microflotation tests. This can imply that without and with supernatant experiments for silane-modified CS were in the same condition. No dissolved species were formed and silane-modified CS is recovered well during filtration due to its higher stability, and good dispersion [50]. For silane-modified CS tests, calcite supernatant contained CS particles and no dissolved calcium species, similar to the test without supernatant.

On the other hand, non-functionalized and aluminate-modified CSs have more tendency to aggregate more and are less likely to recover in calcite supernatant solution after filtration. For these CS tests, the prepared calcite supernatant contained no or less CS and no dissolved calcium species. Thus, a significant calcite supernatant effect was observed for non-functionalized and aluminate-modified CSs. This can be mainly due to the depression of the effect of non-functionalized or aluminate-modified CS itself rather than the formation of dissolved calcium species.

In order to examine the adsorption of calcium species on the mineral surface of hornblende and talc, a calcium species depressant was added in additional tests. Quebracho is known as an excellent depressant for calcium-bearing species and if calcium species are adsorbed to these minerals, theoretically there could be depression. Quebracho is added in the tests with calcite supernatant to see how it affects the recovery of these minerals. When quebracho is added to the recovery of both minerals decreases sharply. It can be assumed that quebracho is absorbed by calcium species before the collector and causes a depressant effect. However, it is unknown whether this effect of quebracho comes from the depression through absorbed calcium species on the mineral surface or from the depression of these minerals themselves.

5.1.4. Effect of talc mineralogical composition on microflotation response

The unexpected complication that arose during the talc microflotation work was the alternating chemical compositions of soapstone samples, which consist primarily of talc. As seen in Figure 38b, the soapstone samples had a distinguishable different appearance and mineralogical composition, as the XRD analysis suggests. Even though samples #1 and #3 had high talc content of more than 93-98%, their associated minerals in the composition were chlorite, and kaolinite, respectively. Despite the high amount of talc content, these two minerals had relatively different responses. For instance, the CS modification effect was positive for sample #1 and, negative for sample #2. This can imply that chlorite and kaolinite have different interactions with colloidal silica modifications if they are located on the mineral surface.

As presented in talc microflotation test results, the effect of most controlled parameters was observed to be the lowest in talc sample #2, which has a mineralogical composition of 53.5% talc and 46.5% clinocllore. From this, a hypothesis could be drawn, that these two minerals in the composition of sample #2 have different responses. To test this hypothesis, additional experiments with the changed order of sodium oleate and quebracho are carried out, as shown in Figure 66. Consequently, the changed order did not result in a significant difference in sample #2. On the other hand, for samples #1 and #3, a significant difference in recovery is observed when the order of quebracho and sodium oleate is switched, which is consistent with previous reports [7] [53]. Therefore, as the results suggest, a possible influence of associated minerals could be present on talc recovery in microflotation.

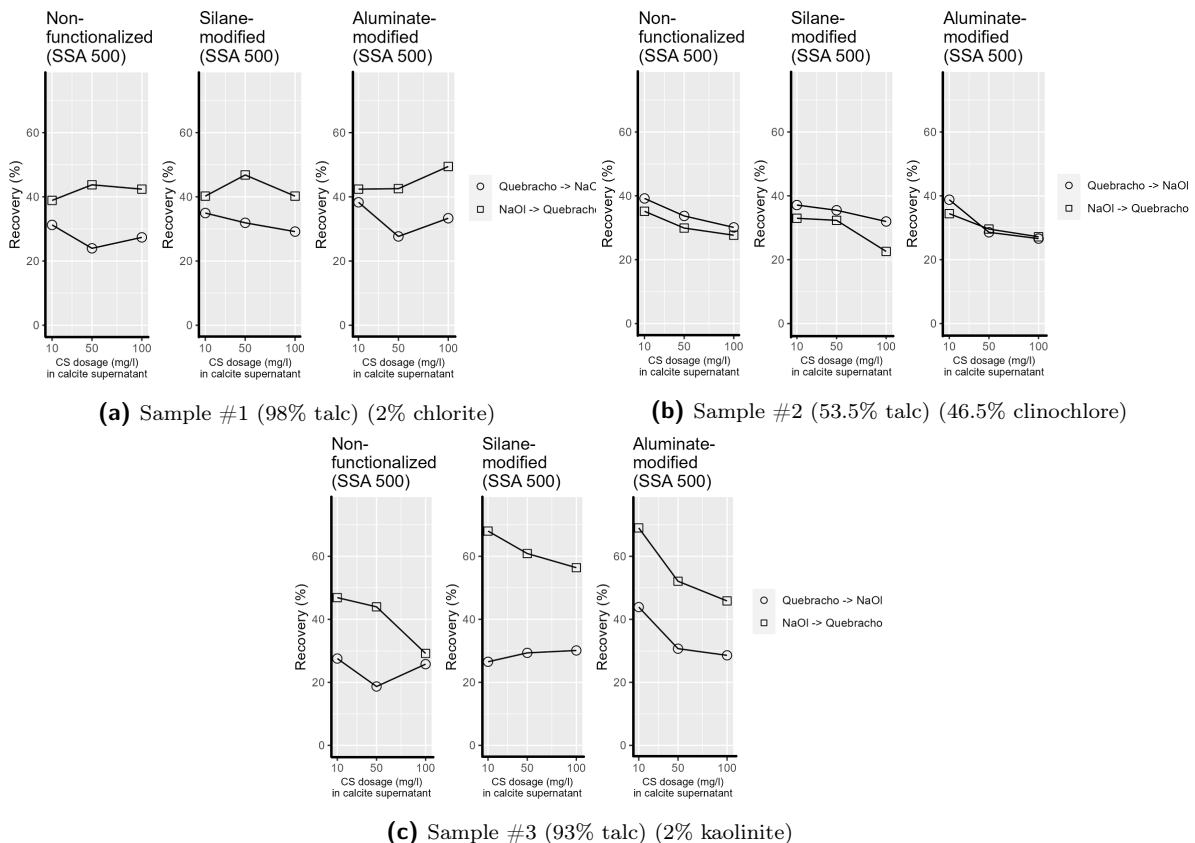


Fig. 66: The effect of changed order on different talc samples

5.2. Evaluation of particle-based model results

Microflotation experiments on pure minerals provide information on only limited micro-processes, compared to actual flotation. In pure mineral microflotation, effects due to bubbles in pulp, froth zones, and interaction between other minerals are not considered. However, the particle-based kinetic model is able to provide more insight into the process on a batch flotation scale.

5.2.1. Effect of CS modification, dosage & SSA in scheelite batch flotation

To understand how colloidal silica modification and dosage affect the flotation kinetics of the main minerals in scheelite batch flotation, the particle-based model was created based on MLA data. The model gives a comprehensive insight into how CS modification, dosage, and SSA are affecting each mineral group. As presented in Figure 49, modified flotation rate constants of scheelite and calcite appear to have relatively similar responses to colloidal silica across different modifications and dosages. The lowest calcite modified flotation rate constant is achieved at a high dosage of aluminate-modified CS (SSA 500), while a slight decrease in scheelite flotation rate is observed as well, compared to the benchmark test without CS.

However, if we take a look at the total recovery in Figure 48, the lowest total recovery of calcite is again observed at a high dosage of aluminate-modified CS (SSA 500). A possible selectivity of scheelite from calcite seems to present based on the kinetic model of the batch flotation tests. Considering the depressing effect of CS on calcite over scheelite, aluminate modification seems to improve colloidal silica performance at high dosages, compared to non-functionalized CS of the same SSA. In the case of silane modification, it appears to be not the case. A previous study reported that a high concentration of aluminate-modified CS can aggregate and form a gel network [49]. The formation of a gel network from colloidal silica could be keeping particles in the pulp zone, preventing possible attachment to the bubbles. This could explain why we see a decrease in recovery of certain minerals for high dosage application of aluminate-modified CS. Alternatively, there could be a selective adsorption mechanism, based on the electrostatic interaction between calcium cation surface and negatively charged colloidal silica. Aluminate modification reportedly results in more negative zeta potential, and this can enhance the adsorption possibility [49]. However, the exact mechanism of observed higher selectivity between scheelite and calcite for aluminate-modified CS remains unclear.

A higher specific surface of aluminate-modified CS was employed in the batch flotation test and a noticeable effect was observed in the flotation kinetics. For calcite, higher SSA of aluminate-modified CS resulted in a higher modified flotation rate constant at both dosage levels. Interestingly, for scheelite, high dosages of both aluminate-modified CSs with different SSA had roughly the same modified flotation rate constant, as previously seen in Figure 49. On the other hand, the total recovery values of scheelite and calcite seem to increase with a higher specific surface area of CS, as seen in Figure 48.

Based on the particle-based model, aluminate-modified CSs in high concentration seem to selectively depress calcite more, as previously presented in Figures 57b and 58b. With respect to total recovery, a high dosage use of aluminate-modified CS (SSA 500) yields the highest selectivity of scheelite against calcite. On the other hand, with respect to flotation kinetics, a high dosage use of aluminate-modified CS (SSA 1100) yields the highest selectivity of scheelite against calcite.

5.2.2. Effect of CS modification, dosage, & SSA on entrainment of amphibole group in batch flotation

Looking into the amphibole recovery alone, the addition of colloidal silica seems to increase the overall recovery probability even at low dosage, as seen in Figure 50. The only exception seems to be the high dosage of aluminate-modified CS, lowering the entrainment back to the level of the test without colloidal silica or even lower. However, this pronounced depressing effect of aluminate-modified CS at high dosage was not observed in hornblende microflotation.

Observed differences can be due to other micro-processes happening in the pulp and froth zones that are affecting the entrainment of such silicates. Moreover, the potential effect of dissolved calcium species in the pulp can be the reason why we see the difference in batch flotation, as the microflotation test results with calcite supernatant suggested.

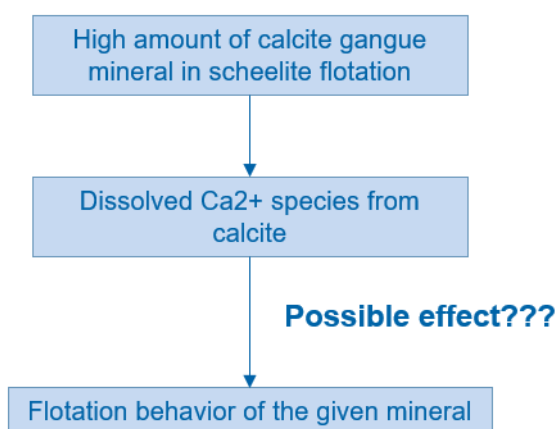


Fig. 67: Possible effect of dissolved calcium species

In addition, batch flotation and microflotation tests were performed at different pH and this may have caused a degree of uncertainty. For consistency with previous studies, microflotation tests are carried out at pH 8, whereas MLA samples are from the batch flotation tests carried out at pH 10.

As seen in Figure 59b, a high dosage of aluminate-modified CS (SSA 500) appears to have the highest selectivity of scheelite against the amphibole group with respect to their total recovery. On the other hand, with respect to flotation kinetics, a high dosage of aluminate-modified CS (SSA 1100) has the highest selectivity of scheelite against the amphibole group, as shown in Figure 60b.

5.2.3. Effect of CS modification, dosage, & SSA on talc in batch flotation

Comparing talc recovery alone, aluminate-modified CS (SSA 500) seems to have a slight negative effect on talc recovery, especially at a high dosage, as previously presented in Figure 48. In these batch flotation tests, the CS dosage effect appears to be significant for aluminate-modified CS, whereas for non-functionalized and silane-modified CS, it is not the case. However, this contradicts the result from talc microflotation tests, where CS modification and dosage effect were slightly positive.

Contradicting results can be due to the effect of other micro-processes happening in pulp and froth zones of batch flotation. It was previously reported that bubble size significantly influences talc recovery based on an experimental study in column flotation [67]. As the microflotation test is limited regarding the effect of bubble size, this could be the reason why there are differences in batch flotation results. Moreover, the calcite supernatant effect was relatively significant in talc microflotation, which means the effect of dissolved calcium species might be causing a different response in the batch flotation.

In addition, it should be noted that talc content in the tests for batch flotation was not the same, due to having two batches of samples. This brings uncertainty to the results from non-functionalized and silane-modified CS tests, as they had a significantly low content of talc in the feed sample.

As reported in talc microflotation, a higher specific surface of aluminate-modified CS did not have a significant effect on the talc recovery. Similarly, in batch flotation, higher SSA of aluminate-modified CS seems to have no significant effect on the maximum recovery of talc particles.

Looking into the selectivity of scheelite against talc for particles more than 0-10 μm , high dosages of aluminate-modified CSs seem to slightly decrease the selectivity index of scheelite against talc, compared to test without CS, as previously presented in Figure 61b. Moreover, higher CS dosage of aluminate-modified CSs seem to decrease the selectivity index of scheelite against talc.

The selectivity index is defined in two ways, calculated either from the total recovery or from the modified flotation rate constant. With respect to these two parameters, different effects of CS modification are observed in particle-based results. Comparing the total recovery values, a high dosage of aluminate-modified CS (SSA 500) seems to bring the biggest improvement in the selectivity of scheelite against both calcite and amphibole groups. On the other hand, considering the modified flotation rate constants, aluminate-modified CS (SSA 1100) has the highest selectivity of scheelite against calcite and amphibole group.

These two definitions of the selectivity index apply to different process designs. For a batch flotation process or tests, the total recovery is often used as a measure of the process efficiency. However, for a continuous process design of froth flotation, flotation kinetic has a significant influence on the total recovery. In the industry, it is common that flotation is carried out in a continuous design, with a series of cells and the residence time of the particles in each cell is limited [68]. Therefore, the more comprehensive parameter for flotation efficiency is the selectivity index calculated from the modified flotation rate constants (k_m), where the flotation kinetic is taken into account [69].

5.3. Evaluation of SOPAT results

5.3.1. Effect of CS specific surface area on particle-bubble hetero-coagulates

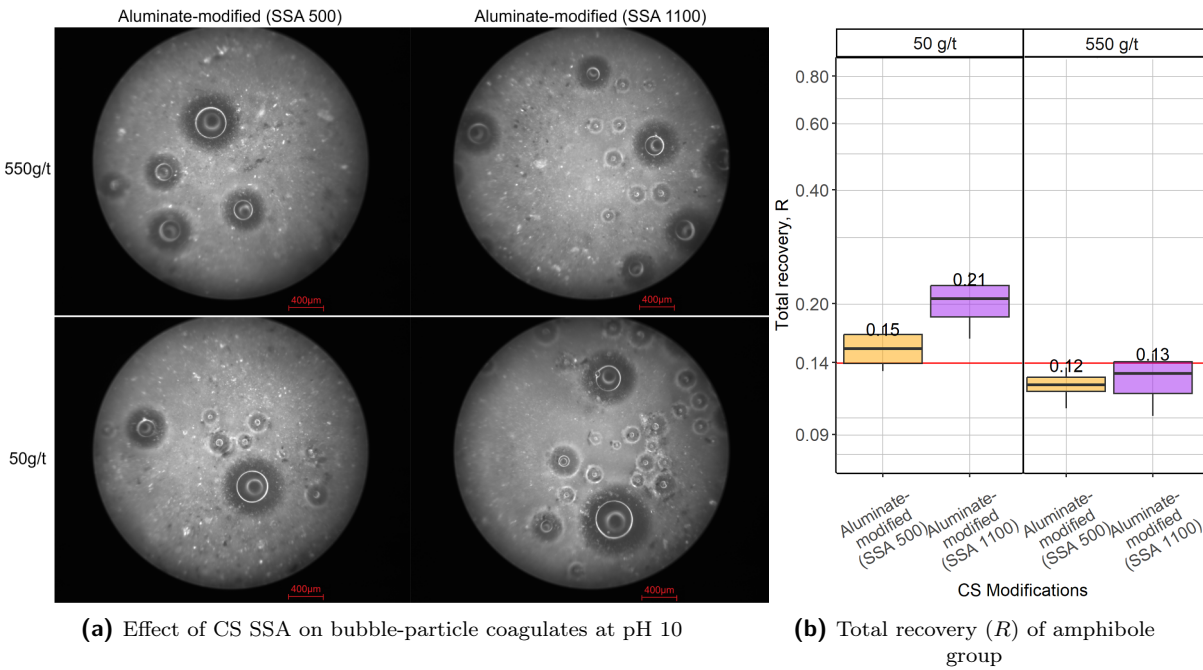


Fig. 68: Observed entrainment of particles due to clusters of particle-bubble coagulates

As seen in the captured images, the pulp zone with higher SSA of aluminate-modified CS appears to have a high number of small bubbles closely packed together. Such coagulates are observed more for low dosage of aluminate-modified CS (SSA 1100) at pH 10, whereas in tests with aluminate-modified CS (SSA 500), these coagulates are not seen. Particle-bubble coagulates appear to form a cluster, where fine particles are entrained. These clusters of closely packed particle-bubble aggregates appear to be the reason why an increase in amphibole recovery is observed at a low dosage of aluminate-modified CS (SSA 1100), as shown in Figure 68.

The rise of such closely-packed particle-bubble coagulates in the pulp zones possibly causes higher entrainment of gangue minerals, including the amphibole group. A close-up of bubble-particle coagulates observed in the test for aluminate-modified CS (SSA 1100) is shown in Figure 69. Loaded bubbles, with sizes ranging from 120-270 μm , are captured in the example image, and dark-coloured, presumably, silicate particles appear to be attached to the bubbles. Some particles seem to be attached to multiple loaded bubbles, keeping them together. This formation can be due to capillary forces and electrostatic interaction between particles on the bubble and the particles in between. Similarly, previous publications suggested that smaller bubble-size distribution could increase bubble-particle collision probability, causing higher recovery of gangue minerals in scheelite froth flotation [49].

Moreover, particle size distribution has a significant impact on scheelite recovery, as scheelite has a brittle property and thus can be readily overground [13]. It was reported that particle size is a significant factor in scheelite flotation performance, as the finer fractions ($<10\ \mu\text{m}$) exhibited significantly lower recovery [13]. This was observed in the result from the particle-based model as well, as the selectivity of scheelite particles with a size of less than $<10\ \mu\text{m}$ was significantly lower.

Therefore, the determination of bubble and particle size distributions in the pulp is necessary to understand the process behaviour in different conditions. Using the captured images from the inline probe of SOPAT, the quantitative investigation on the bubble & particle size distributions and bubble-particle coagulates can be done for further research.

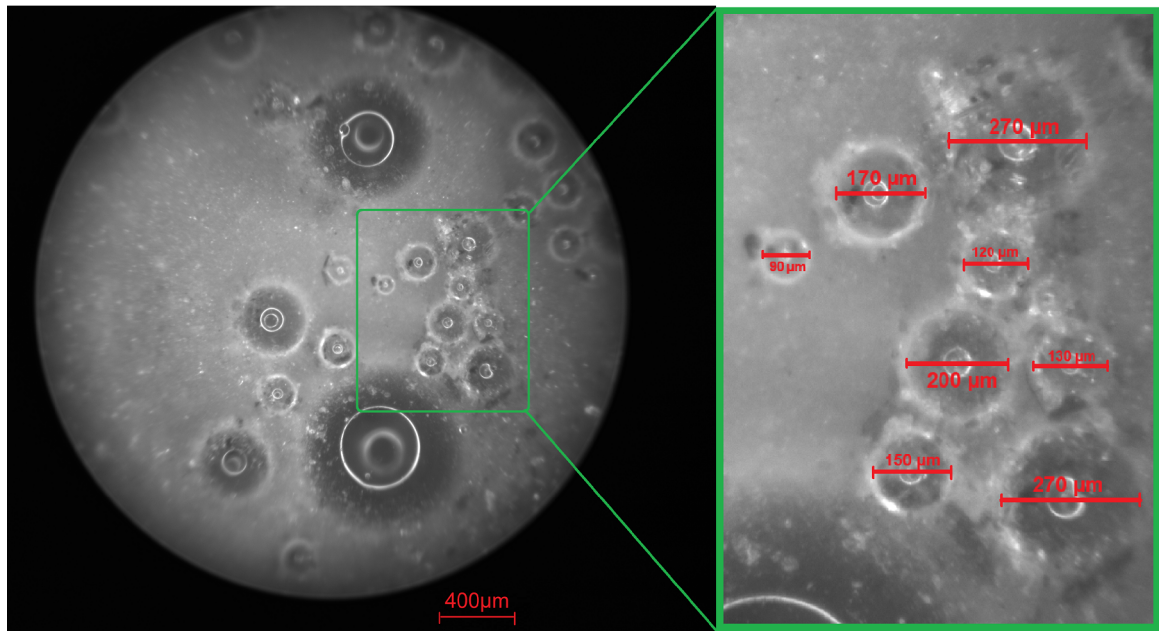


Fig. 69: Close-up of observed bubble-particle coagulates

6. Conclusion and recommendations

6.1. Conclusion

To investigate the effect of dissolved calcium species from calcite on the recovery of gangue minerals in scheelite flotation, a series of experiments are carried out with the aid of DoE on a microflotation scale. To mimic this pulp environment, calcite supernatant was used for the microflotation of hornblende and talc, which are one of the main gangue minerals in scheelite flotation. For both talc and hornblende, a certain degree of calcite supernatant effect is observed in microflotation. The observed calcite supernatant effect can be due to the activation of the mineral surface in the presence of calcium ions. Slight CS modification and dosage effects were observed; however, the effect was not significant compared to the calcite supernatant effect. In the case of aluminate-modified CS, SSA seems to not have a noticeable effect on the talc and hornblende microflotation.

Although microflotation gives empirical information on how pure minerals respond to the process condition, it is limited in mimicking the actual interactions happening in real flotation. Therefore, results from batch flotation experiments were employed for the particle-based kinetic model, where comprehensive insight into the flotation behaviour of minerals with respect to their particle properties. Observed recovery from MLA measurement and predicted recovery from particle-based model matched when comparing the main minerals. With respect to recovery, a high dosage of aluminate-modified CS (SSA 500) appears to have the highest selectivity index of scheelite against calcite and amphibole group, reaching values of 1.6 and 12.7, respectively. However, with respect to both flotation kinetics and recovery, a high dosage of aluminate-modified CS (SSA 1100) has the best selectivity of scheelite against calcite and amphibole group, reaching the selectivity indices of 1.6 and 12.7, respectively.

Moreover, clusters of particle-bubble coagulates were observed at lower concentrations of aluminate-modified CS (SSA 1100) using the SOPAT system. Such an image measurement system with an inline probe could be applicable for the determination of bubble size distribution and investigation of the particle-bubble coagulates for batch flotation tests.

6.2. Recommendations

A calcite supernatant effect was observed in microflotation tests; however, whether the effect comes from the dissolved calcium species remains unclear. Therefore, further investigation of the dissolved calcium species is advised. The amount of generated calcium species in calcite supernatant can be determined, for example using UV-vis spectroscopy.

Quantitative investigation on the particle-bubble coagulates is possible for further investigation. With proper image analysis tools, images generated from SOPAT can provide information about bubble and particle size distributions.

A. Appendix

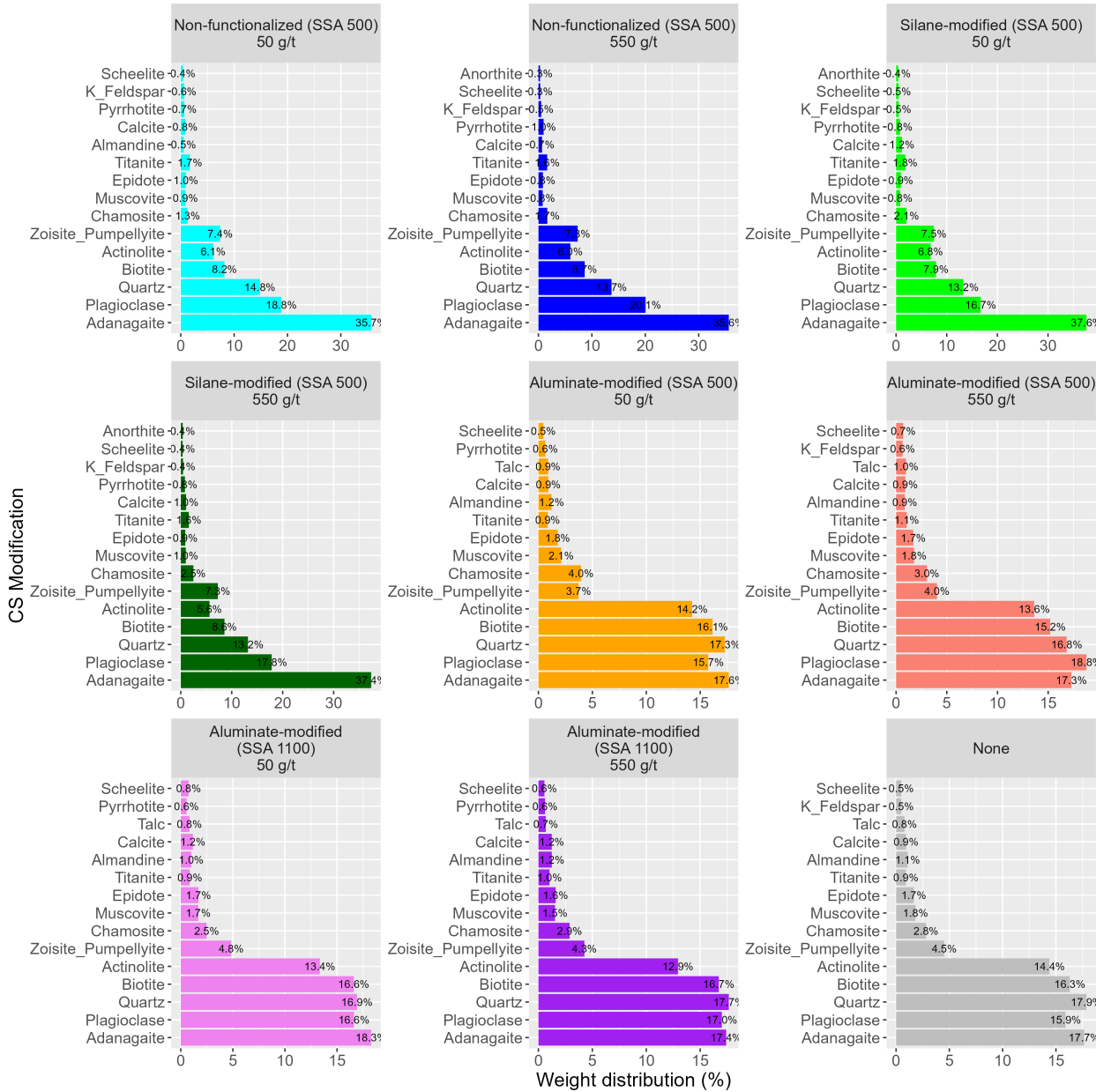


Fig. A.1: Mineralogical composition of the batch flotation feed samples based on MLA

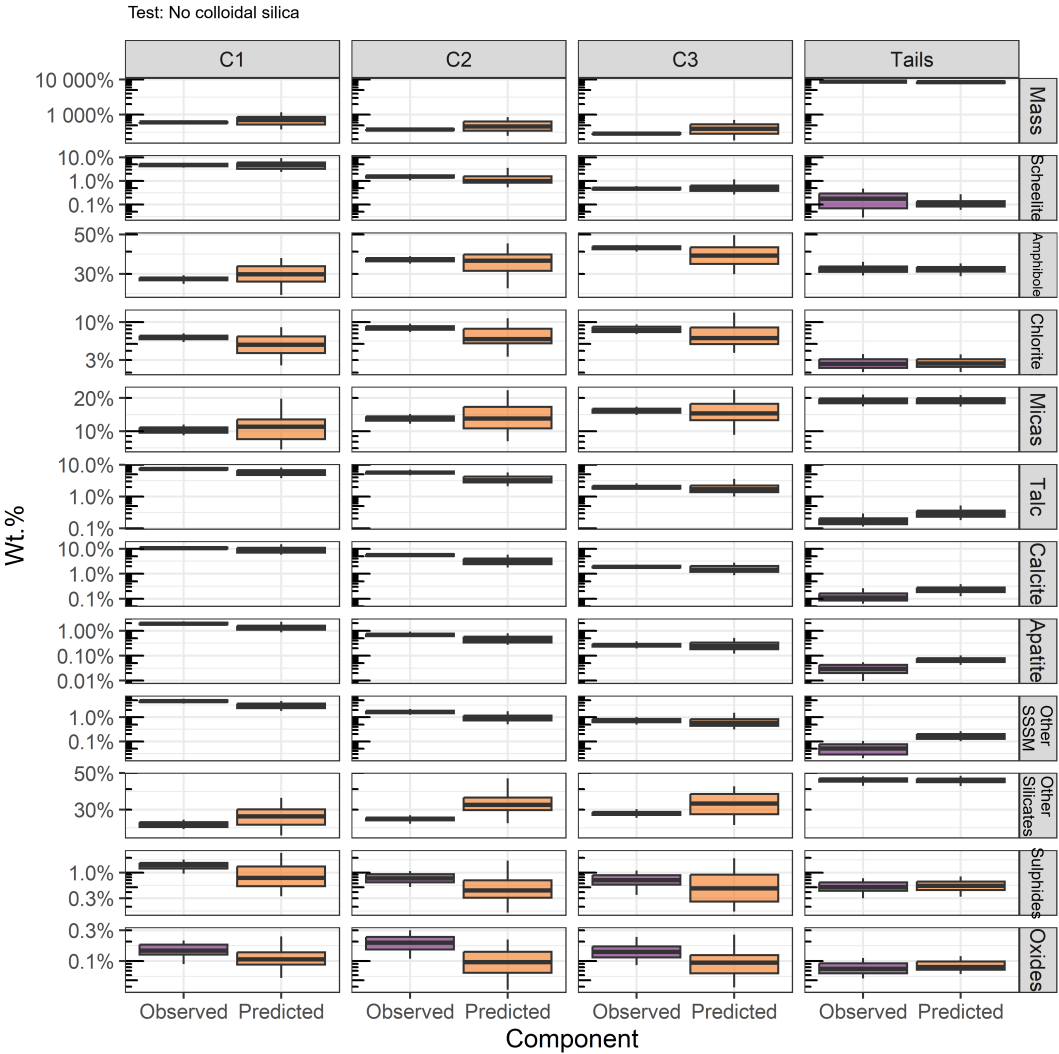
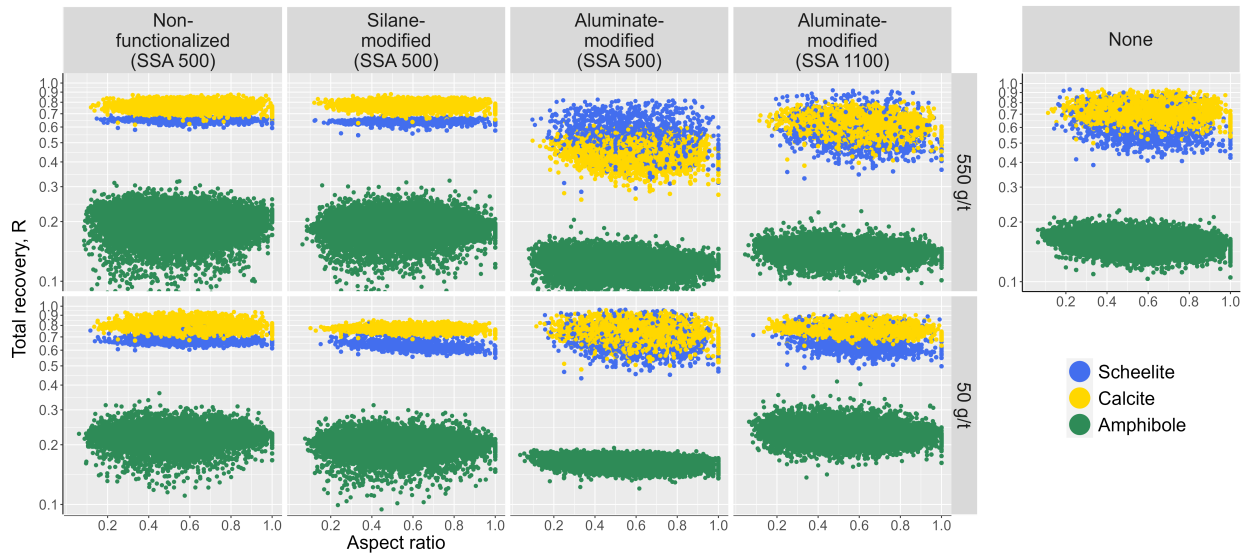
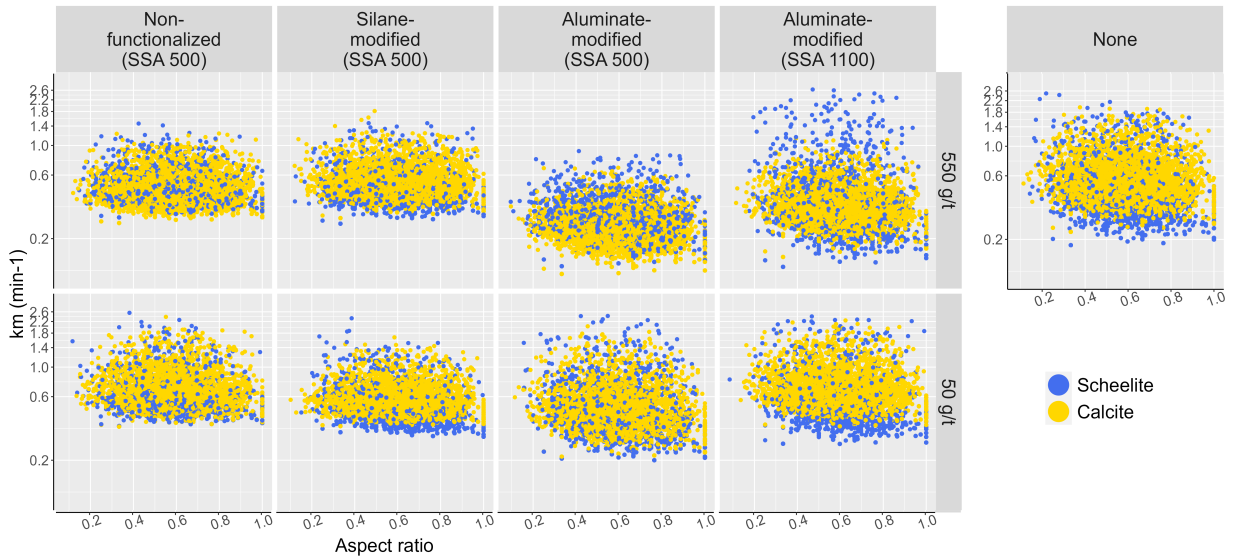


Fig. A.2: Comparison between predicted and observed masses of different mineral groups for the flotation products in test without colloidal silica

(a) Total recovery (R)(b) Modified flotation rate constant ($k_m = k \cdot R_{max}$)**Fig. A.3:** Flotation kinetic of the main minerals respect to aspect ratio

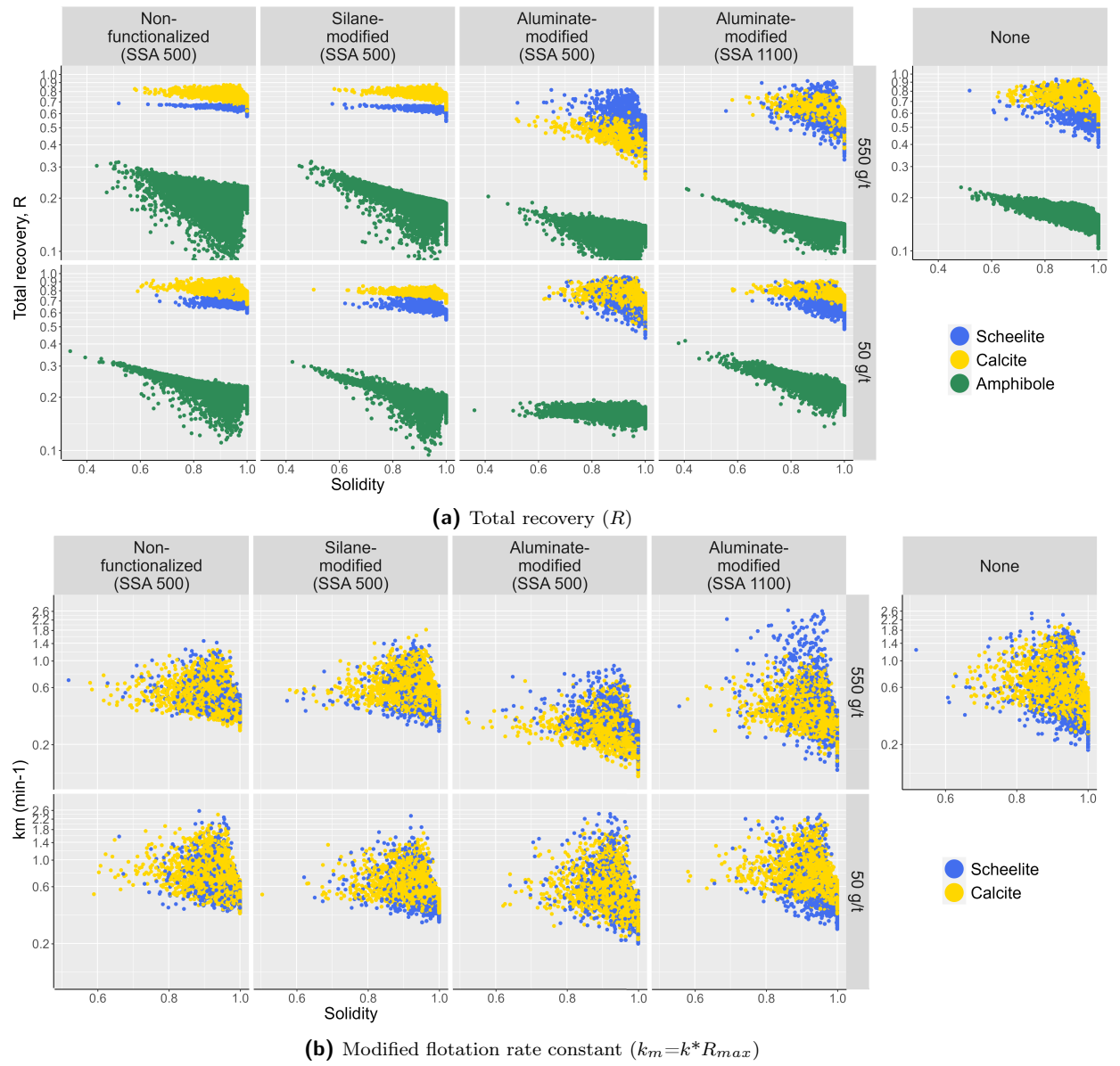


Fig. A.4: Flotation kinetic of the main minerals respect to solidity

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