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FÜR RESSOURCENTECHNOLOGIE

## **Master Thesis**

# **Fundamental Study of Separation of Scheelite Mineral Originated from a European Mine with Froth Flotation Method Using Colloidal Silica**

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## **Declaration**

Hereby, I formally declare that I have developed and written the enclosed thesis without illegitimate help of third party and that no other than the indicated aids have been used for its completion; all thoughts from other sources that have been used literally or indirectly are marked as such. The thesis has not been submitted to any other examination committee in this or similar form

**14 June, 2024**

**Muzammil Nazir**

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## **Abstract**

Tungsten is a valuable critical metal for industrial application, it is considered as a critical raw material in processing stage by the European Unions. The processing of the scheelite faces challenges due to its similar surface properties with the calcite. This research is carried out to study the selective flotation of scheelite against calcite using colloidal silica as reagent, scheelite ores are originated from the European mine. Previously, it was investigated that aluminated modified silica shows selective flotation of scheelite against calcite based upon the specific surface area of CS and particle size distribution of scheelite ores. This study involves the application of gravity separator to produce the feed for batch flotation and measurement of surface charge of reagents. The aim of the study is to improve the scheelite and calcite selectivity.

## Abbreviations

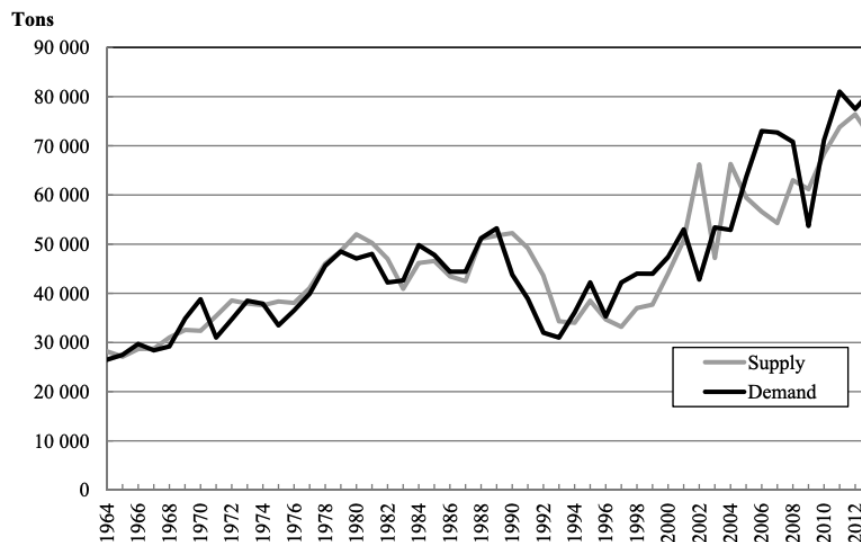
|              |                                         |
|--------------|-----------------------------------------|
| <b>CS</b>    | Colloidal Silica                        |
| <b>SSA</b>   | Specific Surface Area                   |
| <b>HBU</b>   | Hornblende Units                        |
| <b>MVU</b>   | Meta volcanic units                     |
| <b>DLVO</b>  | Derjaguin, Landau, Verwey, and Overbeek |
| <b>ODPB</b>  | Octadecyl pyridinium bromide            |
| <b>DoE</b>   | Design of Experiments                   |
| <b>NF</b>    | Non-functionalized                      |
| <b>S_CS</b>  | Silane-modified Colloidal Silica        |
| <b>Al_CS</b> | Aluminate modified Colloidal Silica     |
| <b>HIF</b>   | Helmholtz Institute Freiberg            |
| <b>HZDR</b>  | Helmholtz Zentrum Dresden Rossendorf    |
| <b>SI</b>    | Selectivity Index                       |
| <b>Hz</b>    | Hertz                                   |
| <b>pXRF</b>  | Portable X-ray Fluorescence             |

## 1 Introduction

Tungsten is a tactical metal due to its substantial applications in the military and various industries. Tungsten is helpful in industrial uses due to its strength and stability against high temperatures as individual elements and alloys (Arora & Gopal Rao, 2004). Cutting tools, and steel hardening are common uses for tungsten. Subsequently, it uncovers its application in the mining, metalwork, exploration, construction, and aerospace sectors (Dvořáček et al., 2017).

The source of tungsten is mined ores, which are extracted from underground mines and contain minerals like scheelite and wolframite. Stockpiles reserves of tungsten that were generated previously by mining companies at times of difference between supply and demand or by authorities for strategic reasons. China, Russia, and the United States are a few nations that have large tungsten reserves (Dvořáček et al., 2017).

In Figure 1.1, difference between the global supply and demand of tungsten can be seen. This difference is coming out because of the economic growth in the world (Shen et al., 2019).



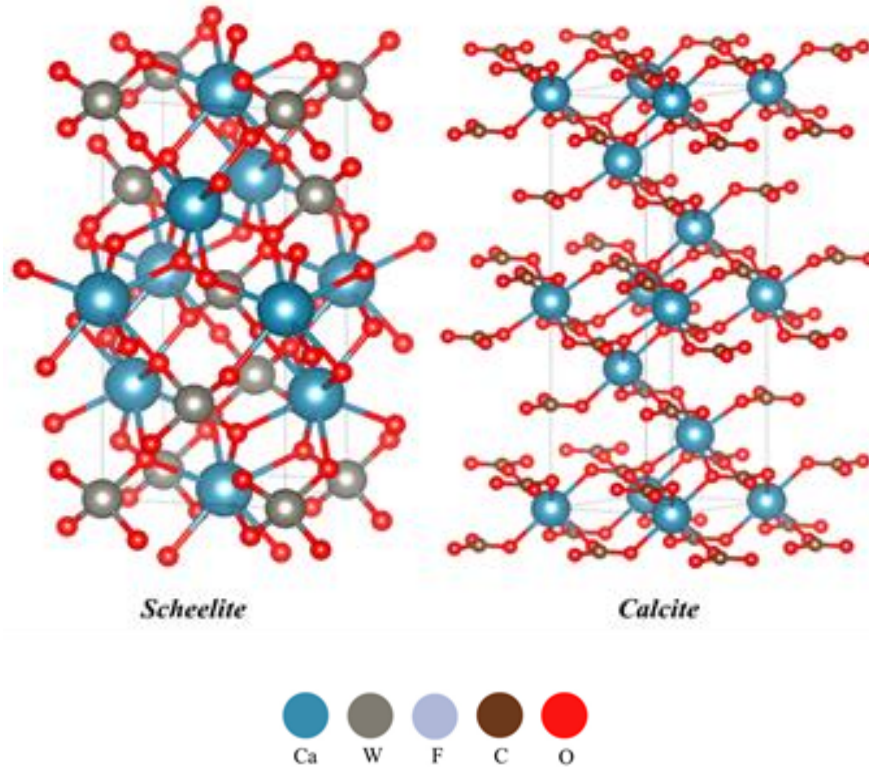
**Figure 1.1:** Global tungsten (W) supply and demand (Dvořáček et al., 2017)

## 1.1 Problem Statement

To produce high-grade tungsten concentrate, the naturally occurring tungsten-bearing minerals must be processed through mineral processing technique. Because tungsten resources are becoming more complex, the  $\text{WO}_3$  content of tungsten concentrates is currently dropping to 50% or even less. Scheelite combines occasionally with wolframite, is the main raw material used to extract tungsten due to the gradual depletion of wolframite ore over the past few decades (Shen et al., 2019). Currently, 430,000 tons of ore has been annually mined with an average grade of 0.38 %  $\text{WO}_3$ . (Gaul, 2008).

Raw materials are decisive for European economy, ensuring jobs and competitiveness. The list of critical raw material for European Union (EU) and a methodology for assessing their criticality, issued by the European Commission (EC), which are essential for the raw materials policy of EU (Blengini et al., 2017). The report of EU on the critical raw materials has included tungsten in this since 2020. The report specifies that tungsten, which falls in the Iron and Ferro-alloy metals group is a critical raw material in the processing stage. China is the key supplier of tungsten for EU, having an 86% share in the market (European Commission, 2020, 2023)

The most common method for the processing of tungsten ores is froth flotation (Mohammadnejad et al., 2018). The main barrier in the flotation of the scheelite is the presence of calcite and gangue minerals (Kupka, Babel, et al., 2020). Calcium-containing minerals show comparable responses to collectors and comparable surface characteristics to scheelite e.g. solubility, surface properties, and zeta potential (Kupka & Rudolph, 2018). Calcite has similar surface properties to scheelite, coming out with significant problems for effective flotation separation of scheelite as shown Figure 1.2 (Foucaud et al., 2020; Yang, 2018; Yao et al., 2023; Yin et al., 2014).



**Figure 1.2:** Surface structure of scheelite and calcite (Lu et al., 2023)

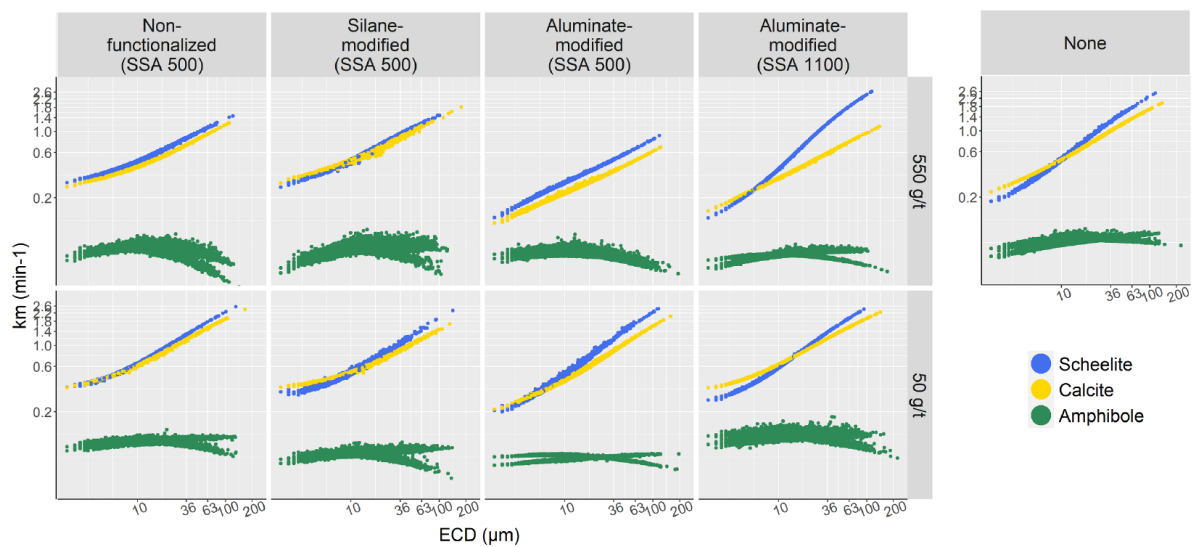
**Table 1.1:** Surface structure parameter of scheelite and gangue minerals (Lu et al., 2023)

| Mineral                               | a           | b | c        | $\alpha, \beta, \gamma$                                           | Space group |
|---------------------------------------|-------------|---|----------|-------------------------------------------------------------------|-------------|
| Scheelite (tetragonal crystal system) | a=b=5.243 Å |   | 11.376 Å | $\alpha = 90^\circ$<br>$\beta = 90^\circ$<br>$\gamma = 90^\circ$  | I41/a       |
| Calcite (tripartite crystal system)   | a=b=4.988 Å |   | 17.061 Å | $\alpha = 90^\circ$<br>$\beta = 90^\circ$<br>$\gamma = 120^\circ$ | R3c         |

The separation of calcium-bearing gangue minerals, mainly calcite ( $\text{CaCO}_3$ ) from scheelite ( $\text{CaWO}_4$ ) is the main challenge. The surface structure parameters of scheelite and calcite is given in **Table 1.1** (Lu et al., 2023).

## 1.2 Aim of Study

The processing department at HIF (Helmholtz Institute Freiberg) investigated colloidal silica as a depressant for calcite in scheelite floatation. (Ben Said et al., 2024). It was found that selectivity of scheelite and calcite is dependent on the specific surface area (SSA) of colloidal silica. Moreover, this is dependent on particle size of the scheelite and calcite as shown in the Figure 1.3 (Batturmur, 2023). The scope of this study is to investigate the effect of the particle size distribution of scheelite ores and SSA of colloidal silica on the selectivity of scheelite against calcite and gangue minerals.



**Figure 1.3:** Modified rate constant against particle size distributions at pH 10 and collector NaOI dosage of 400 g/t (Batturmur, 2023)

In this work, scheelite ore from a European mine will be processed by using the gravity separator. Different fractions with different particle size distributions are produced and use as a feed for the batch flotation tests where the effects of the colloidal silica dosage, and specific surface area is investigated on the most important target variables.

## **2 Literature Review**

### **2.1 Mittersill Mine**

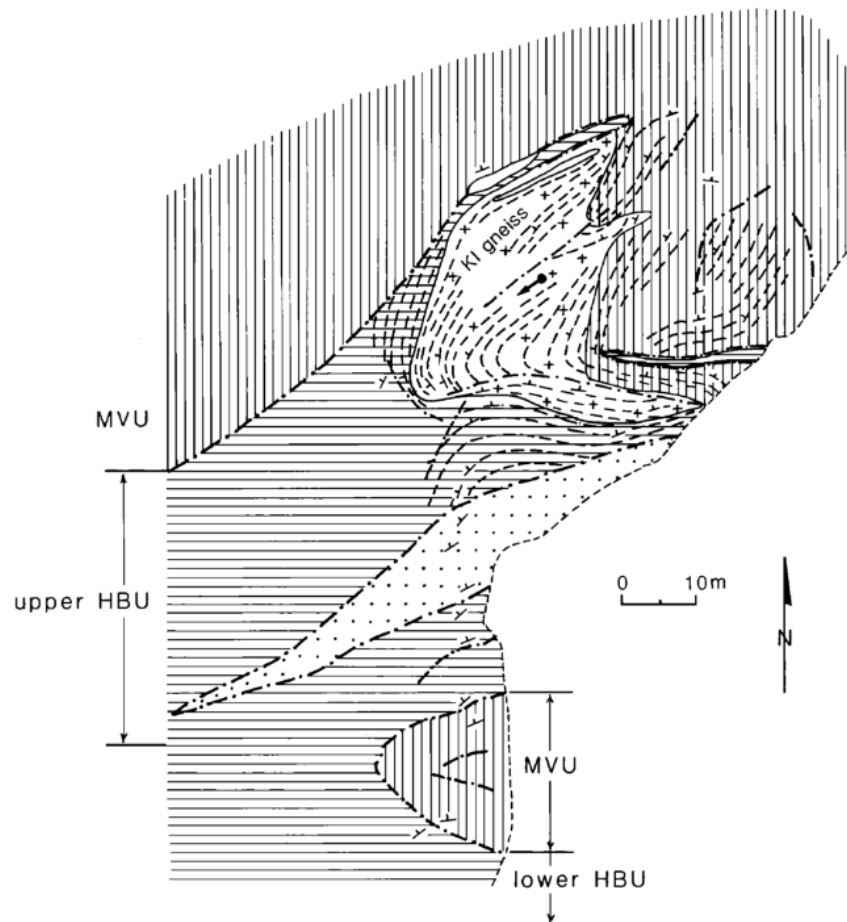
In Austria, the Mittersill mine is situated nearby Salzburg area. The scheelite deposit is located south of Mittersill City on the east and west slopes of Felber Valley. Its position divides the scheelite deposits into eastern and western ore zones (Maucher, 1965).

The Mittersill mine had world's biggest tungsten deposits as well as the largest deposit in Europe (Appel, 1986; Migisha, 1983). With the help of the stream-sediment geochemical approach, this mineral deposit was found. This method looks for possible mineral resources by analyzing sediments comes with by river streams resources (Maucher, 1965).

This scheelite deposit was found in 1967. It was believed that mineral deposit contains tungsten, mercury, and antimony was created underwater because of mafic volcanic activity. The ostfeld open pit and the westfeld underground mine make up the two portions of the mineral deposit. The eastern portion of the valley was the starting point for mineral exploration in 1968. In the eastern section, open pit mining operation was performed from 1975 to 1986. Mine professionals determined that 0.3% was the cutoff grade for  $\text{WO}_3$  in mining. The typical scheelite grade was 0.75%  $\text{WO}_3$ , although it might reach 8.5%  $\text{WO}_3$  in the quartz veins. Exploration for the western portion of the mine began in 1977, and mining began in 1980. The mine's cutoff grade was 0.5%  $\text{WO}_3$ . The average ore grade in this section of the mine was 0.5%  $\text{WO}_3$  (Thalhammer et al., 1989).

#### **2.1.1 Geology of the Mittersill Scheelite Deposit**

Mittersill scheelite deposit is situated in Granatspitz Dom at the northwest slope. The strike direction of the deposit varies from  $50^\circ$  to  $70^\circ$  in its western section and from east to west in its eastern portion. The dips are found between  $45^\circ$  -  $55^\circ$  NW and  $30^\circ$  -  $50^\circ$  N. The geology of the metavolcanic-sedimentary sequence that contains scheelite is shown in Figure 2.1.



**Figure 2.1:** Geology of the metavolcanic-sedimentary sequence MVU (metavolcano-sedimentary unit), HBU (Hornblende Units) (Thalhammer et al., 1989)

The metavolcanic-sedimentary sequence in the western part of the deposit is composed of a lower and upper hornblendite unit with 46 m and upto 170 m thick respectively carrying an imbricated slice of the basic schist unit, and intercalated metavolcanic-sedimentary units of varying thicknesses (29 – 95 m). The majority of the tungsten mineralization is found in the thick top hornblendite unit (Thalhammer et al., 1989).

#### 2.1.1.1 Hornblende

In Mittersil mineral deposit, 75–98% of the hornblendite is composed of dark green amphibole and biotite; the remaining components are limonite, plagioclase, scheelite, pyrite, pyrrhotite, and zoisite (Thalhammer, 1987).

### **2.1.1.2 Metamorphism**

The metavolcanic sedimentary rocks and thrust hornblendite units are arranged in a sequence of overlapping strata, or embricated stacks, on this scheelite-carrying metavolcanic structure. These hornblendite rocks are composed of coarse-grained amphibolites and hornblendite. Fine-grained gneisses and amphibolites comprise the metavolcanic-sedimentary part. This rock experiences numerous metamorphism periods at a pressure of 5.6–6 kbar and a temperature of up to 530 °C (Thalhammer et al., 1989).

### **2.1.2 Mineralization**

The entire meta-volcanic sequence has < 0.3% of WO<sub>3</sub> grade; however, only hornblendite units, those are connected to metamorphic quartz veins and quartz-rich rocks, are considerable and economically important ore concentrations has up to 15% WO<sub>3</sub> grade. Scheelite is the most prevalent ore mineral in the mine and the only noteworthy mineral from an economical view. Scheelite occurrence is always linked to Be-bearing minerals, calcite, fluorite, sulfides, and sulfosalts (Raith & Schmidt, 2010).

### **2.1.3 Mining Methods**

Open pit mining was in process in eastern ore zone from 1975 to 1986. The open pit mining operation (class drill and blast method) was carried with bench height of 10 meter. By the help of hydraulic drill rigs and shovels. For the transportation of mined ore from pit to processing mill dump trucks were used. In 1980, the highest production of 320,000 tons in a year was reached. Stockpiling method helped the continuous milling operations of ores (Raith & Schmidt, 2010).

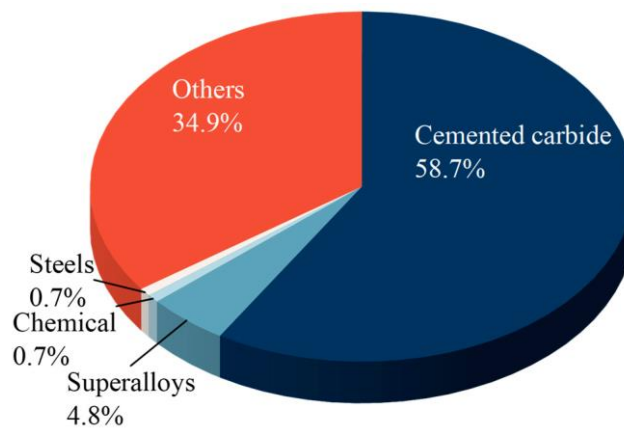
In 1977, underground mine was started in the western ore zone. Other underground mining techniques currently used at the Mittersil mine include longitudinal sublevel stopping bottom to top with smaller sublevel intervals of 12 to 20 m, it is similar method cut and filling mining, and transversal sublevel stopping top to bottom over several sublevel intervals with delayed backfill with typically a mixture of unconsolidated rock waste from underground and hydraulic sand fill (Raith & Schmidt, 2010). Between 60,000 and 120,000 tons of backfill material were filled (Gaul, 2008). The grade of mineral, condition of the mined area, and the geometry of each ore zone influence the choice of mining technique. Relatively flat dip of lower sublevels (between 45° and 55°) is challenging ground conditions, which limits the mining approach. Below the 750 m is the active mining area and exploration is underway (Raith & Schmidt, 2010).

## 2.2 Tungsten

Tungsten is a critical metal has applications in various industries which includes military, electronics, mining, and machinery (Han et al., 2021; Koutsospyros et al., 2006). The graphical representation Figure 2.2 displays the usage of tungsten in various applications in the United States. At the end of 2022, the world would have only approximately 3.7 million tons of tungsten ore reserves as shown in Figure 2.3 (Lu et al., 2023). Total reserves of tungsten owned by different countries is given in the Table 2.1.

**Table 2.1:** Reverses of tungsten in different countries (Lu et al., 2023)

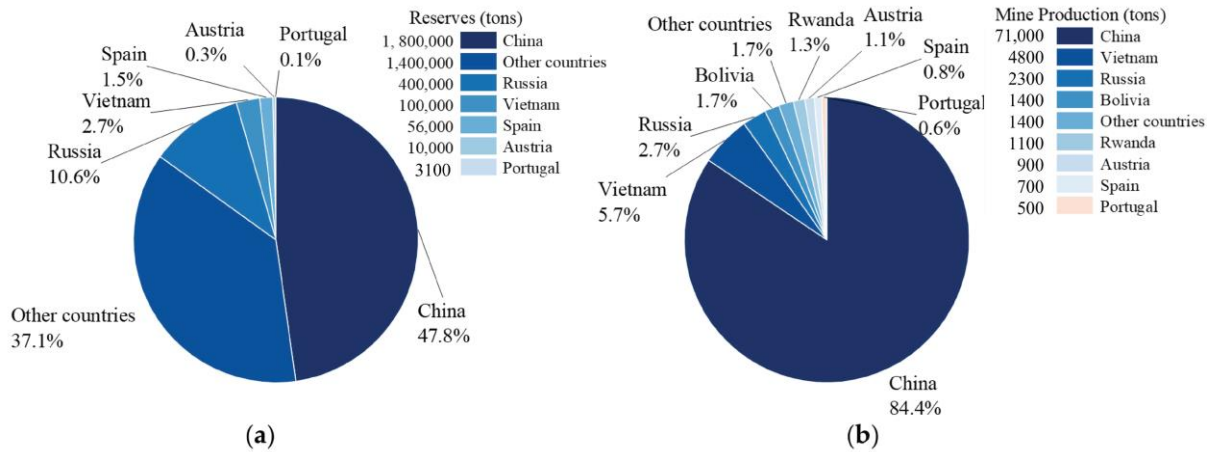
| Countries | Reserves (tons) |
|-----------|-----------------|
| China     | 1.8 million     |
| Russia    | 400,000         |
| Vietnam   | 100,000         |
| Spain     | 56,000          |
| Austria   | 10,000          |
| Portugal  | 3,100           |



**Figure 2.2:** Usage of tungsten in various applications in the United States (Lu et al., 2023)

More than 20 different types of tungsten-containing minerals have been discovered so far. Nevertheless, only wolframite ((Fe, Mn)WO<sub>4</sub>) and scheelite (CaWO<sub>4</sub>) have economic worth. Around 70% of the world's tungsten resources are in scheelite form, although wolframite is about 30% (Lu et al., 2023). Wolframite is the most important source of tungsten resources, because it has high ore grade and is also convenient for mining and processing, although having lower reserves than scheelite. As the world economy expands, the easily accessible

wolframite deposits are gradually depleting. Therefore, efficient utilization of scheelite resources is crucial (Chen et al., 2022; Yang, 2018).



**Figure 2.3:** Reserves and production of tungsten in different countries (Lu et al., 2023)

## 2.3 Gravity Separation

Gravity separation is an ancient technique used to separate minerals based on their specific gravities. This method is attractive due to its low operating costs without and energy requirements, making it environmentally friendly (Falconer, 2003).

During the epoch of past 25 years, new gravity separation equipment has improved these factors, making gravity separation the preferred technique. In Australia, the mineral sands industries are traditionally the main user, other hard rock minerals like tantalum and tin can be recovered using gravity separation. Jigs, shaking tables, hydrosizers, and cyclones are common gravity separators (Falconer, 2003).

## 2.4 Froth Flotation

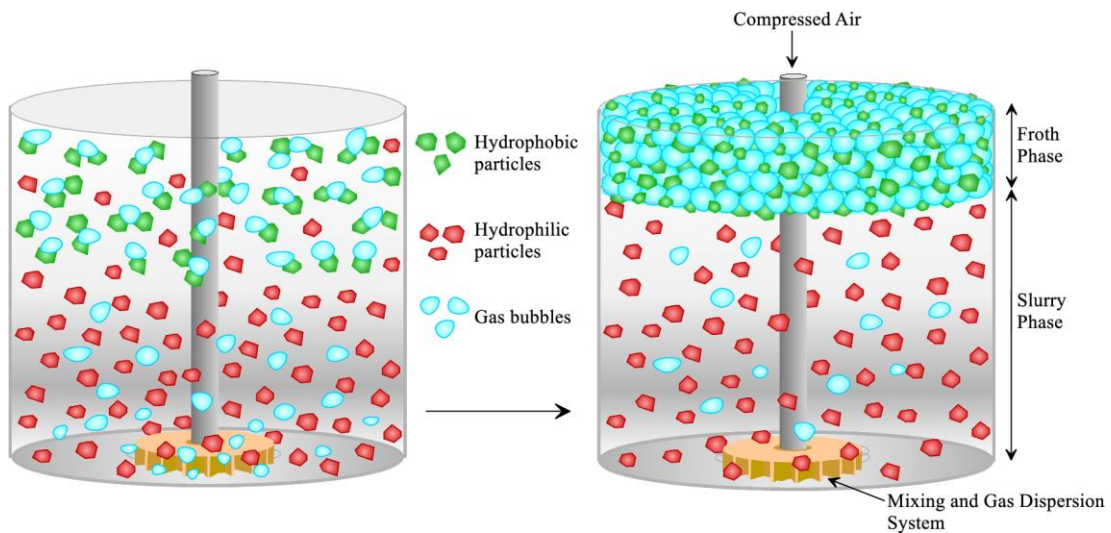
Froth flotation is the most impact mineral process. It is the most revolutionary metallurgical process developed during the 20<sup>th</sup> century. During the early 20<sup>th</sup> century, before the development of froth flotation, bulk oil methods were in use, in which the separation was assisted through the floating of oil or mineral mass by the entrainment of air with the help of the mixing process, the bubble was generated by reducing the pressure and also by the addition of the sulphuric acid to generated carbon dioxide (CO<sub>2</sub>) bubble by reacting the carbonate-based minerals in the ores.

Modern froth flotation started in 1905 from the original patent of Mineral Separation Limited, Australia in 1905. This patent includes the usage of air bubbles instead of chemically generated gas bubbles. The first froth flotation operation was used for the recovery of the fine particles, which were left behind in a gravity concentration plant (Fuerstenau et al., 2007). Despite years of research, it remains bungling and not well understood. Optimization of current processes can lead to major economic gains (Shean & Cilliers, 2011).

#### 2.4.1 Principle of Froth Flotation

In the Froth flotation process, uncountable air bubbles are produced in the froth zone, usually ranging from several millimeters in size, are produced at the bottom of the tank and passed continuously through the slurry. The air bubbles take hydrophobic mineral particles with themselves, and float them on the surface of the tank, and the non-floating (hydrophilic particles settle down at the bottom of the tank. This separation process takes place based on the differences in the surface properties of the minerals in the mixture (Pawlik, 2022).

Hydrophilic mineral particles remain in the tank and are treated as tailings, they could be tailings. These flotation procedures can be seen in Figure 2.4.

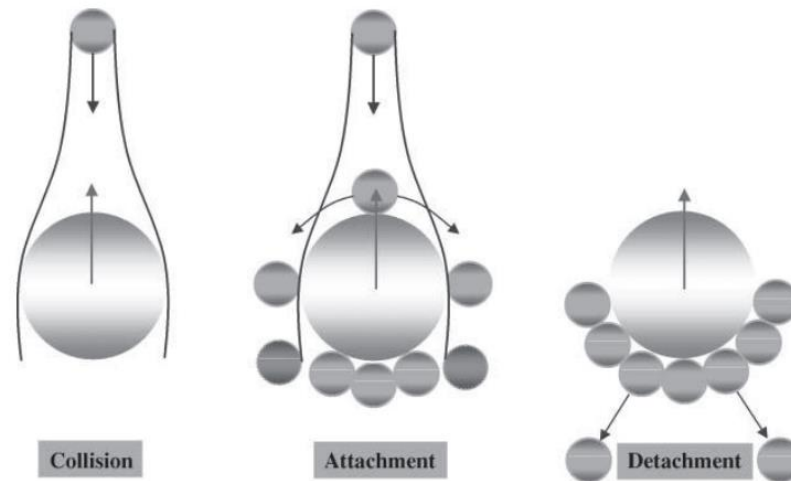


**Figure 2.4:** Schematic diagram of froth flotation (Pawlik, 2022)

#### 2.4.2 Bubble-Particle Interaction

The effective capturing of hydrophobic particles in the air bubbles during flotation is carried out in three separate processes are given below and shown in Figure 2.5 :

- Collision
- Adhesion
- Detachment



**Figure 2.5:** Capture of hydrophobic particles in the air bubbles (Tao, 2005)

### 2.4.3 Particle Bubble Collision

The first step in the flotation process involves the collision of particles with bubbles when come into the surroundings of each other. The process is mainly defined by the hydrodynamics of the flotation. The probability of collision ( $P_c$ ) is a measure of stream functions for quiescent conditions (Yoon, 2000) and microturbulence models for well-mixed conditions (Weber & Paddock, 1983; Yoon & Luttrell, 1989).

### 2.4.4 Particle- Bubble Attachment

Hydrophobic particles make thin and break the liquid film between the particle and the bubble due to attractive surface forces. The particles with less induction time than sliding time get attached to an air bubble. Selectivity of flotation is measured by the difference in attachment probability of various particles ( $P_a$ ), they are found by hydrodynamic forces and surface forces between bubbles and particles (Tao, 2005).

### **2.4.5 Particle – Bubble Detachment**

Air bubbles in a pulp can't carry all the particles attached to them. Detachment happens when the detachment force surpasses the adhesion forces, which can be caused by bubble fluctuations due to particle-bubble collision. The principal factor in the detachment process is the amplitude of oscillation of bubble (Cheng & Holtham, 1995).

## **2.5 Froth Flotation of Scheelite**

Froth flotation has been the leading method used for the enrichment of scheelite since the 1970s (Kupka et al., 2018). With the increasing demand for tungsten in industry and wolframite resources becoming exhausted, research to develop new reagents for scheelite froth flotation is becoming a hot topic for tungsten resource development.

When it comes to the separation of scheelite from minerals having calcium. There are two major challenges; the 1<sup>st</sup> challenge is the similar surface properties of both minerals. During flotation, both minerals have calcium sites on their surfaces inhibitor sites. The second challenge is the high solubilities of scheelite, calcite, and other calcium-bearing minerals, which further enhance the similarities of the mineral surfaces (Ruolin et al., 2021).

Collectors e.g. fatty acids, sulfonates, and phosphoric acid esters are normally used in scheelite flotation. Collector acts to escalate the hydrophobicity of scheelite, which makes it likely for it to attach to air bubbles and float in a froth that can be collected (Kupka et al., 2018).

Now, to develop the selectivity in the flotation process, depressants e.g. sodium silicate and water glass, and silicate-based materials, are used to increase the depression of semi-soluble salts e.g. calcite and gangue minerals (Kupka, Kaden, et al., 2020).

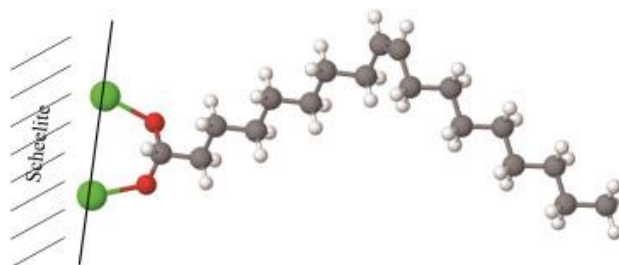
The surface charge (zeta potential) of scheelite is measured to be negatively charged throughout the pH range, it can be an outcome of the presence of excess  $\text{WO}_2^-$  ions over its surface. Active  $\text{Ca}^{2+}$  cationic sites, and the negative zeta potential of the scheelite minerals allow usage of cationic or anionic collectors for scheelite froth flotation (Arnold & Warren, 1974).

### **2.5.1 Collectors**

Cationic collectors can be used for froth flotation scheelite because of electrostatic interaction. Amines can also float silicates, oxides, and other gangue minerals that's why on the industrial scale, scheelite cannot be effectively used because of less selectivity (Atademir et al., 1981).

Pyridinium salts have applications to float potash, phosphates, sulfides, oxides, silicates, and coal during froth flotation. Nevertheless, to date, such pyridinium salts have been examined in the form of octadecyl pyridinium bromide (ODPB). Whereas octadecyl pyridinium bromide (ODPB) was effective in flotation of scheelite under pH 10 but with low selectivity. The reason is, its low selectivity, octadecyl pyridinium bromide was not considered for future research (Atademir et al., 1981).

Oleic acid in the form of sodium oleate has significant applications in scheelite flotation as a collector. As an anionic collector, it gets adsorbs on cationic sites ( $\text{Ca}^{2+}$ ) of the scheelite, as shown in Figure 2.6. The collector's carboxylate group bridges two calcium ions on the surface, coordinating with them through its oxygen atoms (Kupka & Rudolph, 2018).



**Figure 2.6:** Bridging coordination of sodium oleate at the scheelite surface (Colors: Ca = green, O = red, C = grey, H = white) (Kupka & Rudolph 2018)

At lower concentrations, the surface of scheelite makes a bilayer collector, this bilayer plays an important role in the extraction of scheelite, and it also increases the selectivity of scheelite against calcite. Scheelite is unable to float above pH 12 because of the formation of hydroxide ions.

### 2.5.2 Depressants

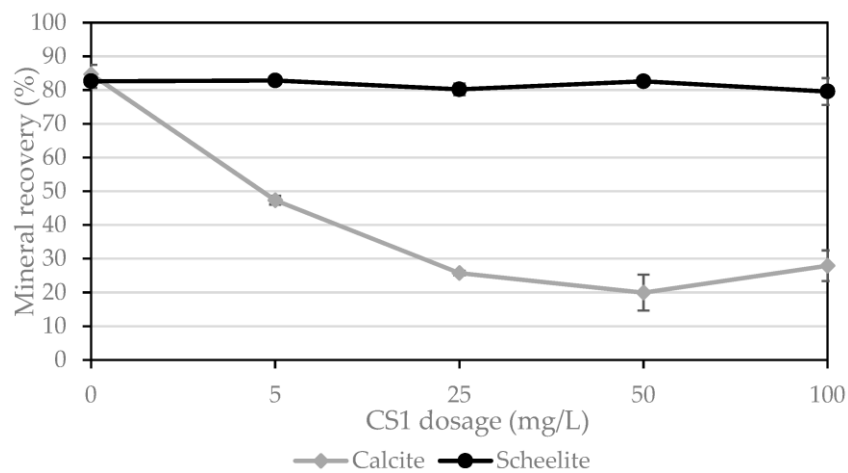
On the industrial level, sodium silicate is most common depressant used against calcite in the scheelite flotation (Martins & Amarante, 2013; Yongxin et. al., 1983).

In the scheelite flotation industry, sodium silicate can be used as a depressant for calcite in different forms, i.e. by varying the concentration of  $\text{SiO}_2$  and  $\text{Na}_2\text{O}$  (Marinakos & Shergold, 1985). Increasing the dosage of sodium silicate as a depressant in scheelite flotation can reduce the selectivity of scheelite and calcite by over depression of scheelite (Filippov et al., 2018; Gao et al., 2016; Han et al., 2017; Patil et. al., 1985; Yongxin et. al., 1983).

Researchers have acidified the sodium silicate to enhance the ability to depress calcite in the scheelite flotation. To accomplish it, supersaturated silicate acid  $\text{Si}(\text{OH})_4$  is prepared, which is achieved by using a 10% sodium silicate solution that has acidified with 1 M sulfuric acid. Also by mixing the sodium silicate with oxalic acid or sulfuric acid (Liu et al., 2016; Martins & Amarante, 2013)

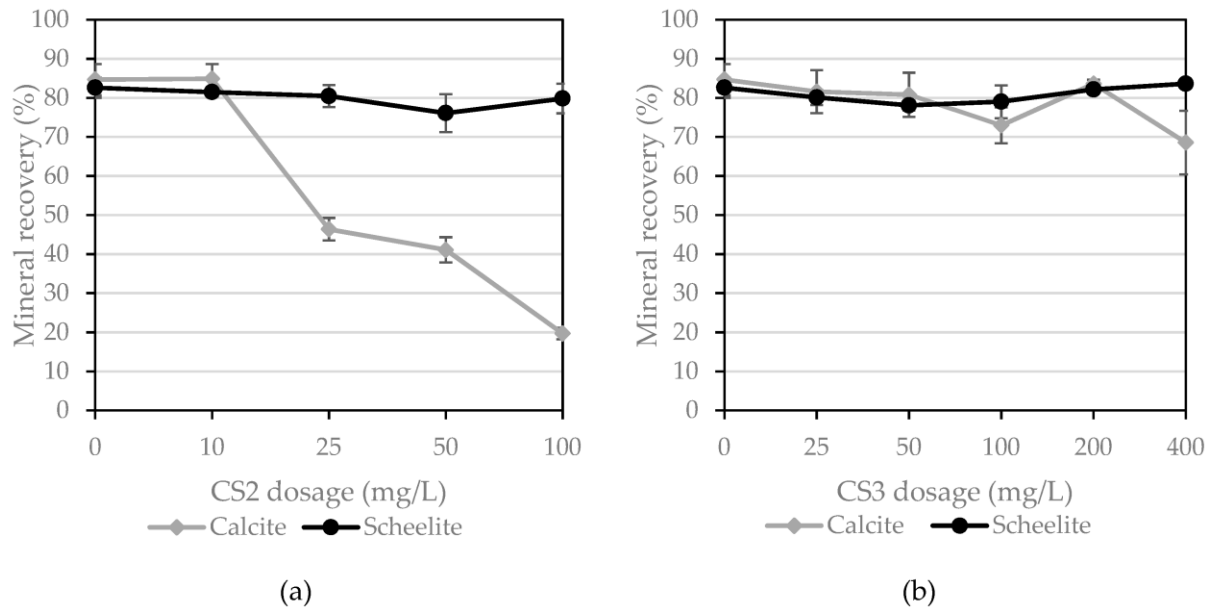
### 2.5.3 Colloidal Silica as Depressant

The effect of colloidal silica on the separation of scheelite and calcite was monitored in micro flotation (Kupka, Kaden, et. al., 2020). Results are shown in Figure 2.7 that colloidal silica depresses the calcite, and scheelite is not affected by the depressant, regardless of how much of it is added. Furthermore, calcite shows variation even the small change in colloidal silica dosage. Based on these findings, the author looked into the effect of different sizes, dosages of colloidal silica, and pH.



**Figure 2.7:** Single-mineral flotation recovery of calcite and scheelite depending on the Levasil CS30-324P® (CS1) dosage (at pH = 8, collector =  $1 \times 10^{-4}$  sodium oleate) (Kupka, Babel, et al., 2020)

The average colloidal silica sizes of CS-1 is 9 nm, CS-2 is 30 nm, and CS-3 is 55 nm, respectively. Single mineral micro flotations were conducted with CS-2 and CS-3 and shown in Figure 2.8. Only higher dosage of the CS-2 depress the calcite, while CS-3 shows negligible depression when at higher dosage.



**Figure 2.8:** Single mineral micro flotation was conducted with CS-2 and CS-3 (Kupka, Babel, et al., 2020)

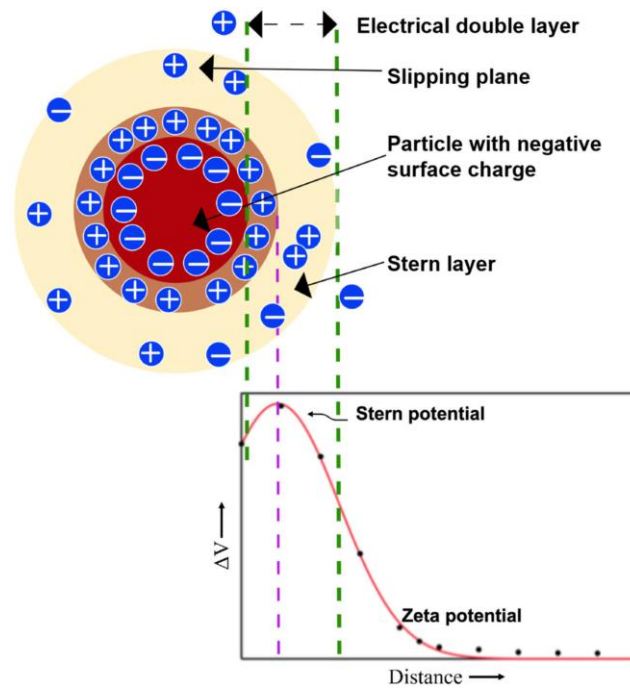
## 2.6 Surface Charge

The strength of shear plane of particle during electrophoresis is called Zeta Potential, it is a process in which an electric field moves charged particles (ions), and these are the independent characteristics (Williams, 2016).

Surface charge is the density of charge on the particle surface. Zeta potential which ignores the charge density of the system, offers a helpful interpretation for colloidal stability while being only indirectly assessed. The dielectric constant, the viscosity of the suspended liquid, and the electrical potential at the slipping plane all affect the material's mobility (Figure 2.9). This slipping plane is the interface between the liquid and the moving substance; it is the location where the diffuse layer combines with the Stern layer (Bhattacharjee, 2016).

The Stern layer is bound with colloid but is not rigidly bound to the diffuse layer. Zeta potential, the electrical potential at this junction, is consequently associated with particle mobility.

Derjaguin, Landau, Verwey, and Overbeek (DLVO) theory states that the equilibrium of the electrical double-layer and van der Waals counteracting forces determines the stability of an electrostatic structure (Adamczyk & Weroński, 1999) (Figure 2.9).



**Figure 2.9:** Zeta potential (Lunardi et al., 2021)

Using Henry's equation of an electrical field to calculate zeta potential indirectly from electrophoretic mobility, which is the particle velocity divided by the electric field strength,  $E$ . (Lunardi et al., 2021)

$$\frac{U}{E} = \frac{2\varepsilon\zeta\kappa a}{3\eta}$$

$\frac{U}{E}$  is the electrophoretic mobility ( $\text{m}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$ ),

$\zeta$  is the zeta potential (V),

$\varepsilon$  is the solvent dielectric permittivity ( $\text{kg} \cdot \text{m} \cdot \text{V}^{-2} \cdot \text{s}^{-2}$ )

$\eta$  is the viscosity ( $\text{kg} \cdot \text{m}^{-1} \cdot \text{s}^{-1}$ )

$F(\kappa a)$  is Henry's function (dimensionless)

## 2.7 Experimental Design

Design of Experiments (DoE) is a statistical technique used to design, develop, and optimize various systems, processes, and products. It is a multidimensional technique applied in different situations, e.g., design for comparisons, variable screening, optimization, and improved design. It is an application of applied statistics to conduct scientific analyses on a system, or product by controlling input variables to examine their outcomes on the measured response variable (Y) (Yi et al., 2021).

The purpose of the Design of Experiment (DoE) is to select the experimental conditions, experiments are conducted with these conditions, and the results are statistically analyzed. Usually, resources and equipment are required to perform experiments in order to save the resources and perform the experiments in a sustainable way. It's important to reduce the number of experiments and utilize the limited data to get more information. Design of Experiments (DoE) works with various mathematical and statistical theories, which are applied in DoE (Yi et al., 2021).

When dealing with DoE, there are certain terminologies, such as factor, level, and response.

- A factor is any controlled input variable that influences the output of an experiment
- Response is an output variable that needs to be optimized in the experiments.
- Levels are the factors that are controlled during the experiment

Full factorial design is accurate because it studies all possible groupings of factors and their levels. This wide-ranging method let all the knowledge of the main effects and interactions. Full factorial design effectively finds the ideal output ratio, validating its precision in complex optimization tasks.

Other design of experiments (DoE) techniques, such as Plackett-Burman designs, have distinctive balances between efficiency and accuracy. These methods are used when a full factorial design is invalid due to the high amount of experiments. Each method has its strengths and drawbacks, depending on the particular application and complication of the experiment.

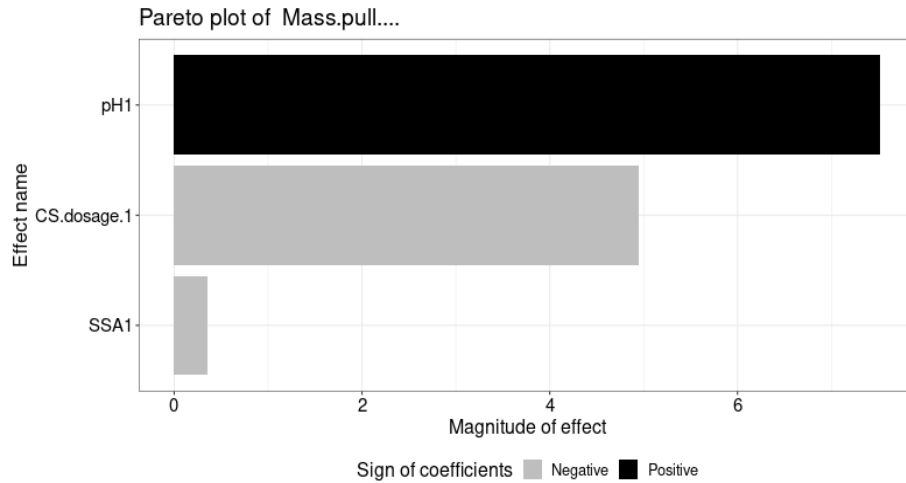
The selection of DoE methods depends upon the requirements of the experiment, including the number of factors, the nature of interactions, and resources. The full factorial design is extremely accurate because it considers all possible combinations (Yi et al., 2021).

### 2.7.1 Full Factorial DOE

To thoroughly evaluate the impact of various factors and their interactions on the response variable, a full factorial design of experiment was utilized. This method allows for the assessment of both main effects (individual factor influence) and interaction effects (combined influence of two or more variables) because it systematically analyzes all potential combinations of factor levels (Ahmaddani & Dwijayanti, 2024). This thorough investigation offers insightful information on the intricate interactions between variables, resulting in a stronger comprehension of the system being examined (Siang et al., 2018).

### 2.7.2 Pareto Diagram

The pareto diagram is a statistical method to analyze, compare, and quantify the effect of the investigated factors by calculating the magnitude of effect shown in Figure 2.10. This method is commonly used to quantify the impact of variables observed in design of experiment DoE.



**Figure 2.10:** Pareto diagram representing the magnitude of effect (Ben Said et al., 2022).

Magnitude of effect is calculated by the difference between the mean values of output factor at maximum and minimum level.  $\mu_{max}$  show the mean value at maximum level, and  $\mu_{min}$  show the mean value at minimum level (Ben Said et al., 2022)..

$$\text{Magnitude of effect} = \frac{\mu_{max} - \mu_{min}}{2}$$

## 2.8 Kinetic Rate Flotation Model

The kinetic model precisely define the basic nature of froth flotation in a well-stirred flotation environment. In a well-stirred flotation environment, capturing of solid particles by bubble in suspension is possible. The concentration of particle in pulp is related to capturing process of particles by bubble. Particles of different types will have different capturing rates, mainly due to differences in floatability initiated by differences in the contact angle caused by the surface of particles. It can be suggested that particle size has a major role in the flotation process (King & Cross, 2003).

The kinetic models associate flotation with chemical reactors. Flotation is compared with the reaction between bubbles and particles, which has been extensively examined in the literature. These kinetic models are used to develop controlling mechanisms in industrial settings. The overall rate equation for flotation process can be expressed as:

$$\frac{dC_p(t)}{dt} = -k(t)C_p^m(t) C_b^n(t)$$

In above equation,  $C_b(t)$  and  $C_p(t)$  is the concentration of the bubbles and particles at time  $t$ , respectively.

The exponents,  $m$  and  $n$  are the respective orders for particles and bubbles, and pseudo rate constant  $k(t)$  depends on the different parameters controlling the flotation process.

Literature suggests that the process of particle-bubble collision is a first-order kinetic reaction concerning the concentration of particles and bubbles remains constant.

$$R(t) = R_{\infty} \left[ 1 - \int_0^{\infty} f(k) \exp(-kt) dk \right]$$

At time  $t$ , the recovery will be equal to the above equation: when  $k$  value of the material to be floated is made up of particles then  $k$  could be signified by a continuous distribution function,  $f(k)$ .

Practically, the classical first-order kinetic flotation model, represented by eq ..., is frequently employed. A number of experiments are carried out to get the recovery values at various time intervals to fit the model.

$$R_t = R_{\max}(1 - e^{-kt})$$

$k$  is the 1<sup>st</sup> order rate constant for flotation,

$R_{\max}$  stands for flotation rate constant,  $t$  for time,  $R_t$  is the recovery of the mineral at time  $t$ , and  $R_{\max}$  is the maximum achieved recovery of mineral at  $t = \infty$  (Polat & Chander, 2000)

Results of the batch flotation are frequently examined using kinetic models. The model fit to an experimental recovery-time curve and gives two parameters:  $k$  (first-order flotation rate constant) and  $R_{\max}$  (maximum recovery). It can be often false to compare  $R_{\max}$  or  $k$ , which is obtained under different conditions. A modified flotation rate constant,  $k_m$ , is calculated to resolve this concern. It can be expressed as the product of  $R_{\max}$  and  $k$ .

$$k_m = R_{\max} \cdot k$$

The selectivity index (SI) of the desired mineral to the undesired mineral in flotation system is defined as the ratio of the modified rate constant of the desired mineral to the undesired mineral.

$$\text{Selectivity Index} = \frac{k_m (\text{Desired Mineral})}{k_m (\text{Undesired Mineral})}$$

Batch flotation data can be analyzed using kinetic models. The selectivity index and the modified flotation rate constant are helpful in flotation studies. They are useful for evaluating factors that have control over flotation processes (Xu, 1998).

### 3 Material and Methods

#### 3.1 Reagents

For zeta potential measurement, 1 M hydrochloric acid (HCl) and sodium hydroxide (NaOH) are used as pH modifiers provided by Carl Roth GmbH. 0.01 M KCl solution was used as the solvent. Eight types of Levasil® Colloidal Silica (CS) provided by Nouryon differ in modification and specific surface area (SSA), as shown in Table 3.1.

**Table 3.1:** Colloidal silica modifications

| Modifications                              | SiO <sub>2</sub> Concentration | Specific Surface Area (m <sup>2</sup> /g) |
|--------------------------------------------|--------------------------------|-------------------------------------------|
| <b>Non-functionalized Colloidal Silica</b> |                                |                                           |
| NF-CS-500                                  | 15%                            | 500                                       |
| NF-CS-250                                  | 30%                            | 250                                       |
| NF-CS-750                                  | 15%                            | 750                                       |
| <b>Silane modified Colloidal Silica</b>    |                                |                                           |
| S_CS_500                                   | 15 %                           | 500                                       |
| S_CS_220                                   | 40 %                           | 220                                       |
| <b>Aluminate modified Colloidal Silica</b> |                                |                                           |
| Al_CS_1100                                 | 7 %                            | 1100                                      |
| Al_CS_500                                  | 15 %                           | 500                                       |
| Al_CS_250                                  | 30 %                           | 250                                       |

For batch flotation, 4-methyl-2-pentanol or methyl isobutyl carbinol (MIBC) as frother, 5 w/w % of sodium oleate (NaOl) as collector, and Levasil® aluminate modified colloidal silica modifications (Al\_CS\_1100 & Al\_CS\_500) provided by Nouryon. 1 M hydrochloric acid (HCl) and sodium hydroxide (NaOH) are used as pH modifiers provided by Carl Roth GmbH.

#### 3.2 Experimental Procedure

##### 3.2.1 Zeta Potential

The colloidal silica suspensions were prepared in 0.01 M KCl solution. The calculated volume and measured weight of eight different Colloidal Silica (CS) reagents and KCl solution are given in Table 3.2.

**Table 3.2:** Composition of colloidal silica suspension

| Modifications                              | Volume (Milliliter) | Weight (grams) |
|--------------------------------------------|---------------------|----------------|
| 0.01 M KCl                                 | 204                 | 201.72         |
| <b>Non-Functionalized Colloidal Silica</b> |                     |                |
| NF-CS-500                                  | 5.36                | 5.86           |
| NF-CS-250                                  | 2.68                | 3.26           |
| NF-CS-750                                  | 5.36                | 5.78           |
| <b>Silane Modified Colloidal Silica</b>    |                     |                |
| S-CS-500                                   | 5.36                | 5.78           |
| S-CS-220                                   | 2.53                | 2.53           |
| <b>Aluminate Modified Colloidal Silica</b> |                     |                |
| Al-CS-1100                                 | 10.72               | 10.71          |
| Al-CS-500                                  | 5.36                | 5.26           |
| Al-CS-250                                  | 2.68                | 3.30           |

The Colloidal Dynamics AcoustoSizer II shown in Figure 3.1 was set up, cleaned and calibrated with deionized water. Colloidal silica suspensions were poured into the chamber and dispersed till pH stabilized. pH was adjusted with the pH modifiers; zeta potential was measured across the pH from 11 to 2.



**Figure 3.1:** Colloidal Dynamics AcoustoSizer II

### 3.2.2 Experimental Plan Development

Gravity separation and batch flotation experiment tests were conducted with the help of the full-factorial design of the experiment method. The design of experiment (DoE) was designed by open-source shiny R platform for the design of experiment created by HIF (Helmholtz Institute Freiberg) to study the relationship between input and response variables. The results are analyzed by using a shiny R platform that evaluates the design and plan of the experiment, calculating the main and interaction effects of the process parameters and their statistical importance. This platform is an open-access source (Ben Said et al., 2022).

### 3.2.3 Gravity Separation

The shaking table used in the gravity separation of the feed ore is shown in Figure 3.3. To avoid agglomeration, a slurry of scheelite ore and water with the ratio 1:3 of pulp density was prepared and dispersed with the help of a motor stirrer for 3 minutes and fed to the shaking table. Firstly, the shaking table experiments were performed on the basis of the full factorial-based experimental plan given in the Table 3.3 to investigate the effect of the experimental parameters the inclination degree of the shaking table, water flow rate, and frequency of the shaking table

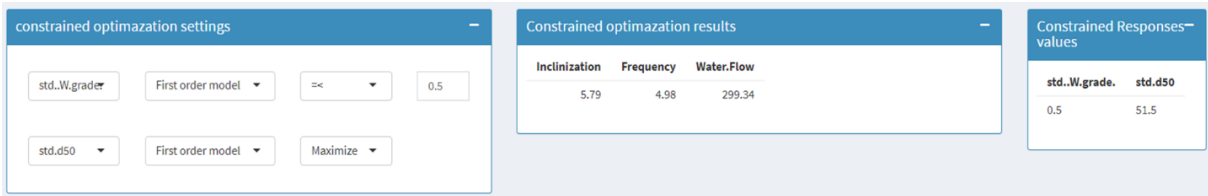
**Table 3.3:** Operating parameter of the shaking table (Full Factorial DoE)

| Parameter                          | Unit                | Factor Levels |         |
|------------------------------------|---------------------|---------------|---------|
|                                    |                     | Minimum       | Maximum |
| Inclination angle of shaking table | Degree of angle (°) | 4             | 10      |
| Water flow rate                    | Liter/hour          | 150           | 300     |
| Frequency                          | Hz                  | 3             | 5       |

**Table 3.4:** Optimized operating parameter for shaking table

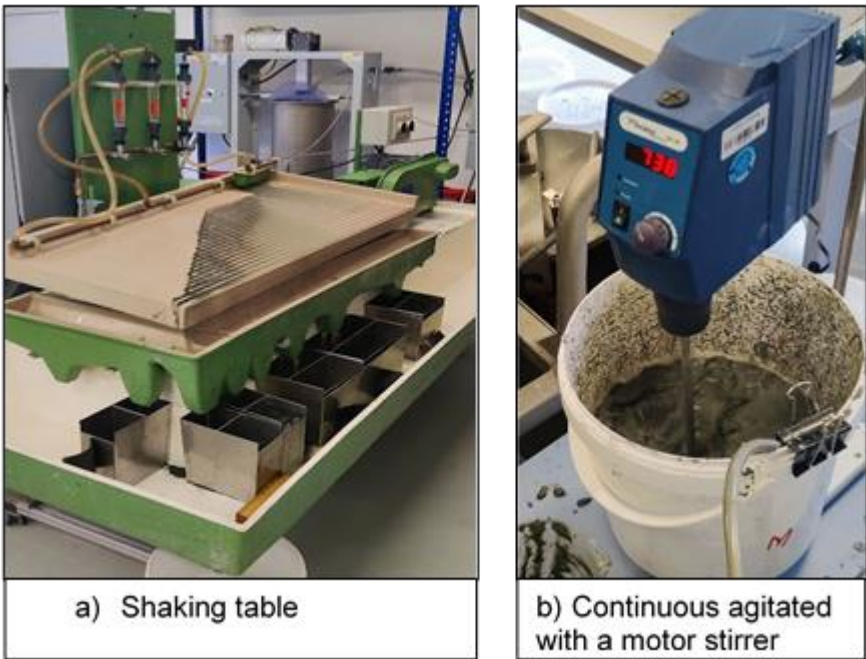
| Parameter                          | Unit                | Level |
|------------------------------------|---------------------|-------|
| Inclination angle of shaking table | Degree of angle (°) | 6     |
| Water flow rate                    | Liters/hour         | 300   |
| Frequency                          | Hz                  | 5     |

After finding out the desired and optimal parameters from R platform – Shinny app (Ben Said et al., 2022) shown in Figure 3.2. The shaking table test was performed on the optimized parameters given in Table 3.4, in which refined samples were fed to the shaking table with the help of a dosing pump (positive displacement pump) to the feed box.

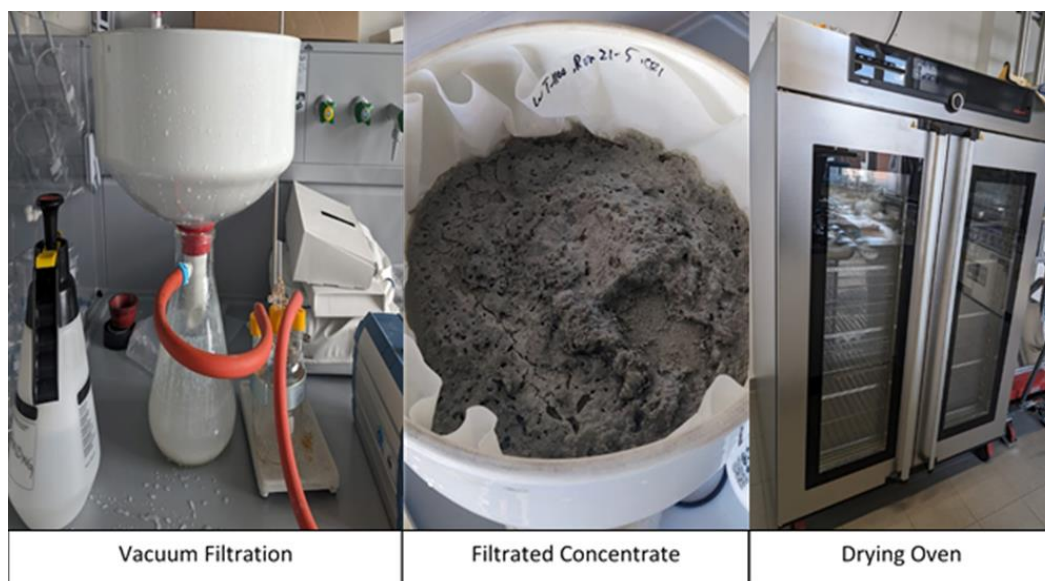


**Figure 3.2:** Optimized parameter from R platform - Shinny app (Ben Said et al., 2022).

At the time of the experiment, a bucket of slurry is continuously agitated with a motor stirrer at around 700 rpm as shown in Figure 3.3, connected it with the help of a dosing pump (Positive displacement pump) to feed it in the feed box. Shaking products from each fraction were collected into a separator bucket and filtered with the vacuum filtration method and dried overnight at the temperature of 70 °C shown in Figure 3.4.



**Figure 3.3:** Gravity separation experimental setup



**Figure 3.4:** Filtration and drying

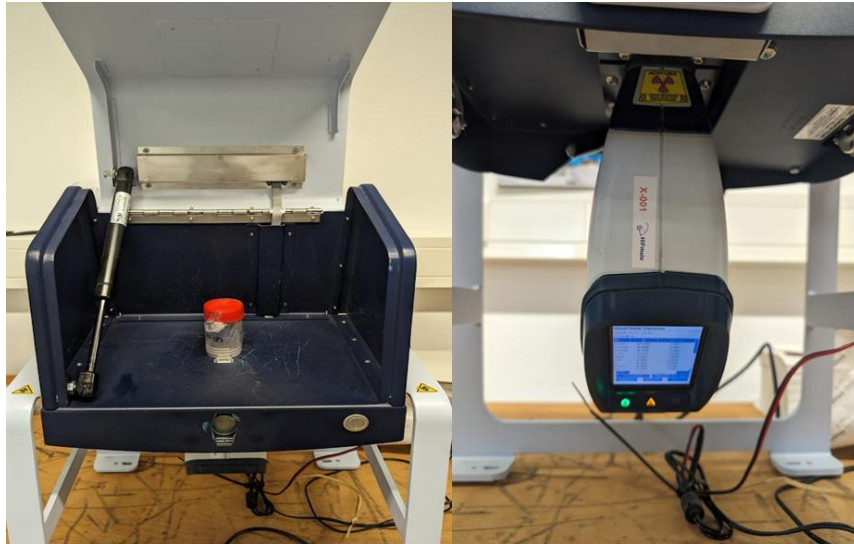
### 3.2.4 Mineral Characterization

For elemental compositional analysis and particle size distribution analysis, uniform and homogenized 5-7 g samples were split by Riffle splitter shown in Figure 3.5



**Figure 3.5:** Riffle splitter

Elemental compositional analysis of shaking table products and batch flotation concentrate were performed by Bruker S1 Titan XRF analyzer as shown in Figure 3.6.



**Figure 3.6:** Bruker S1 Titan XRF analyzer

The samples were packed in a sample container were positioned on the S1 Titan XRF analyzer, the cover was shut, and the 60-second analysis was started by pulling the trigger. Three repetition measurements were for each sample. To measure the particles at the various locations within the plastic container, the samples were well shaken after each repetition measurement. The obtained XRF data were processed to develop interpretations and corresponding recoveries and grades.

Laser diffraction particle size distribution analysis of the shaking table products were performed by device HELOS, Symptech GmbH shown in Figure 3.7.



**Figure 3.7:** HELOS-VARIO/KR, Symptech GmbH - Laser diffraction particle size distribution analyzer

### 3.2.5 Batch Flotation

After performing elemental compositional analysis on the shaking table products they were homogenously split into 500 grams samples with the help of a large size riffle splitter as shown in Figure 3.8.



**Figure 3.8:** Riffle Splitter (Large)

The process parameters for batch flotation of scheelite ores are pH, CS dosage, and specific surface (SSA) are given in **Table 3.5**.

**Table 3.5:** Parameter of the batch flotation (Full Factorial DoE)

| Parameters               | Units             | Factor Level |         |
|--------------------------|-------------------|--------------|---------|
|                          |                   | Minimum      | Maximum |
| pH                       |                   | 8            | 10      |
| Colloidal Silica dosages | g/t               | 50           | 550     |
| SSA                      | m <sup>2</sup> /g | 500          | 1100    |

The batch flotation apparatus is shown in Figure 3.9 The batch flotation experiment takes place with a sequence of well-defined steps. Firstly, wash-water bottles, fill-water bottles, and pH adjustors were prepared, and weighed. The flotation cell is properly cleaned to avoid any

possible contamination that could affect the results and empty weighted. After cleaning, an amount of deionized (DI) water was added to the flotation cell.

The sample material was then carefully weighed up to 500 grams for precise measurements. The entire sample fraction was afterward added to the flotation cell containing the DI water. More DI water is added until the liquid level reaches the mentioned "blue sign" on the flotation cell. The weight of the cell with the sample and water is taken and noted. To ensure proper stability during the experiment, the flotation cell was securely fastened onto the flotation instrument.

The flotation process carried on agitation at 750 rpm. Next, the specific instructions displayed on the Raspberry Pi screen, the pH of the pulp is adjusted to the conditions. The flotation cell was then waited to complete the pH conditioning time as shown by the Raspberry Pi. Subsequently, the depressant was dosed according to the desired conditions, followed by a conditioning time of the depressant according to Raspberry Pi's instructions. Similar procedures were followed for the collector and frother, ensuring conditioning time according to the Raspberry Pi.

When the conditioning time finished, the airflow rate was set to 5 liters per minute from the bottom of the flotation cell. Three trays were tagged to collect the flotation concentrates after the regular intervals. During the froth flotation, the concentrate collection was routinely cleaned with water-wash, and fill-water bottle was used to maintain the appropriate water level within the flotation cell and clean the walls of the flotation cell.

Finally, after collecting three concentrates fractions, concentrate trays, the weight of the wash water, fill water bottles, and pH adjustors were taken and noted. The collected flotation concentrates and tailings are filtrated and put in dryers for further processing. This procedure makes it a well-organized and well-documented batch flotation experiment.



**Figure 3.9:** Batch flotation apparatus (Magotteaux FloatCell)

### 3.2.6 Element to Mineral Conversion Methodology

Elemental composition obtained by the pXRF are converted into the mineralogical composition based upon the linear algebra equation (Eq. 1). A is the chemical composition of mineral, b is the chemical assays and x is the mineralogical content of the material.

$$A * x = b \quad \text{Eq. 1}$$

Elemental compositions are converted into minerals classes, based upon its chemical composition of the minerals given in the Table 3.6. The stoichiometric formula of minerals were applied to calculate the composition (Ben Said et al., 2024).

**Table 3.6:** List of elements and minerals (Ben Said et al., 2024)

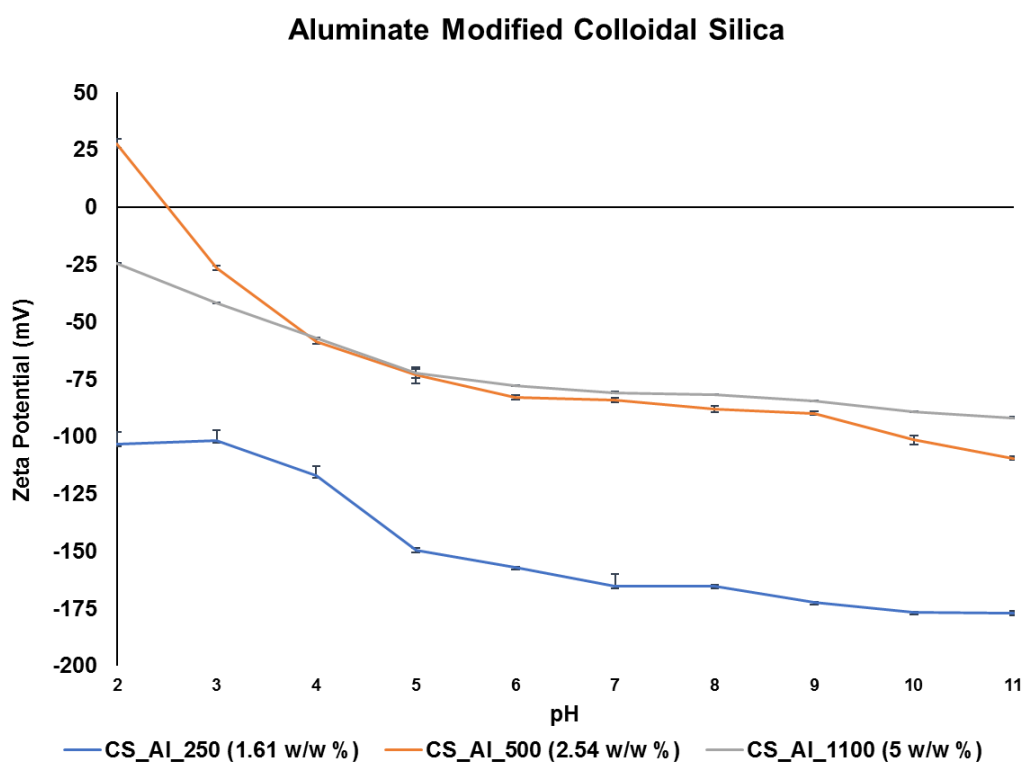
| Elements   | Mineral        |
|------------|----------------|
| Ca         | Calcite        |
| Scheelite  | W, Ca          |
| Apatite    | Ca, P          |
| Hornblende | Ca, Fe, Mg, Mn |

## 4 Results of Experiment

### 4.1 Zeta Potential Measurements

#### 4.1.1 Zeta Potential of Aluminate-modified Colloidal Silica

Figure 4.1 illustrates the zeta potential measurements of the aluminate-modified colloidal silica with specific surface area of 250, 500 and 1100 m<sup>2</sup>/g from pH 2 to 11. Moreover, Zeta potentials of CS\_AI\_500 and CS\_AI\_1100 shows comparable and similar results between pH 4 to 9. However, after pH 4 CS\_AI\_500 shows a rapid increase, has an isoelectric point between pH 2-3, and a maximum zeta potential of 27.6 mV. CS\_AI\_250 shows the lowest zeta potential measurement and it stays negative through the pH range of 2 to 11.

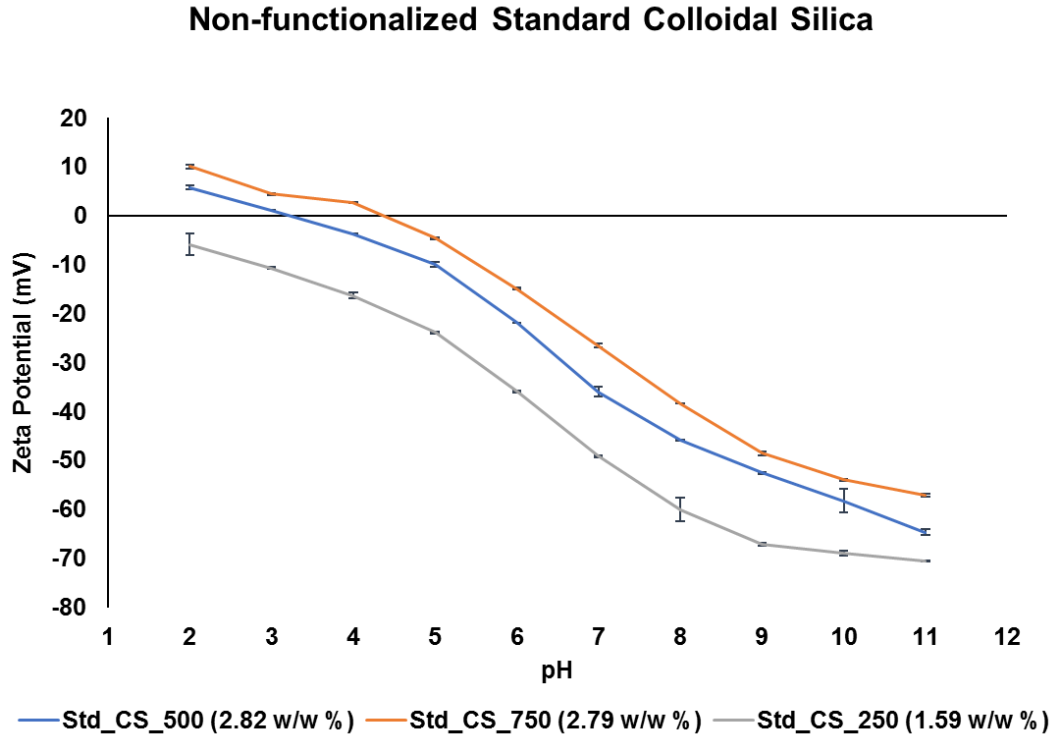


**Figure 4.1:** Zeta potential of aluminate-modified colloidal silica

#### 4.1.2 Zeta Potential of Non-functionalized Colloidal Silica

Figure 4.2 shows the results of the zeta potential measurements for non-functionalized colloidal silica. It demonstrates that the zeta potential of the non-functionalized standard colloidal silica suspensions depends on the specific surface area with an increasing zeta potential with higher specific surface area.

For std\_CS\_250, the surface charge stays in the negative throughout the pH 2 to 12, it varies between -70.5 to -5.85 mV. Meanwhile, std\_CS\_500 shows an isoelectric point between pH 3 to 4, and std\_CS\_750 has an isoelectric point between pH 4 to 5.

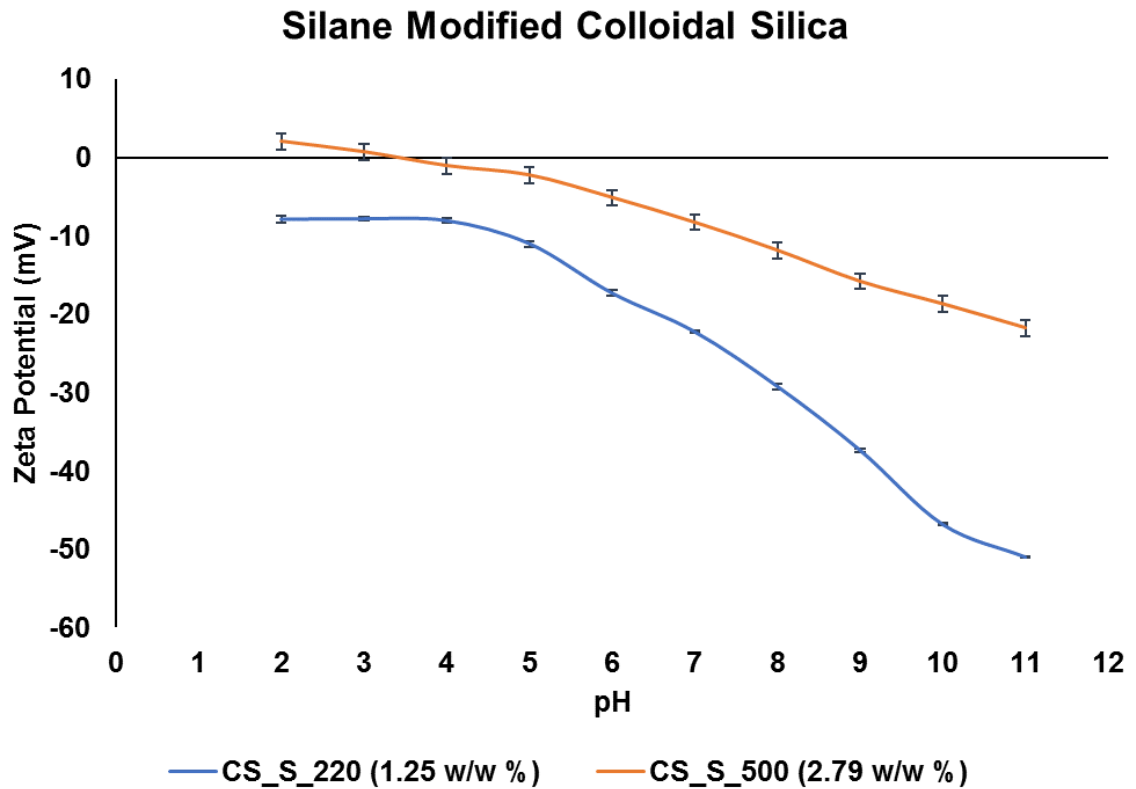


**Figure 4.2:** Zeta potential of Non-functionalized colloidal silica

#### 4.1.3 Zeta Potential of Silane-modified Colloidal Silica

Figure 4.3 shows the zeta potential measurement of silane-modified colloidal silica. CS\_S\_220 modification with a specific surface area of 220 m<sup>2</sup>/g shows a negative trend throughout pH from 2 to 11. CS\_S\_500 indicates an isoelectric point between pH 3 and 4.

From pH 2 to 6, both species exhibit a comparable trend. At pH 5, CS\_S\_220 and CS\_S\_500 have a zeta potential of -11.03 mV and -2.26 mV respectively. At pH 11, the difference in zeta potential becomes higher.

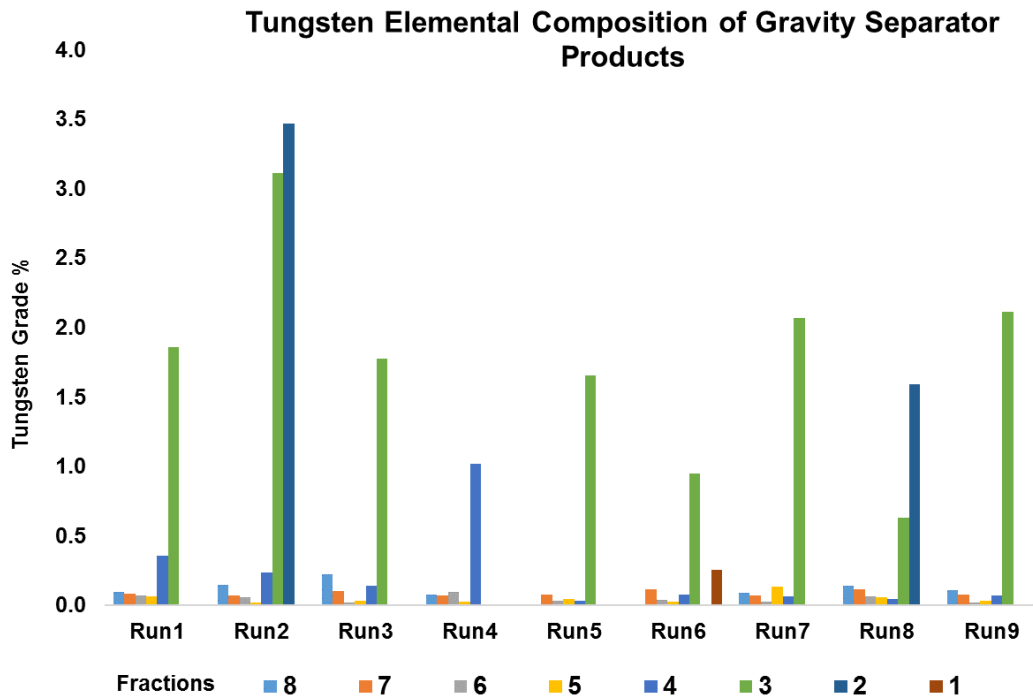


**Figure 4.3:** Zeta potential of silane-modified colloidal silica

## 4.2 Gravity Separation

### 4.2.1 Elemental Compositional Analysis

The given results shown in Figure 4.4 are the tungsten (W) grade % in eight size fractions collected from nine shaking table experiment runs from experiment design as shown in Table 4.1. Figure 4.4 shows that fractions with the highest tungsten content were consistently observed in Fraction 3 across multiple runs but for the Run 2, fraction 3 and 4 have high tungsten grade.



**Figure 4.4:** Tungsten grade % for experimental runs on the different parameters

In general, fractions 8, 7, 6, and 5 consistently have lower tungsten grade % across all experimental runs. The measured tungsten grade in these fractions varies from 0.02% to 0.22%. Run 2 displays high tungsten grade in both Fraction 2 (3.47%) and Fraction 3 (3.11%).

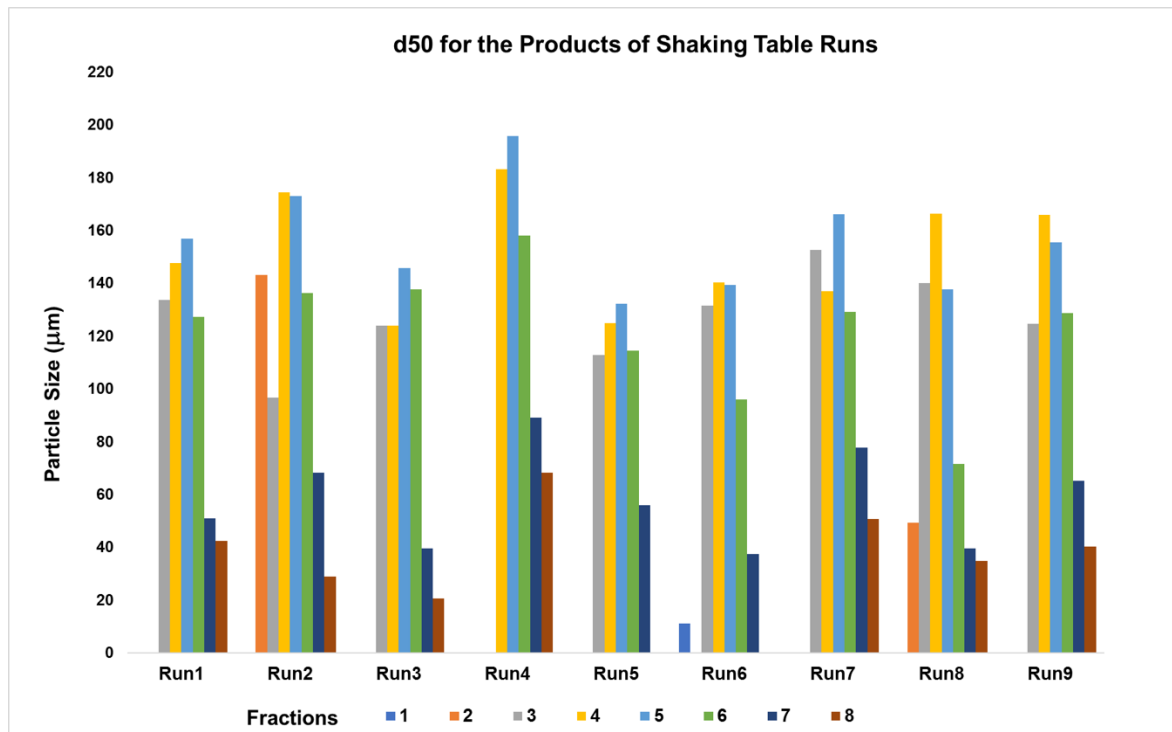
**Table 4.1:** Tungsten grade % in different shaking table products across all runs

| Tungsten Grade % |           |      |      |      |      |      |      |      |
|------------------|-----------|------|------|------|------|------|------|------|
|                  | Fractions |      |      |      |      |      |      |      |
|                  | 8         | 7    | 6    | 5    | 4    | 3    | 2    | 1    |
| Run1             | 0.10      | 0.08 | 0.07 | 0.06 | 0.36 | 1.86 |      |      |
| Run2             | 0.14      | 0.07 | 0.05 | 0.02 | 0.24 | 3.11 | 3.47 |      |
| Run3             | 0.22      | 0.10 | 0.02 | 0.03 | 0.14 | 1.78 |      |      |
| Run4             | 0.08      | 0.07 | 0.09 | 0.02 | 1.02 |      |      |      |
| Run5             |           | 0.07 | 0.03 | 0.04 | 0.03 | 1.65 |      |      |
| Run6             |           | 0.11 | 0.04 | 0.03 | 0.08 | 0.95 |      | 0.25 |
| Run7             | 0.09      | 0.07 | 0.02 | 0.13 | 0.06 | 2.07 |      |      |
| Run8             | 0.14      | 0.11 | 0.06 | 0.06 | 0.04 | 0.63 | 1.59 |      |
| Run9             | 0.10      | 0.08 | 0.02 | 0.03 | 0.07 | 2.11 |      |      |

#### 4.2.2 Particle Size Distribution Analysis

Figure 4.5 presents the data of particle size distribution of the shaking table products. The measurements were taken across nine different runs with different operating parameters. Rows Run1 to Run9 correspond to specific runs of the shaking table varying under operational parameters. Similarly, all test runs exhibit variations in their  $d_{50}$  values, illustrating the influence of operating parameters on the shaking table's performance.

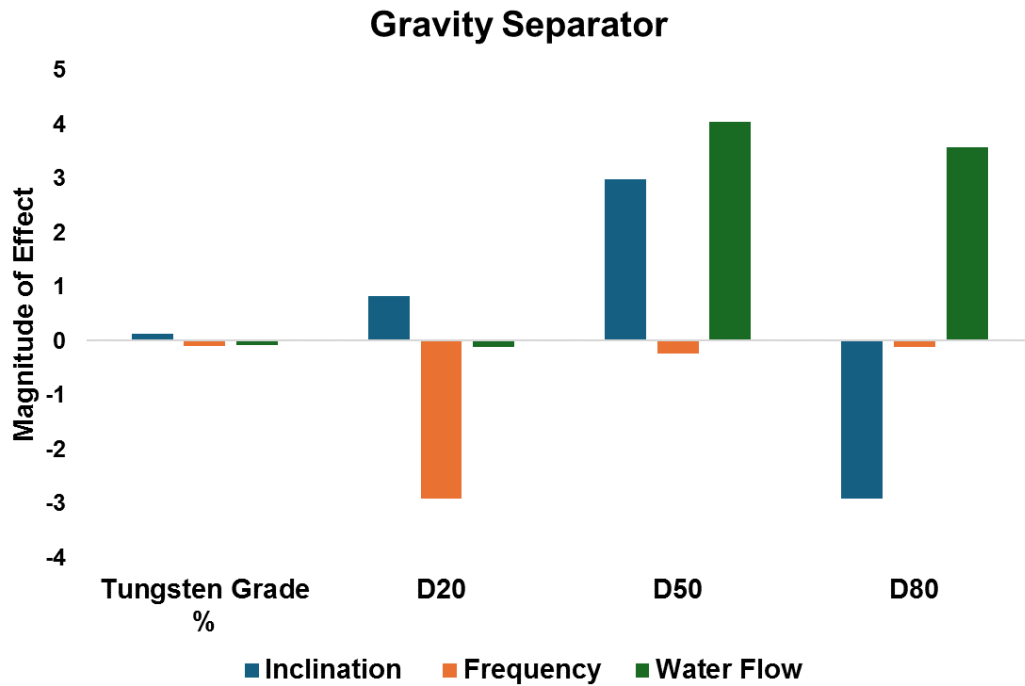
Run 8 shows that the  $d_{50}$  value in fraction 2 is 49.24  $\mu\text{m}$ . Looking into fraction 3, the  $d_{50}$  value increases to 140.08  $\mu\text{m}$ . The highest  $d_{50}$  value for this run is observed in fraction 4, at 166.40  $\mu\text{m}$ . Consequently, fractions show a regular decrease in the  $d_{50}$  values.



**Figure 4.5:** Particle size distribution of shaking table products for experimental runs on the different parameters

Figure 4.6 shows the impact of process parameters i.e., inclination, frequency and water flow on the target variables tungsten grade %,  $d_{50}$  and  $d_{80}$ . The effect of the operating parameters on the tungsten grade % is low, On the other hand, inclination has a positive impact on  $d_{20}$ , and  $d_{50}$  and a negative impact on  $d_{80}$ . An increase on water flowrate has a prominent positive impact on  $d_{50}$  and  $d_{80}$  and a small negative influence on  $d_{20}$ . Meanwhile, frequency has a negative effect on the fine particle size distribution. For coarser particles the effect of the frequency is insignificant.

The basis of finding the optimized parameters is the wide range of particle size distribution and equal distribution of tungsten grade in all the fractions. The objective of the optimized parameter to investigate the effect of particle size distribution on the flotation of scheelite.

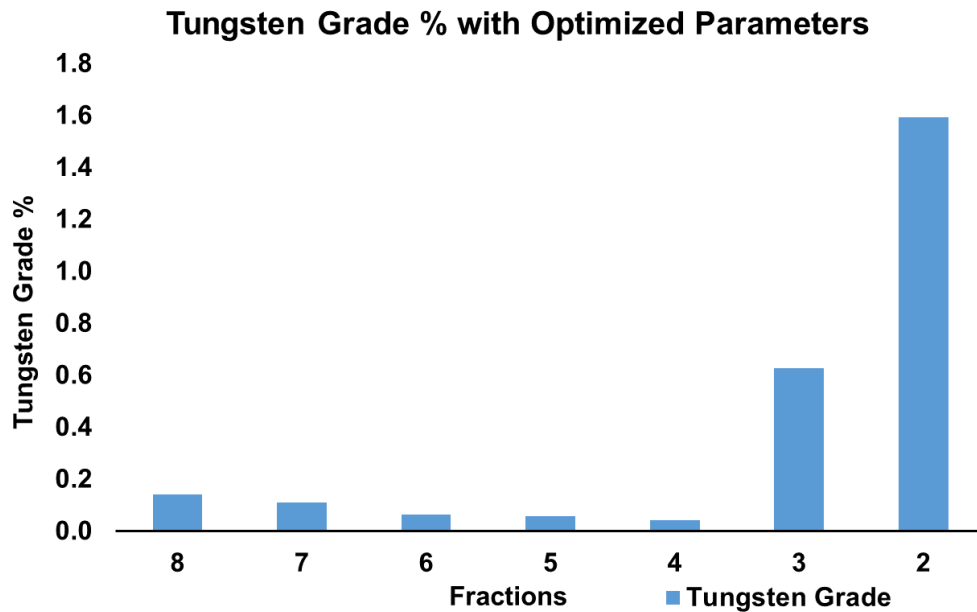


**Figure 4.6:** Effect of gravity separator parameters on tungsten grade % and particle size distribution

### 4.3 Gravity Separation test with optimal conditions

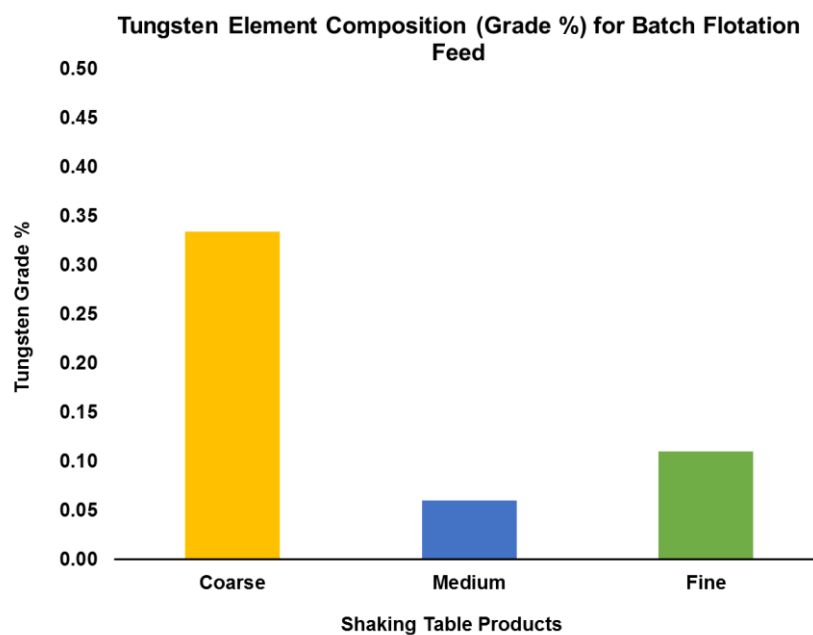
#### 4.3.1 Elemental Compositional Analysis

Figure 4.7 shows elemental compositional analysis of shaking table experiment with optimal setting or parameters. It shows that coarse size shaking table products have higher tungsten grade and medium size shaking product have lowest tungsten grade. Fine size shaking table products have comparatively high tungsten grade than medium size products.



**Figure 4.7:** Tungsten grade % of shaking table products with optimized settings

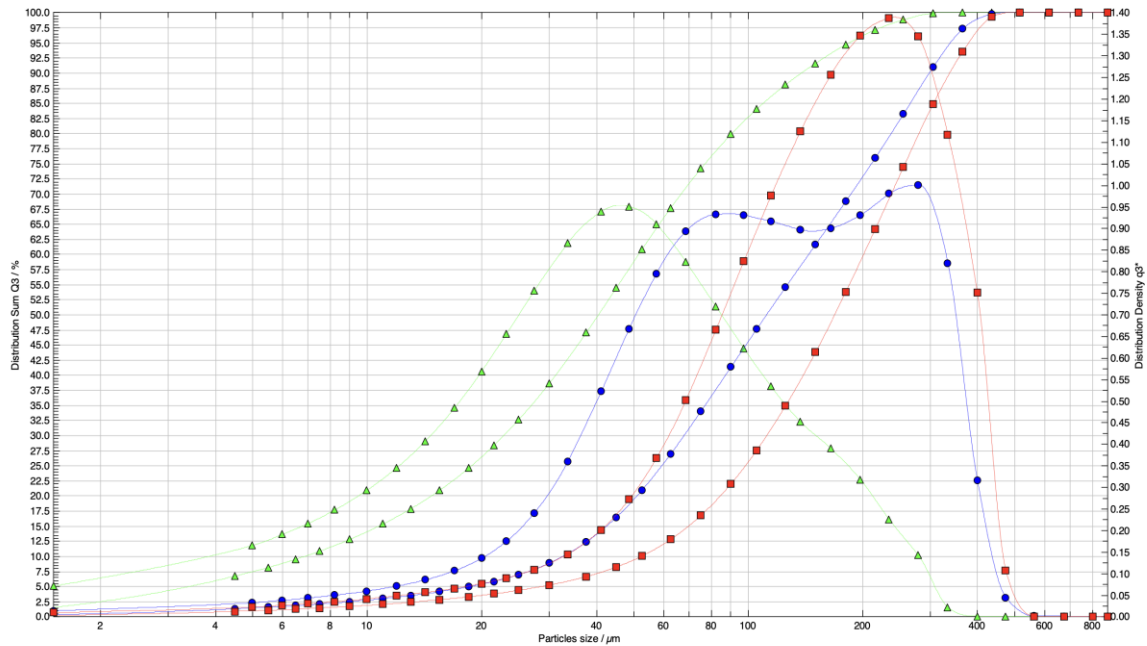
The Figure 4.8 shows tungsten grade of the shaking table products that was mixed and categorized into 3 parts: coarse, medium, and fine. Fractions 3 and 4 were mixed together, 5 and 6 were mixed together and fraction 7 stayed separate. Coarse-size shaking table products have the highest composition of tungsten that is 0.33 %, fine-size shaking table products have 0.11 % and the lowest tungsten fraction is found in medium-size shaking table products which is 0.06 %



**Figure 4.8:** Tungsten element composition batch flotation feed

### 4.3.2 Particle Size Distribution Analysis

Figure 4.9 represents the particle size distribution of coarse, medium, and fine shaking table products. It shows coarse and medium-sized shaking table products have almost the same  $d_{80}$ , but there is a difference between the  $d_{50}$  and  $d_{20}$  of both shaking products. It shows that medium-sized shaking table products have a bimodal distribution.



**Figure 4.9:** Particle size distribution graph for shaking table products with optimized setting represented as  - Fine size shaking table product;  - Medium size shaking table product;  - Coarse size shaking table product

### 4.4 Batch Flotation

Batch flotation of the scheelite ores was conducted under different pH and with colloidal silica dosages of different specific surface areas (SSA), under the fixed collector and frother dosages. The behavior of the scheelite, calcite, and hornblende recoveries and grades, froth properties, and kinetic flotation model were studied and analyzed.

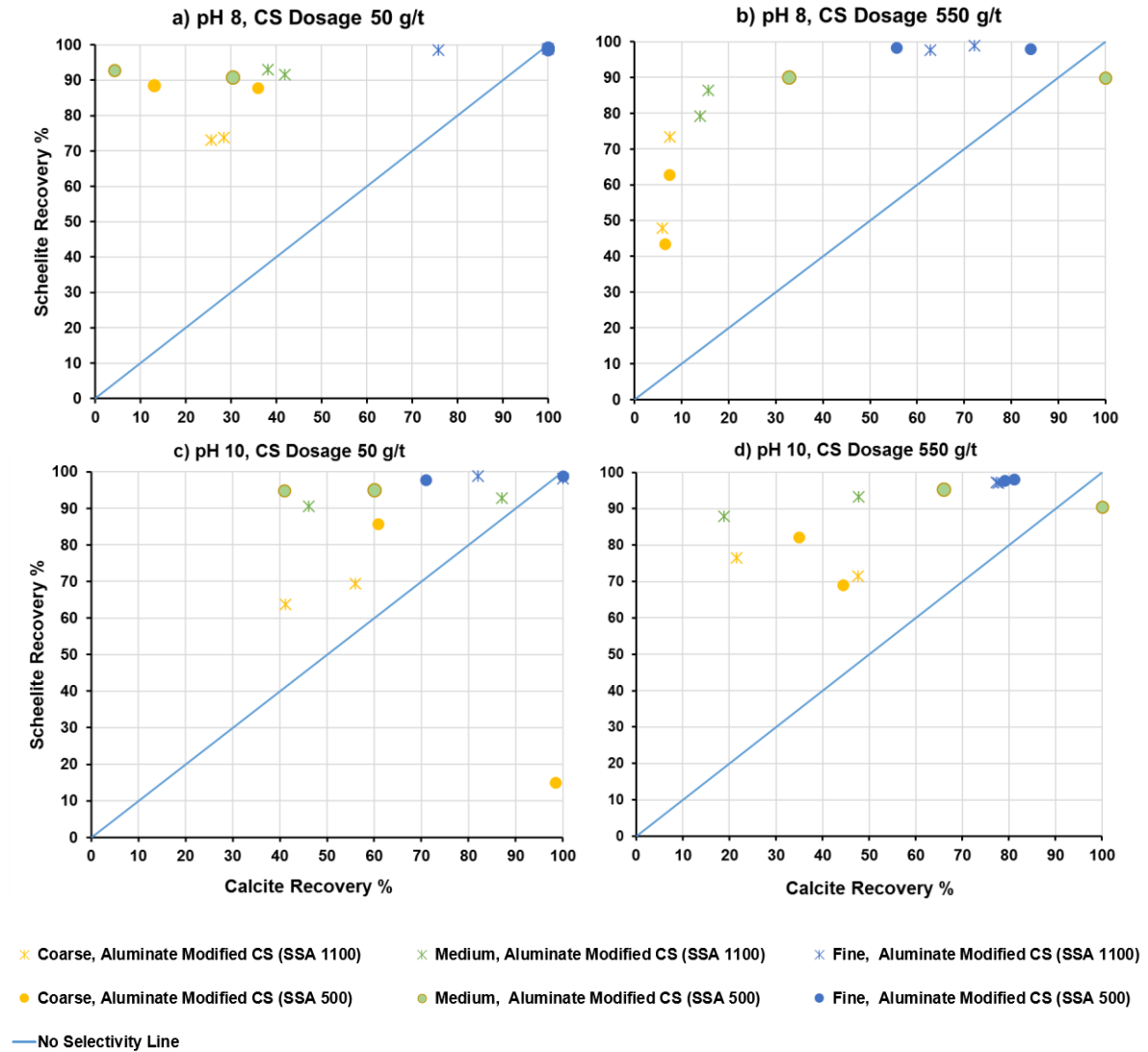
#### **4.4.1 Selectivity Curves**

##### **4.4.1.1 Selectivity of Scheelite against Calcite**

Figure 4.10 shows a relationship between the scheelite and calcite recovery. It can be seen that in graph a) coarse-size fraction with aluminate modified CS (SSA 500 & 1100) and medium-size shaking table products with aluminate modified CS (SSA 500) show good selectivity of scheelite against calcite, with a good depressing effect of calcite, calcite recovery is less than 30 %. Overall, fine-size shaking table products and medium-size shaking table products with aluminate-modified CS (SSA 1100) show low selectivity of scheelite against calcite with higher recovery of calcite and scheelite.

In graph (b), aluminate-modified CS (SSA 500 & 1100) on the coarse-size shaking table products has a good depressing effect, but lower scheelite recoveries. Meanwhile, aluminate-modified CS (SSA 1100) on the medium-size shaking table products have relatively good scheelite selectivity against calcite.

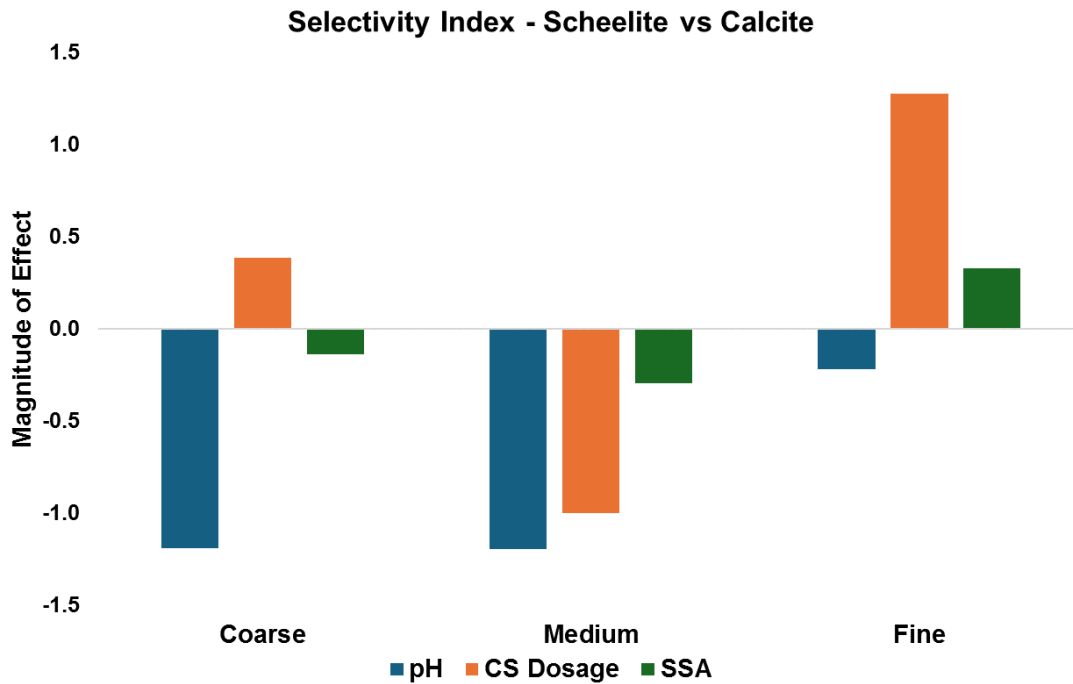
At higher pH in graphs (c) and (d), it is observed that CS has a low selectivity. At higher pH and CS dosage in graph d) coarse and medium-size shaking table products have a relatively better selectivity.



**Figure 4.10:** Selectivity of the scheelite against calcite

Figure 4.11 shows the magnitude of the effect of the pH, CS dosage, and SSA on the SI of scheelite against calcite on different size fractions of the shaking table. It shows that an increase in pH negatively influences the SI of calcite and scheelite for all three size shaking table products. Meanwhile, colloidal silica positively impacts the coarse and fine-sized shaking table products. CS dosage has a more pronounced positive impact on the fine-sized shaking table product which is more than 1 but less than 0.5 magnitude of SI on coarse-sized shaking table products. Nevertheless, an increase in CS dosage for medium-sized shaking table products decreases the SI between scheelite and calcite.

The effect of the SSA is not very pronounced; coarse and medium-sized shaking table products are influenced negatively but it has a positive impact on the fine-sized shaking table product.

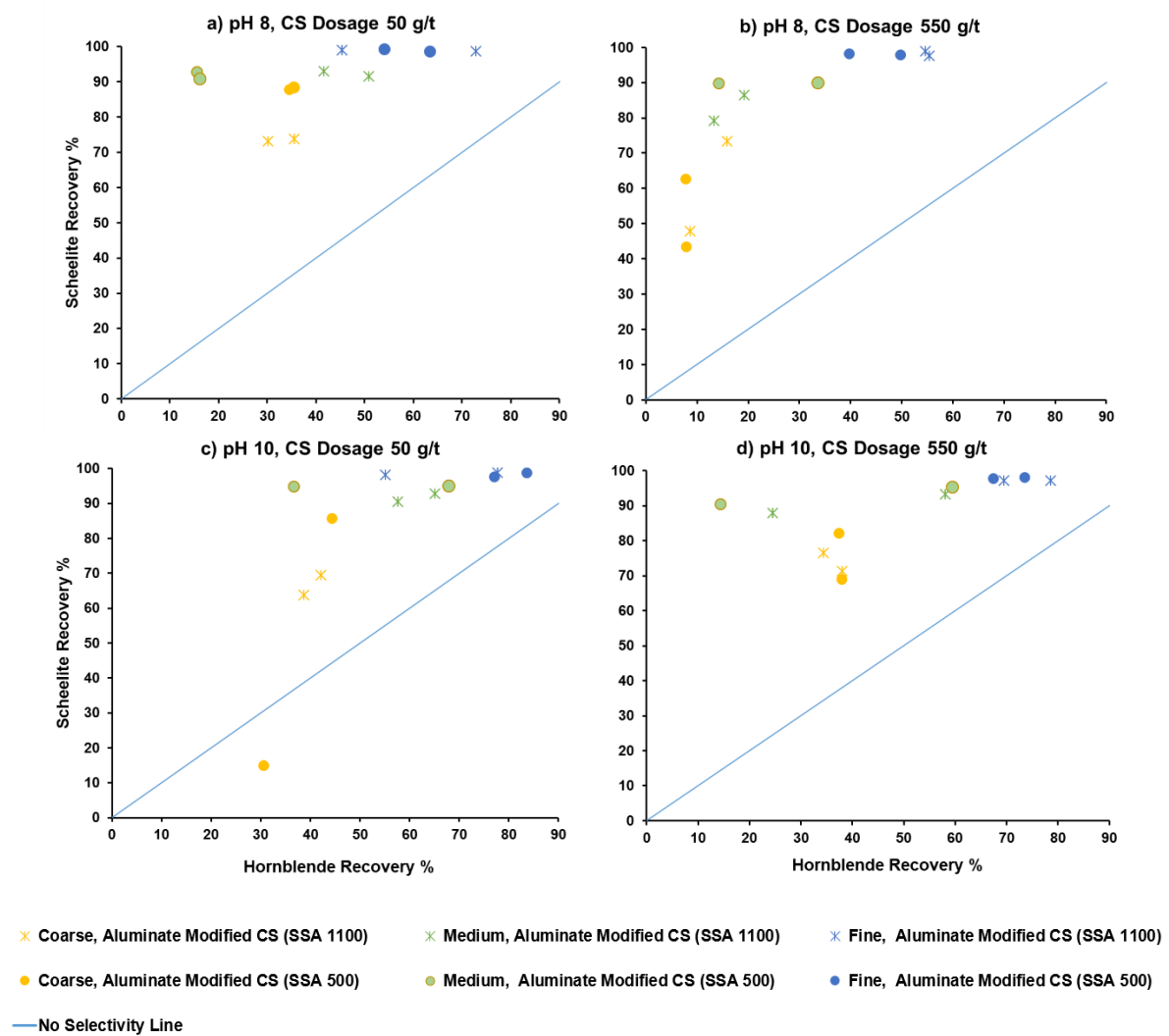


**Figure 4.11:** Magnitude of pH, CS modification, and dosage effects on the calcite recovery

#### 4.4.1.2 Selectivity of Scheelite against Hornblende

Figure 4.12 explains the selectivity of scheelite against hornblende. It demonstrates that at low pH 8, CS has a better depressing effect on hornblende against the scheelite for medium-sized shaking table products. However, a higher CS dosage of 550 g/t with coarse-size shaking table products has a relatively low scheelite recovery but a good depressing effect against the hornblende.

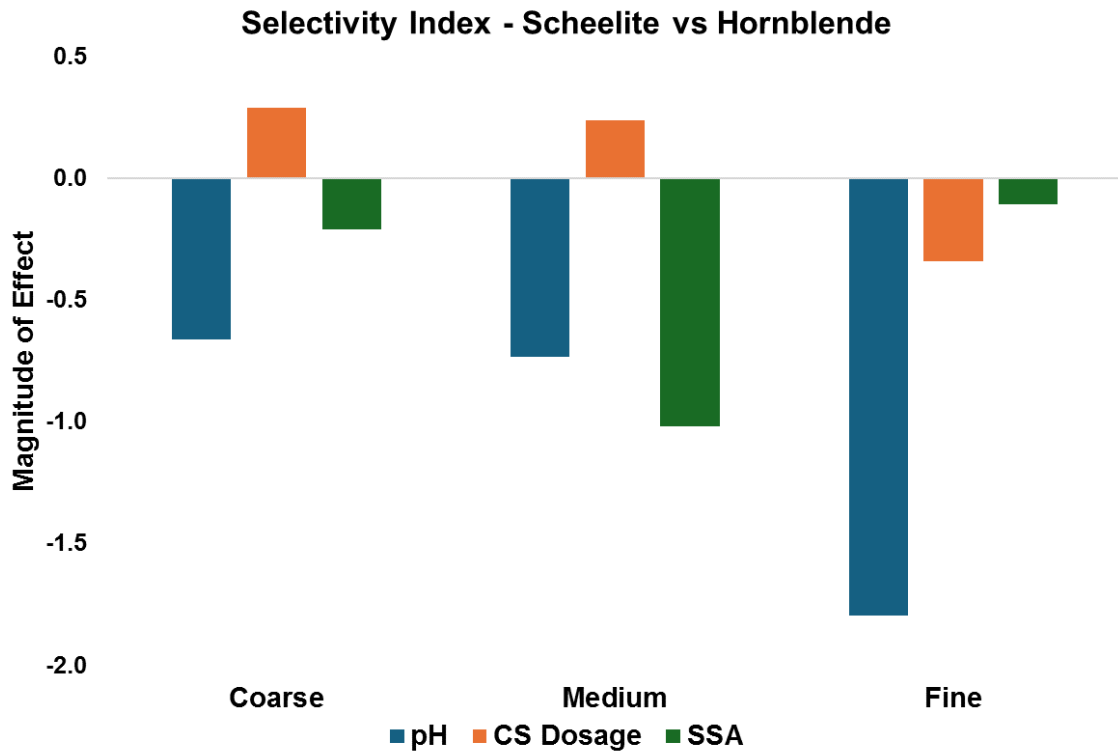
In graph c), coarse-size shaking table products show low selectivity of scheelite against hornblende but they can be outliers.



**Figure 4.12:** Selectivity of the scheelite against hornblende

Figure 4.13 describe the magnitude of effect of the pH, CS dosage, and SSA on the SI of scheelite and hornblende on different size fraction of shaking table. It shows the selectivity index (SI) of scheelite against hornblende for all sizes of shaking table products, which are impacted negatively by increasing pH and specific surface area. In fine-sized shaking table products, the effect of pH is more prominent which decrease the SI of scheelite against hornblende by the magnitude of 2, meanwhile, coarse and medium size shaking table products have slightly decreasing effect of SI magnitude of 0.5. SSA has a notable negative impact on medium-sized shaking table products, which is almost SI magnitude by 1.

For the coarse and medium-size shaking table products, CS dosage increases the selectivity index by up to 0.25 points but reduces the SI for fine-sized shaking table products by 0.25.

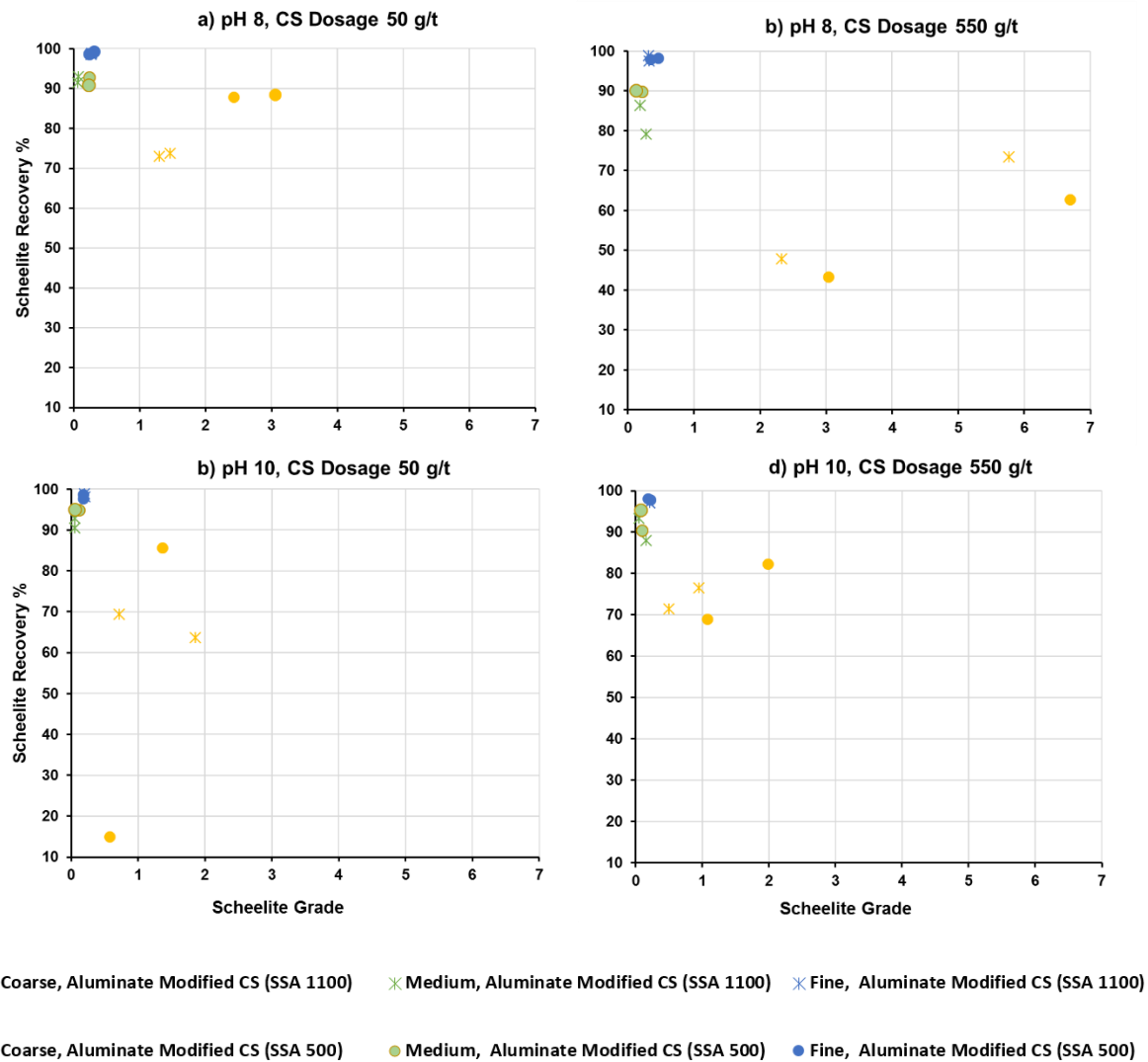


**Figure 4.13:** Magnitude of pH, CS modification, and dosage effects on the selectivity index for scheelite and hornblende

#### 4.4.2 Upgrading Curves

##### 4.4.2.1 Scheelite Upgrading Curve

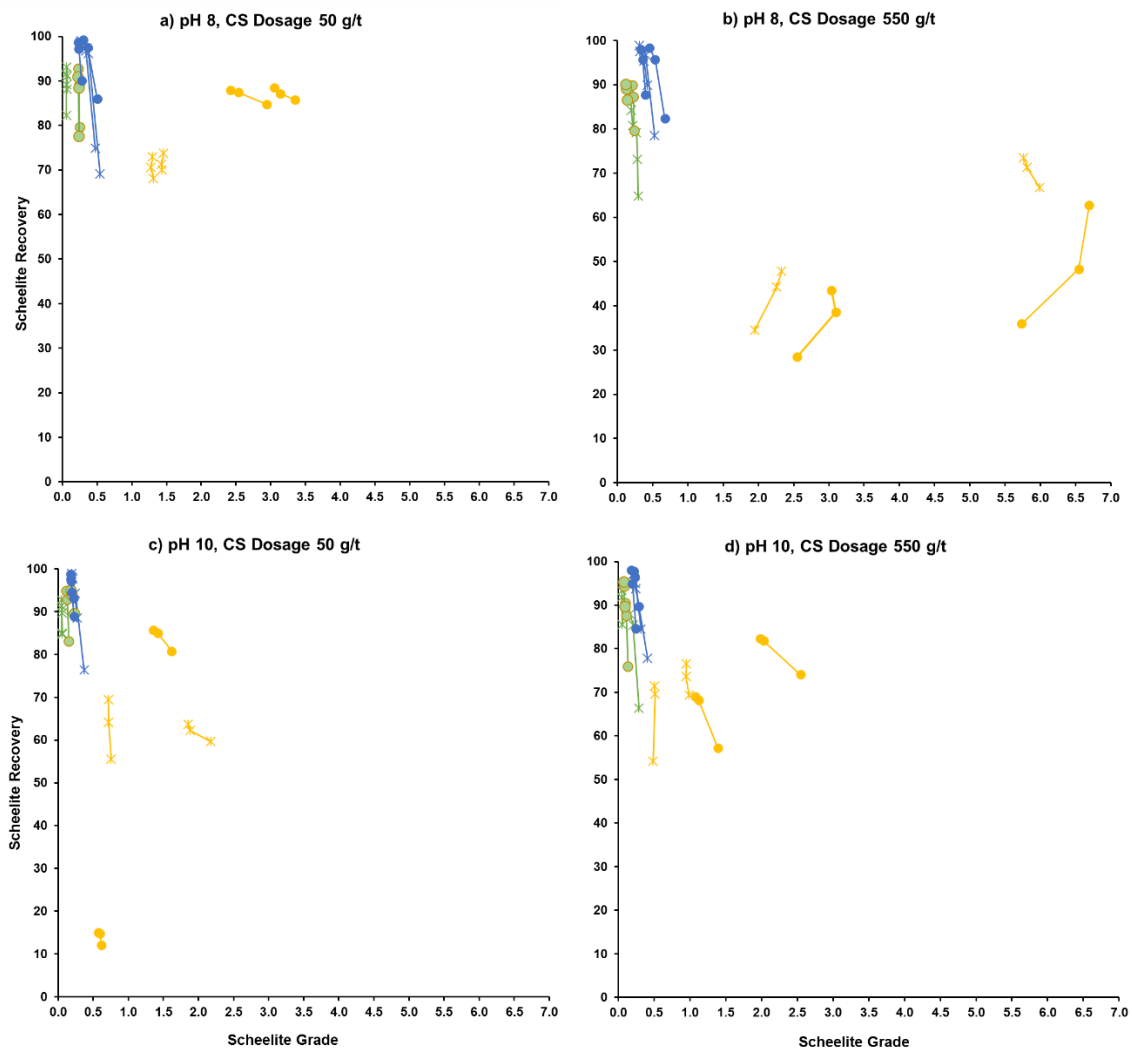
Figure 4.14 show the relationship between the scheelite recovery and grade. It demonstrates that coarse-sized shaking table products have a higher scheelite grade %, but a relatively low scheelite recovery. Meanwhile, fine and medium-sized shaking table product has very high scheelite recovery, but low scheelite grade %.



**Figure 4.14:** Upgrading curve of Scheelite

The cumulative upgrading curves of scheelite recovery and grade of different shaking table products are shown in Figure 4.15. For coarse-size shaking table products, the recovery of the scheelite increases with time, and the grade of scheelite also increases at low pH and high CS dosage for both CS modifications.

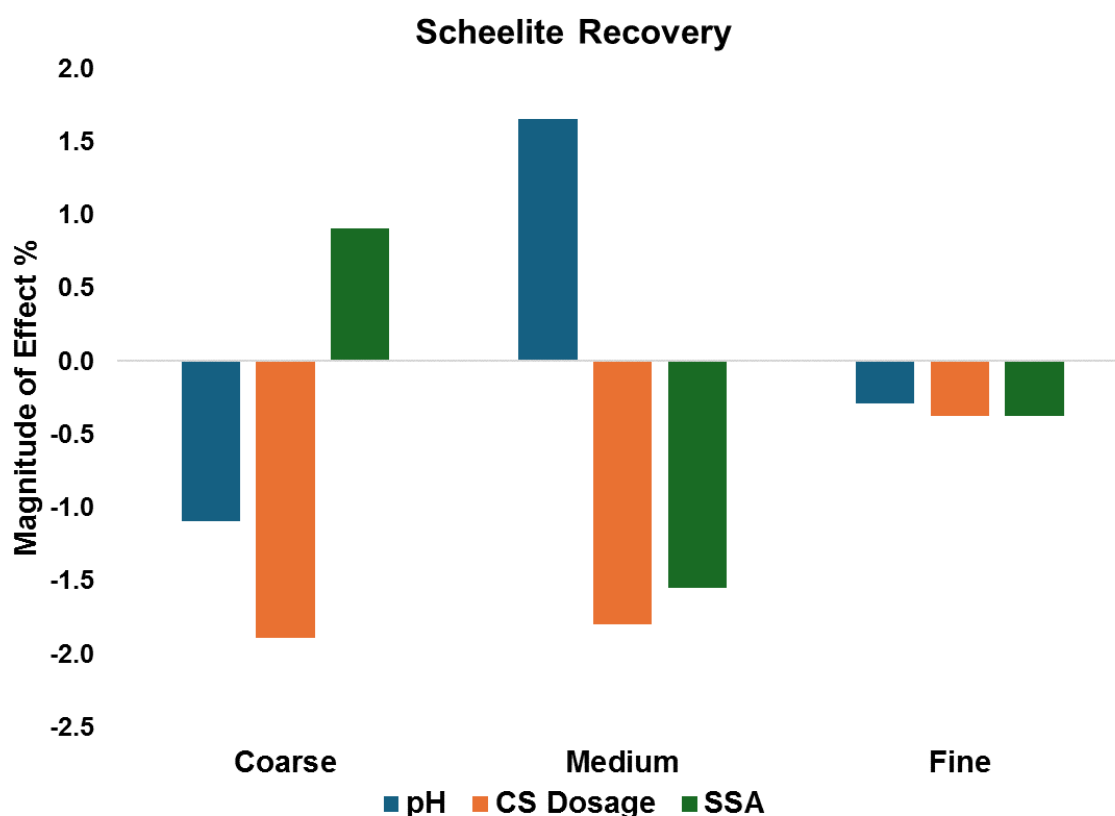
In other operating conditions of batch flotation, the grade of scheelite for coarse-size shaking table products decreases as the recovery of scheelite increases. For medium and fine-size shaking table products the grade of scheelite remains constant with time as recovery of the scheelite is increasing.



**Figure 4.15:** Cumulative upgrading curve of scheelite

Figure 4.16 describes the magnitude of effect of the operating parameters on the scheelite recovery of different size fraction of shaking table. It illustrates that scheelite recovery is positively influenced only by increasing the specific surface area (SSA) and pH in the coarse and medium-sized shaking table products respectively. Scheelite recovery % is negatively affected by increasing the colloidal silica (CS) dosage in all three sizes of shaking table products but significantly impacts the coarse and medium size shaking table products. In fine-sized shaking table products, all three parameters show less than 0.5 % of the magnitude effect. Conversely, in coarse and medium-sized shaking table products an acute change in parameter affects the whole scenario for scheelite recovery. In Figure 4.16, some interesting

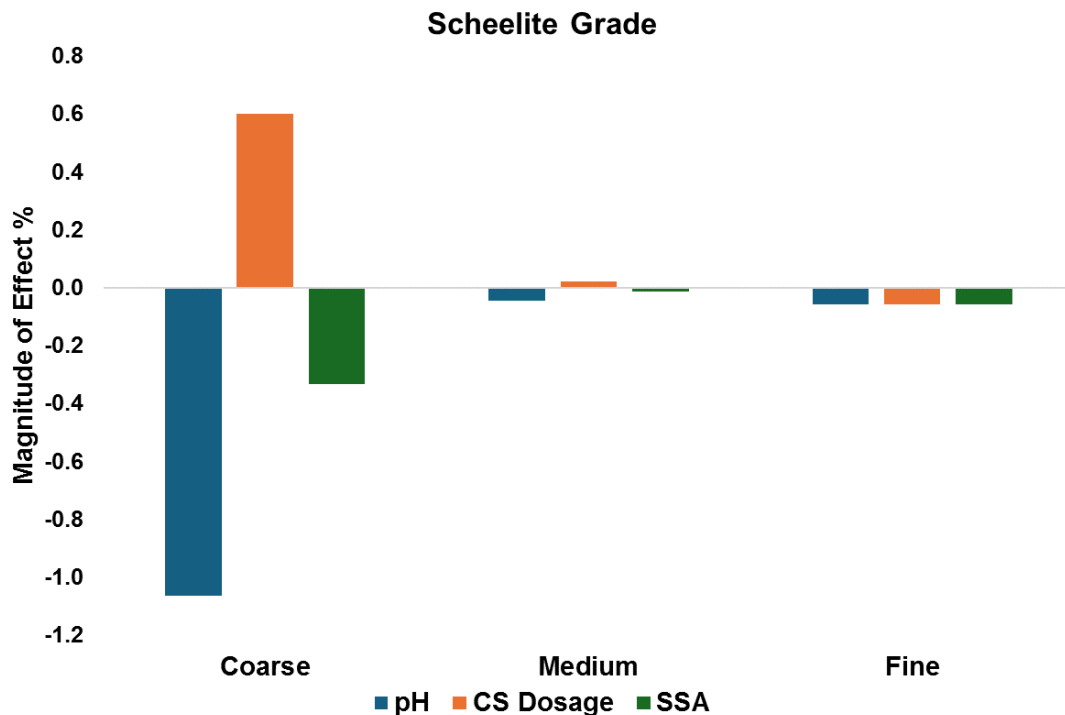
observations can be seen that increasing the specific surface area (SSA) for medium and fine-sized shaking table products reduces the scheelite recovery, but higher SSA increases the scheelite recovery for the coarser size shaking table products. Also, the pH shows a big positive impact on the medium size shaking table products.



**Figure 4.16:** Magnitude of pH CS modification and dosage effects on the Scheelite recovery

Figure 4.17 shows the magnitude of effect of the operating parameter on the scheelite grade for different size fraction of shaking table. It demonstrates a curious effect on the coarse size shaking table products. Increasing the pH and SSA of colloidal silica modifications decreases the scheelite grade up to 1 % and 0.30% respectively. However, increased CS dosage from 50 g/t to 550 g/t has increased the scheelite grade in the concentrates up to 0.6 %.

Scheelite grade is only positively influenced by changing the CS dosage for coarse size shaking table products. Otherwise, scheelite grade has been negatively influenced in all sizes of shaking table products and with all parameters.



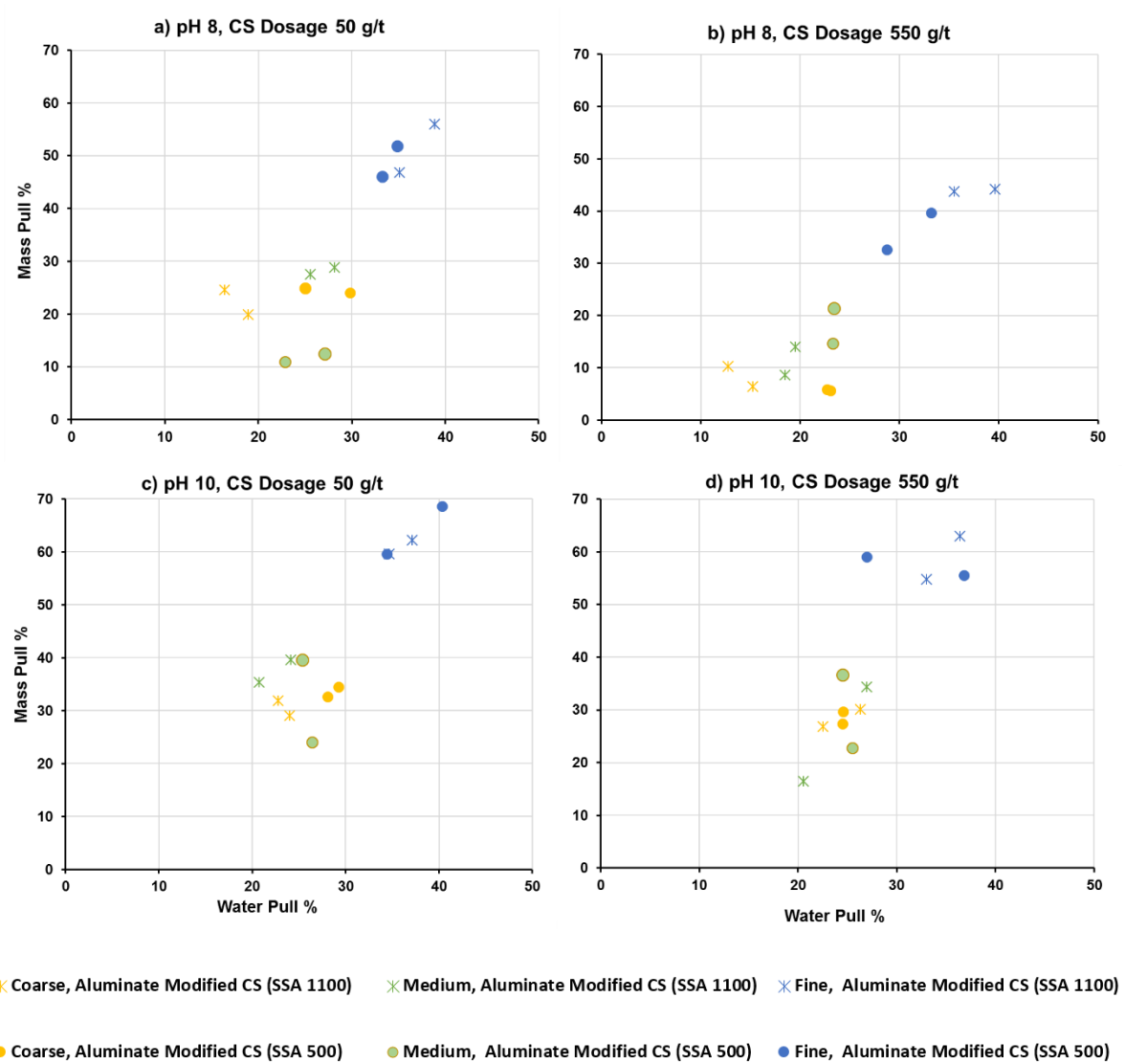
**Figure 4.17:** Magnitude of pH CS modification and dosage effects on the scheelite grade %

### 4.4.3 Froth Properties

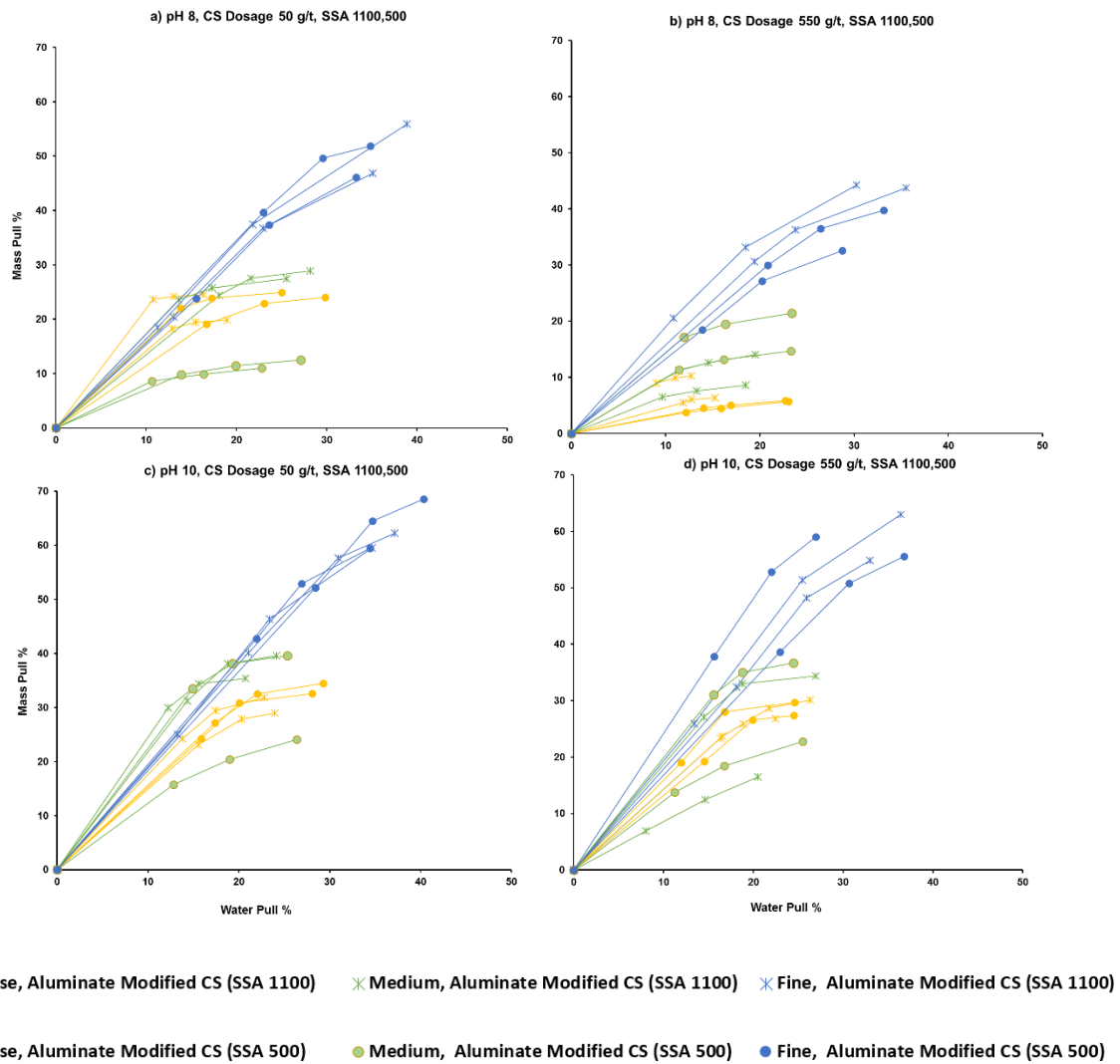
#### 4.4.3.1 Water Pull versus Mass Pull

Figure 4.18 and Figure 4.19 show the overall and cumulative mass & water pull respectively. The mass pulls and water pulls of batch flotation at different parameters in Figure 4.18 and Figure 4.19 show that increasing the pH results in a more loaded froth. However, high CS dosage and low pH results in the least loaded froth.

Fine-sized shaking table products show higher mass pull and water pull, followed by medium and coarse-sized shaking table products.



**Figure 4.18:** Water pull versus mass pull %

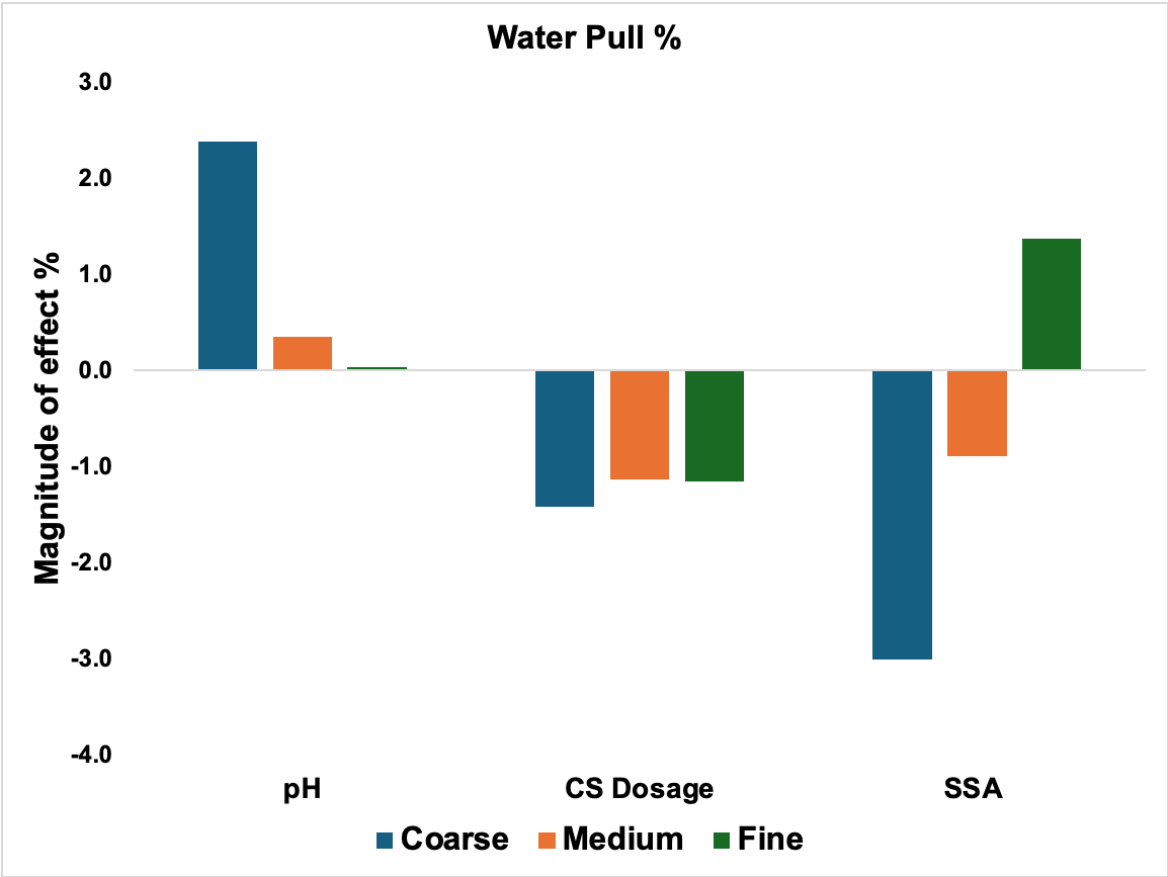


**Figure 4.19:** Cumulative water pull versus Mass pull %

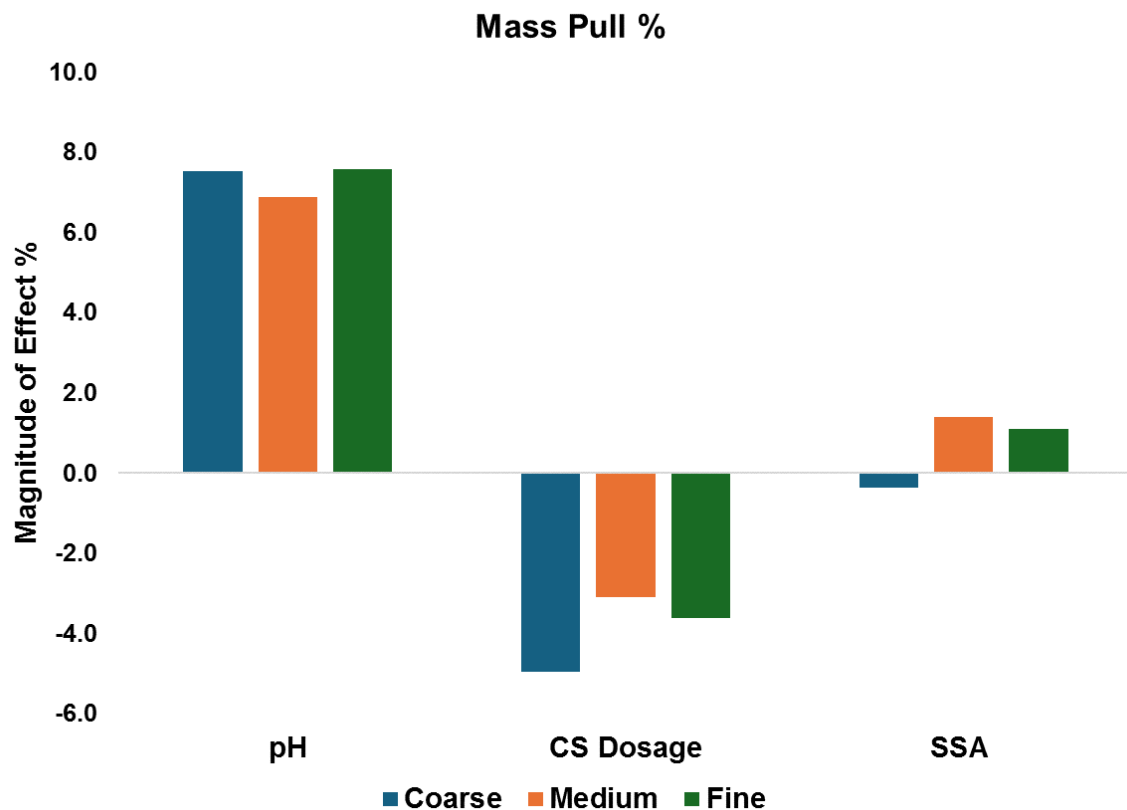
Figure 4.20 and Figure 4.21 show the magnitude of the effect of the operating parameters of batch floatation on the water and mass pull % of different sizes of shaking table products respectively. It can be observed that pH and CS dosage have a similar behavior on the water pull and mass pull. There is an observation that impact on the mass pull is more positively pronounced than the water pulls, e.g., pH has a less than 1 % of magnitude effect on water pull of medium and fine-sized shaking table products, however, it has more than 7 % of the impact on the mass pull, which leads to more loaded froth.

Now, SSA impacts negatively the mass and water pull for coarse-sized shaking table products, but it is less than 1 % for the mass pull but more pronounced on water pull, up to 3 %, which results in a less loaded froth.

The effect of the specific surface area on the fine-sized shaking table products is similar for mass and water pull and is impacted almost by 1 % in both cases. In the case of the medium-sized shaking table products, an increase in SSA enhances the mass pull but reduces the water pull by up to 1 %, which results in more loaded froth.



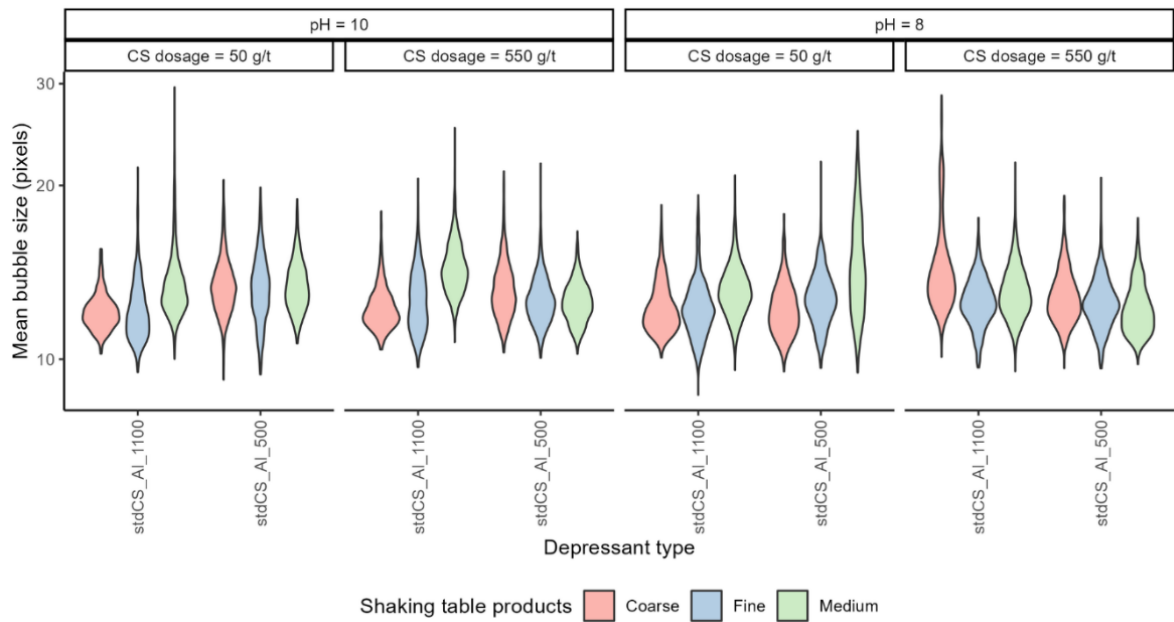
**Figure 4.20:** Magnitude of pH, CS modification, and dosage effects on the Water Pull



**Figure 4.21:** Magnitude of pH, CS modification, and dosage effects on the Mass Pull

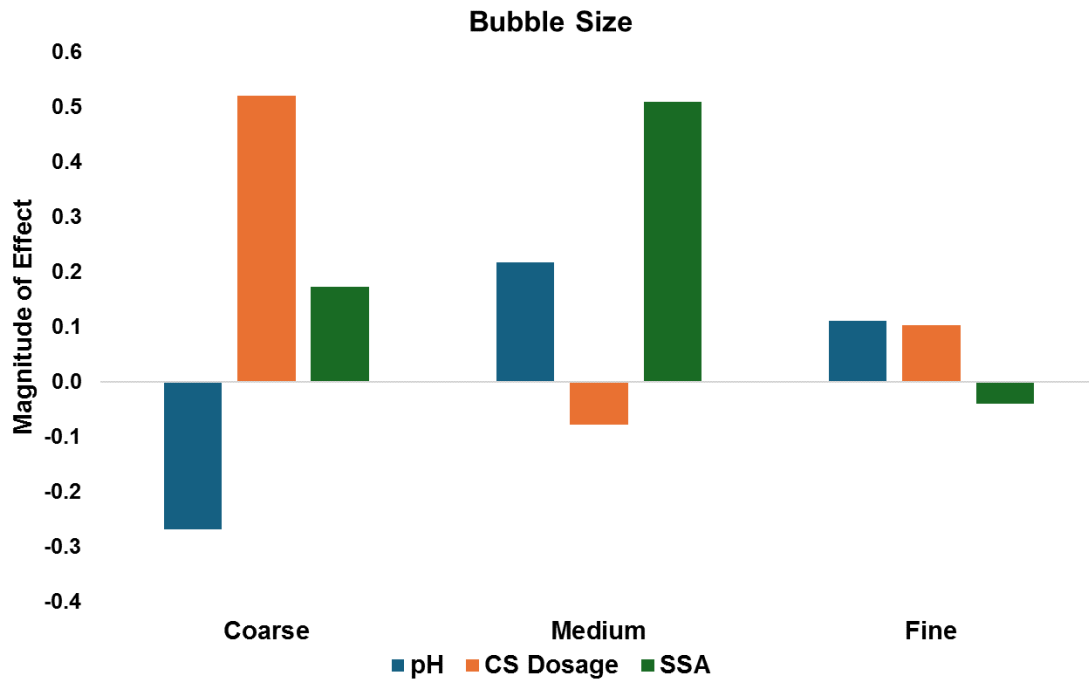
#### 4.4.3.2 Bubble size distribution in the froth zone

The effect of the specific surface area of CS, dosage, and pH is shown in Figure 4.22. The bubble size of the coarse-sized shaking table products is relatively smaller than other sizes of shaking table products. The highest bubble size is observed in the medium-sized shaking table products. At pH 8 and higher CS dosages, coarse-sized shaking table products have a higher bubble size with SSA 1100 in the froth zone.



**Figure 4.22:** Mean bubble size

Figure 4.23 demonstrates the magnitude of the effect of operating conditions on the bubble size. It shows that bubble size is more prominently affected by operational parameters in coarse and medium-sized shaking table products. The bubble size of the coarse-sized shaking table products is more prominently influenced by CS dosage and pH. It can be observed that CS dosage and pH increase the bubble size in coarse-size shaking table products. On the other side, a rise in the pH has a decreasing effect on the bubble size for coarse size fraction. The bubble size of the medium-size shaking table products is negatively influenced by CS dosage. Meanwhile, pH and SSA have opposite effects than the medium size shaking table products. pH and SSA has a positive effect on the bubble size. Figure 4.23 shows that pH, CS dosage, and SSA do not have a much-pronounced effect on the bubble size of fine-sized shaking table products. pH and CS dosage increased the bubble size and decreased by SSA.

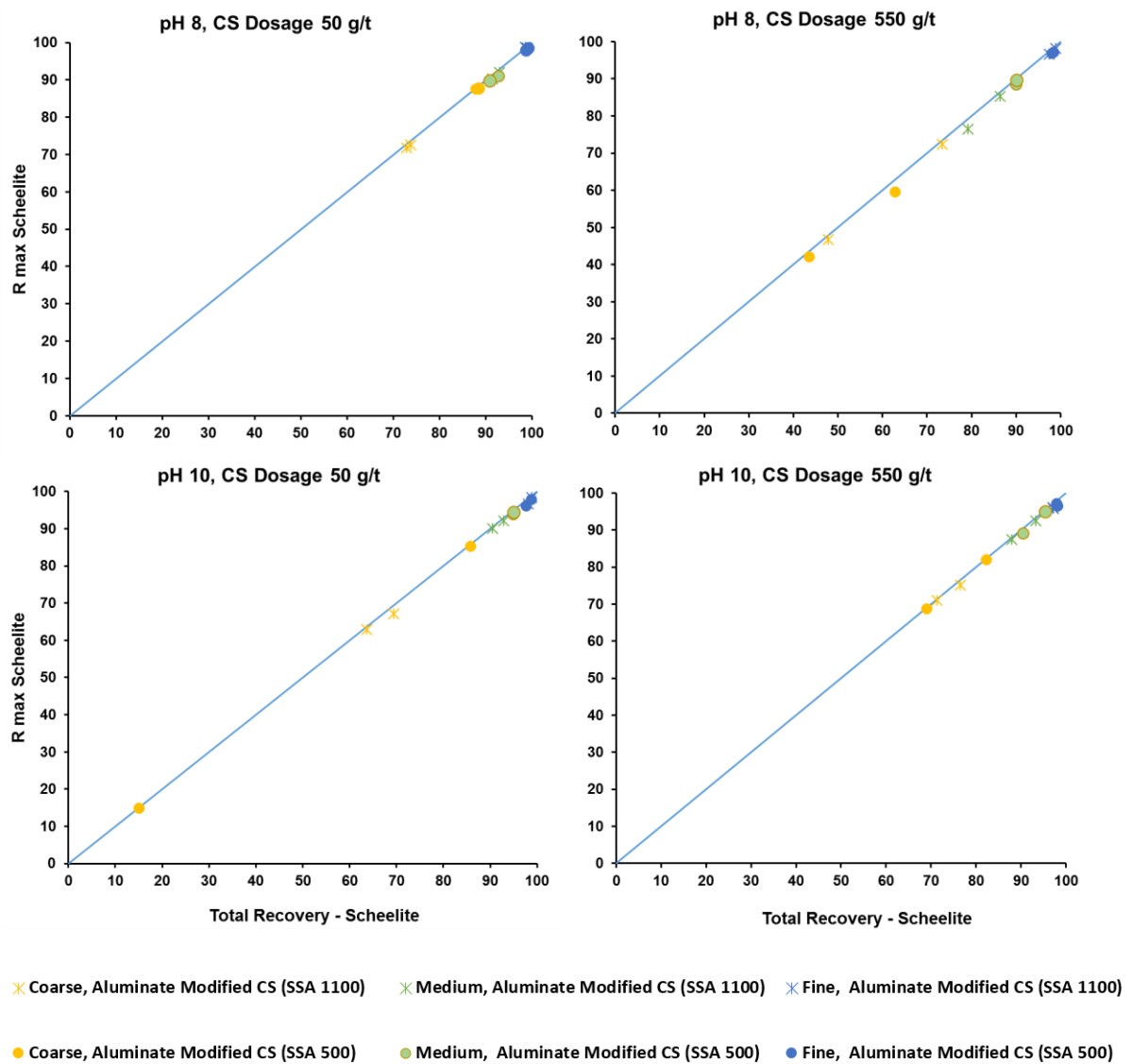


**Figure 4.23:** Magnitude of pH, CS modification, and dosage effects on the Bubble size

#### 4.4.4 Kinetics Model for Batch Floatation

##### 4.4.4.1 Validation of the first-order kinetic model fitting

The probable estimated recovery is fitted to the kinetic model for validation in Figure 4.24. Doubts about the flotation kinetic parameters, e.g., maximum recovery and flotation rate constant, may come out by fitting the kinetic model curve using discrete recovery values. A kinetic model for batch floatation is applied to predict the cumulative recovery values at cumulative times of 1, 3, and 7 minutes. The kinetic model fitting is made by using a first-order kinetic model. The maximum recovery,  $R_{\max}$ , determined from the fitted kinetic model, is plotted against the total recovery of scheelite in Figure 4.24.



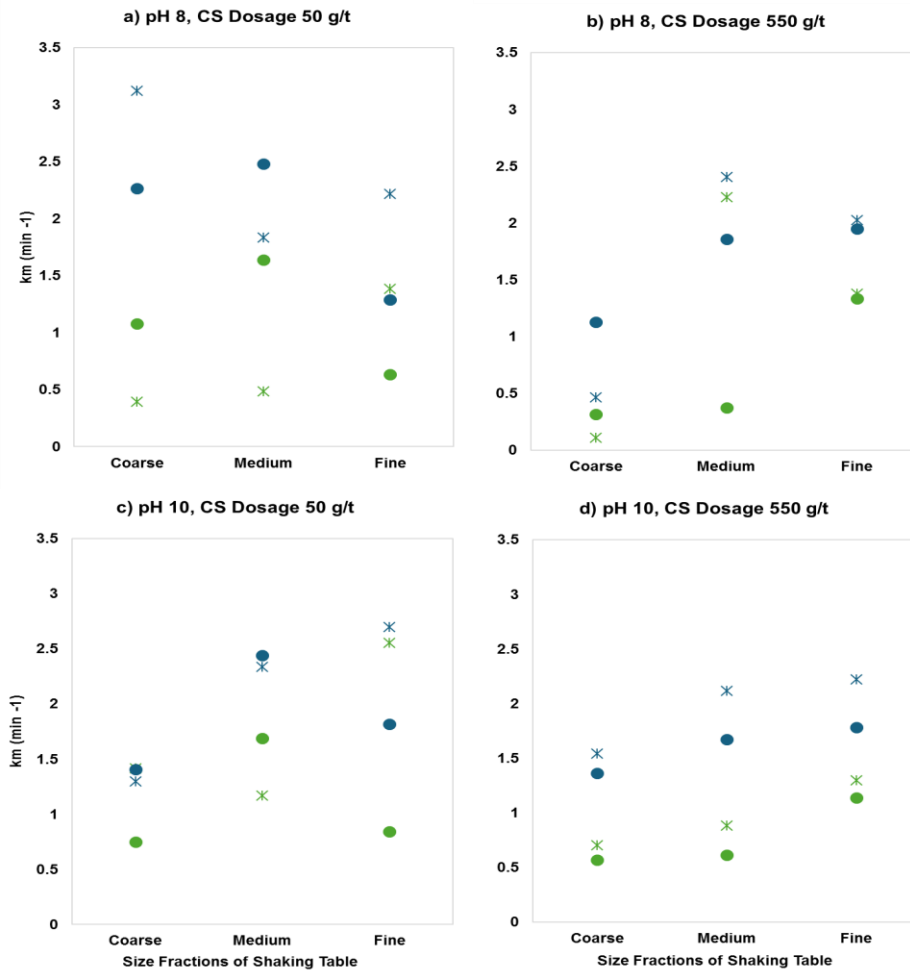
**Figure 4.24:** Total recovery vs  $R_{\max}$  of scheelite

#### 4.4.4.2 Modified Rate Constant of Scheelite and Calcite

The modified flotation rate constant of scheelite  $K_m$  for the 1<sup>st</sup> order rate equation for different shaking table products is shown in Figure 4.25. It shows that coarse-size shaking table products have higher  $K_m$  for scheelite in graph a) at pH 8 and CS dosage of 50 g/t. For medium-sized shaking table products, there is a modified rate constant  $K_m$  shift from low to high CS dosage. There is a consistent behavior of the modified rate constant  $K_m$  in fine-size shaking table products that CS SSA 500 has a higher constant value.

The modified rate constant  $K_m$  for the 1<sup>st</sup>-order rate equation for calcite in batch floatation has a trend e.g. for coarse-size shaking table products, there is a modified rate constant  $K_m$  shift for calcite going from pH 8 to 10. Also, a shift can be seen for medium size shaking table

products, by increasing the CS dosage from 50 to 550 g/t. The fine-size shaking table products have a similar trend but at a higher CS dosage the difference between the modified rate constant  $K_m$  for calcite is very small.



✕ Scheelite, Aluminate Modified CS (SSA 500) ✕ Calcite, Aluminate Modified CS (SSA 500)

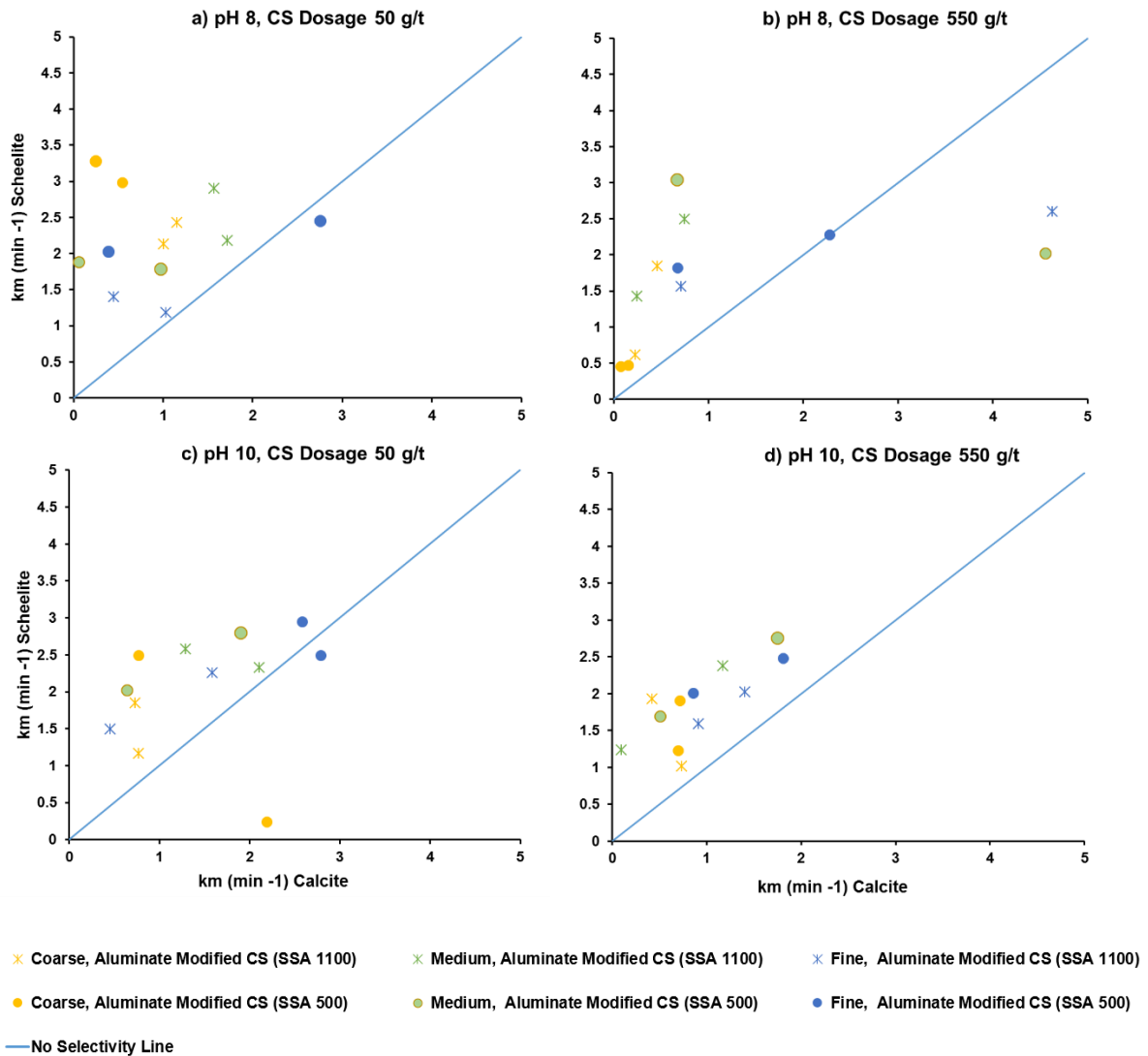
● Scheelite, Aluminate Modified CS (SSA 1100) ● Calcite, Aluminate Modified CS (SSA 1100)

**Figure 4.25:** Modified rate constant  $K_m$  for scheelite and calcite

The modified rate constant  $K_m$  based selectivity of scheelite and calcite is shown in Figure 4.26. The better selectivity is based upon distance from the no selectivity. It shows that increasing the CS dosage limits the value of the modified rate constant of calcite. In Graph a), the best selectivity is seen for the coarse-size shaking table product with CS modification with SSA 500, but in graph b) coarse size products have a bad selectivity. But medium-size shaking

table products, have relative better scheelite selectivity against calcite in all operation conditions.

The fine-sized shaking table product with CS SSA 500 has a low scheelite selectivity against calcite. For fine-size shaking table products at higher pH and CS dosages, have comparably better scheelite selectivity against calcite as compared to other operating conditions.

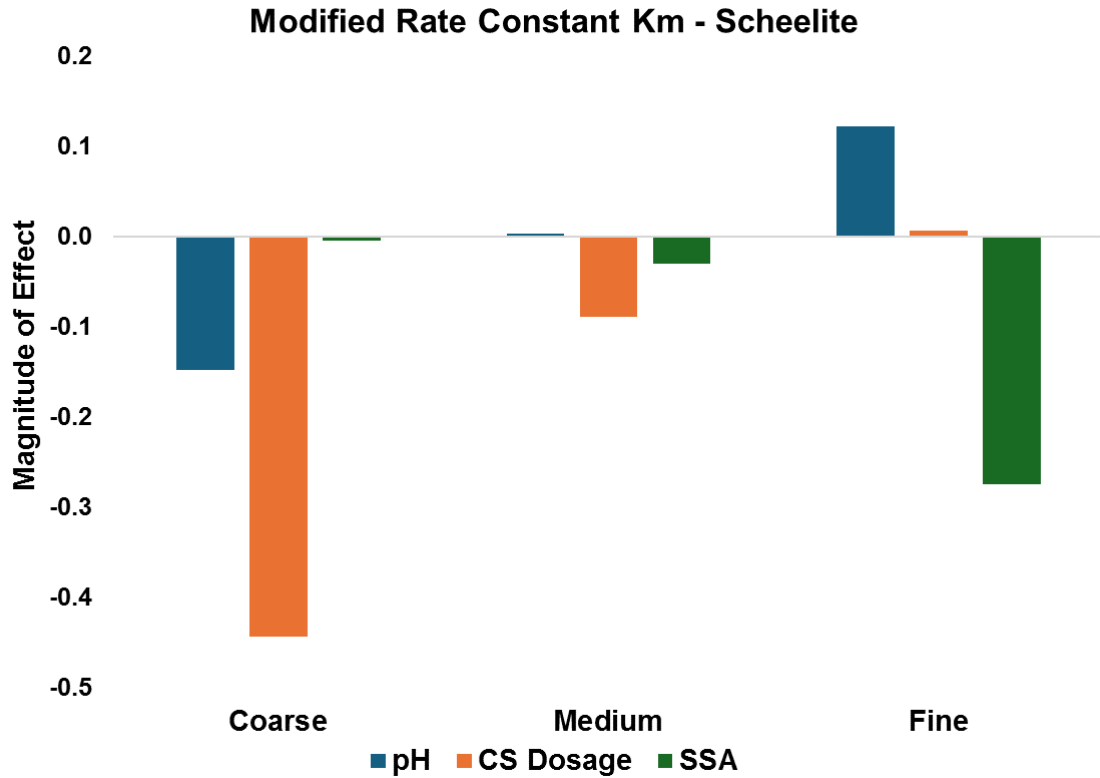


**Figure 4.26:** Selectivity diagram for the modified rate constant  $K_m$  scheelite versus calcite

The magnitude of the effect of the parameter on the modified rate constant  $K_m$  of scheelite is given in Figure 4.27. For coarse-size shaking table products, pH, SSA and CS dosage have a decreasing effect. But pH and CS dosage show more prominent negative effect on the modified rate constant  $K_m$ .

For medium-sized shaking table products, an increase in the pH, CS dosage and SSA reduces the modified rate constant  $K_m$  and but CS dosage effect is more negatively pronounced.

SSA has a prominent negative effect on the modified rate constant  $K_m$  for fine-sized shaking table products, but pH, and CS dosage increase the modified rate constant  $K_m$  for scheelite.

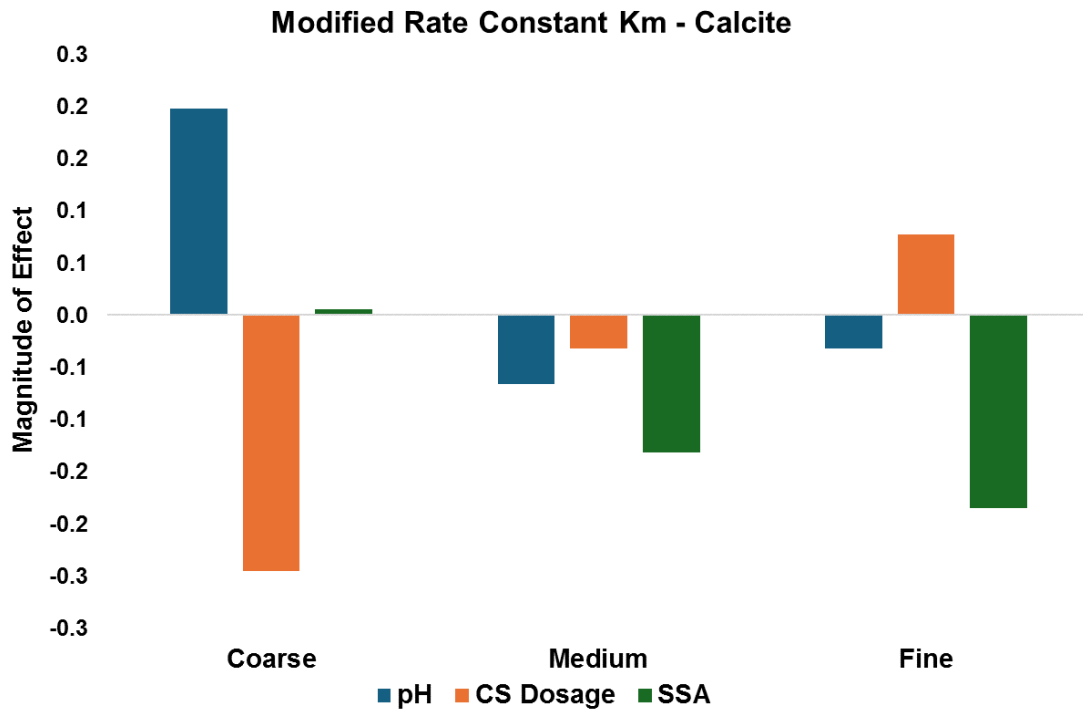


**Figure 4.27:** Magnitude of pH, CS modification, and dosage effects on the modified rate constant  $K_m$  – scheelite

Figure 4.28 demonstrates the magnitude of the effect of the operating parameter on the modified rate constant  $K_m$  of calcite. It shows that coarse-size shaking table products have a pronounced effect on the pH and CS dosage. Increasing pH and SSA increase the modified rate constant  $K_m$  of calcite. Increasing CS dosage considerably decreases the modified rate constant  $K_m$  of calcite.

Figure 4.28 shows that the modified flotation rate constant  $K_m$  of calcite for medium-size shaking table products have a decreasing effect by increasing the pH, CS dosage, and SSA.

For fine-size shaking table products, SSA has a significant decreasing effect by and pH has small decreasing impact. Meanwhile, CS dosage increases the modified rate constant  $K_m$  of calcite.

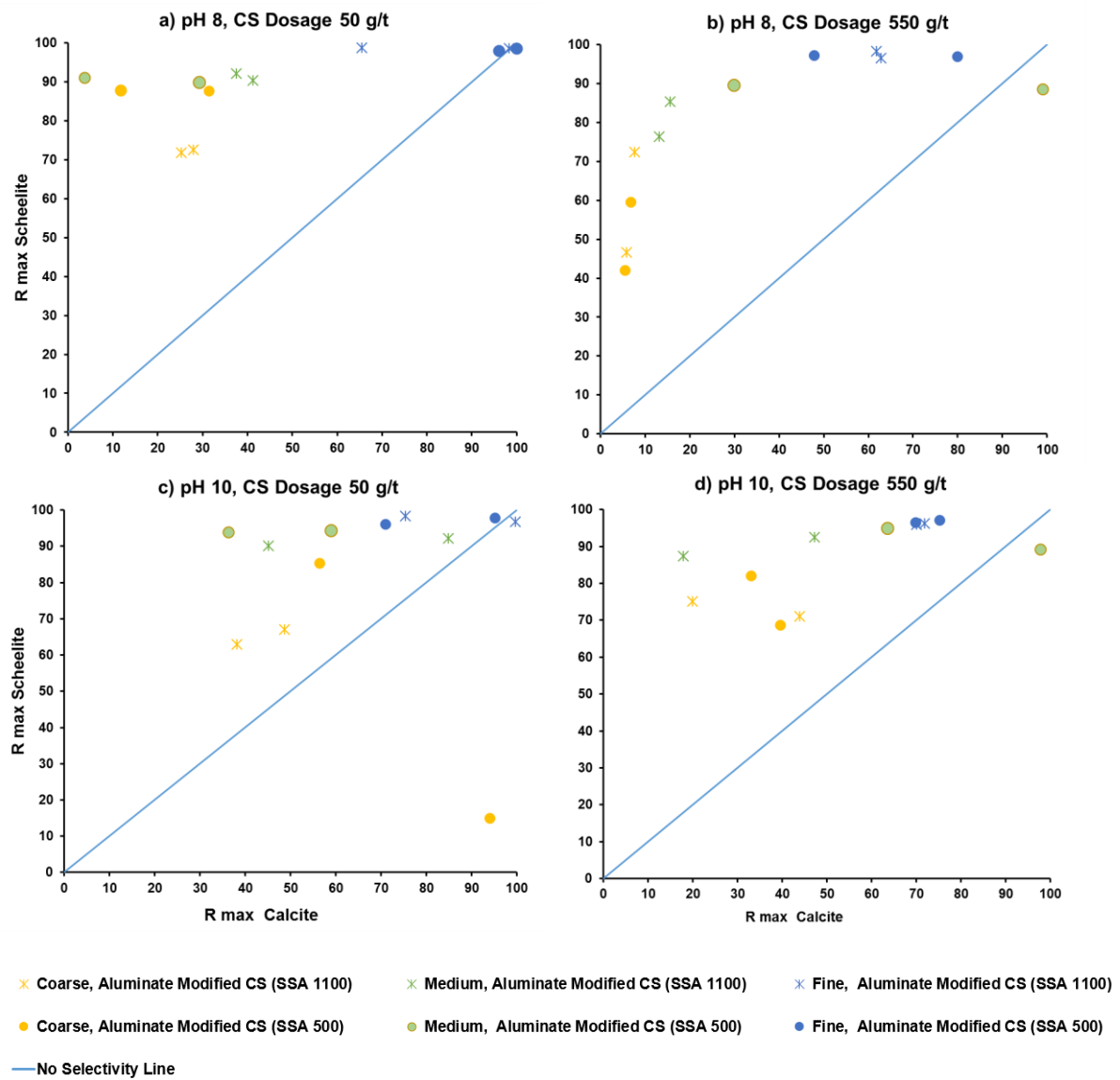


**Figure 4.28:** Magnitude of pH, CS modification, and dosage effects on the modified rate constant  $K_m$  – calcite

#### 4.4.4.3 Maximum recovery of Scheelite and Calcite

The maximum recovery  $R_{\max}$  based selectivity of scheelite and calcite is shown in Figure 4.29, which describes that coarse-sized shaking table products give better scheelite selectivity against calcite at pH 8. In graph b) the least maximum calcite recovery  $R_{\max}$  is calculated at pH 8 and CS dosage of 550 g/t, but the maximum recovery  $R_{\max}$  for scheelite also drops to its minimum value.

At higher pH, coarse and medium-sized shaking table products have low selectivity. The fine-sized shaking table product has a high maximum scheelite recovery  $R_{\max}$ , but  $R_{\max}$  for calcite is also very high, which reduce the scheelite selectivity against calcite.

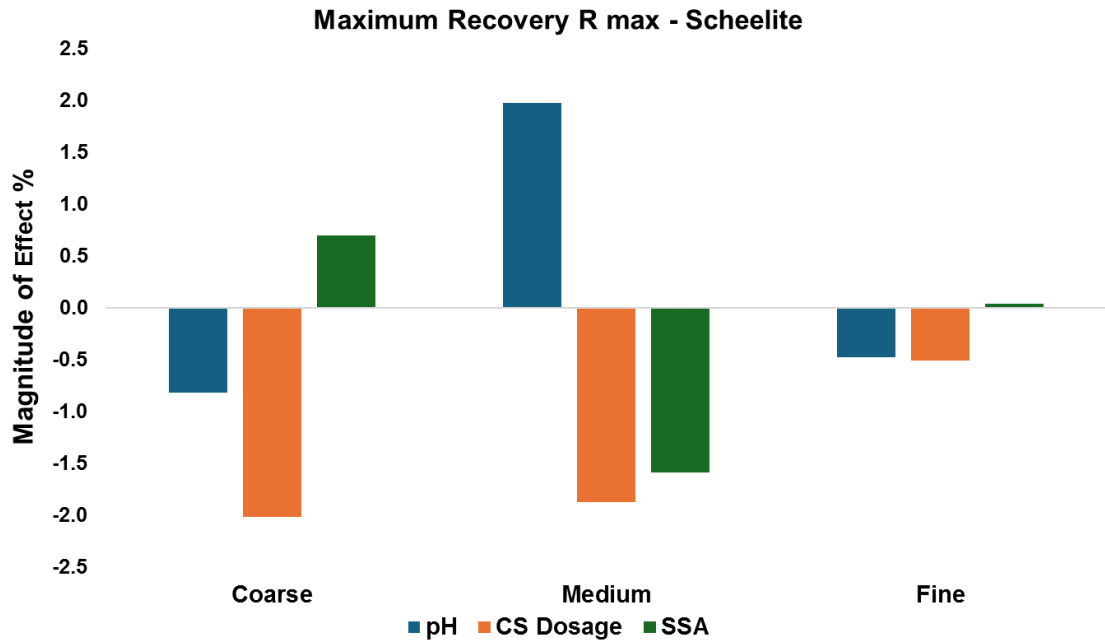


**Figure 4.29:** Selectivity diagram based on maximum recovery  $R_{\max}$  of scheelite and calcite

Figure 4.30 shows the magnitude of the effect of the operating parameter on the maximum recovery  $R_{\max}$  of scheelite. It shows that an increase in the CS dosage decreases the maximum recovery  $R_{\max}$  for all sizes of shaking table product. While pH decreases the  $R_{\max}$  for fine and coarse-sized shaking table products by 0.47 % and 0.82 % respectively. However, it increases the  $R_{\max}$  value for the medium-size shaking table product by 1.9 %.

Now, an increase in the SSA increases the  $R_{\max}$  value for the coarse and fine-size shaking table products by 0.7% and 0.03 % respectively. However, it decreases the  $R_{\max}$  for scheelite by 1.6 %.

CS dosage has a more significant negative impact on the coarse and medium-size shaking table products with up to 2 % and 1.9 % effect respectively, fine-sized shaking table products have a decreasing effect of 0.5 % of the maximum recovery  $R_{\max}$ .

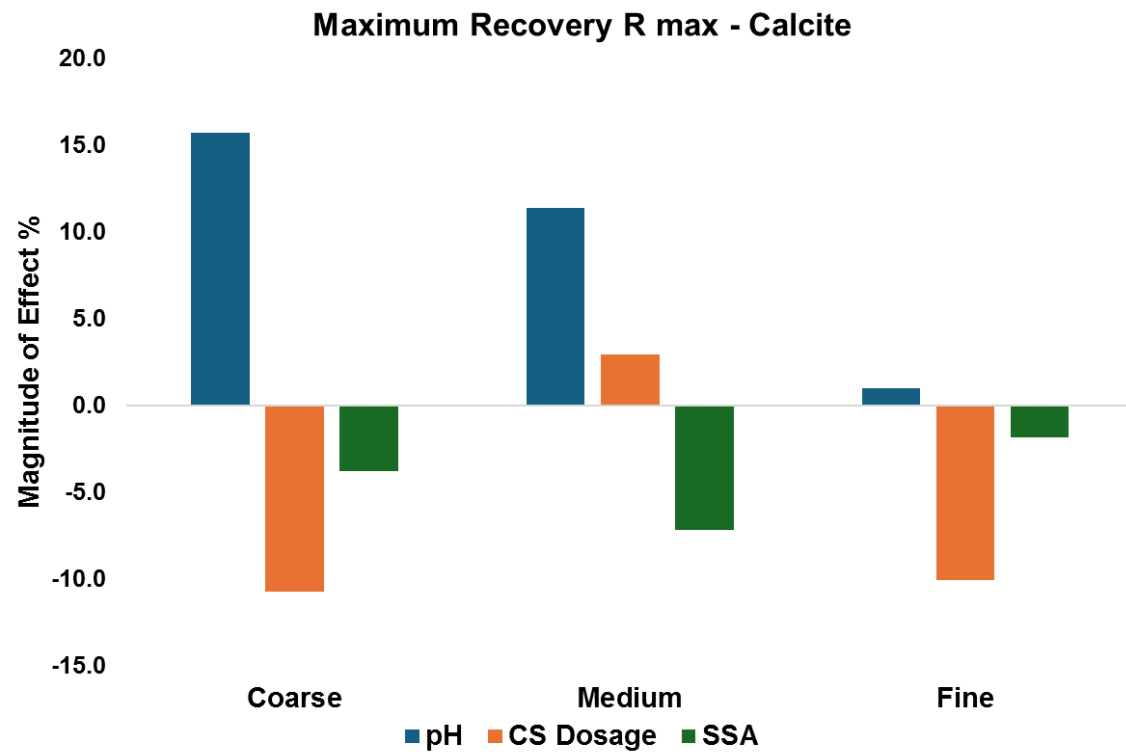


**Figure 4.30:** Magnitude of pH, CS modification, and dosage effects on the maximum recovery  $R_{\max}$  – scheelite

Figure 4.31 describes the magnitude of the effect of the operating parameter on the maximum recovery  $R_{\max}$  of calcite. It shows the pH has pronounced positive effects on the maximum recovery  $R_{\max}$  of calcite on the coarse and medium-size shaking table products by 15.5 % and 11.4 % respectively, fine-sized shaking table products also have an increasing effect on the maximum recovery  $R_{\max}$  of calcite by 1 % of the magnitude.

Increasing SSA has a decreasing effect on the maximum recovery  $R_{\max}$  of calcite on coarse, medium, and fine-sized shaking table products by 3.8 %, 7.2 %, and 2 % respectively.

CS dosage has a more prominent and negative impact, on the coarse and fine-sized shaking table products, of 10 % each, but medium-size shaking table products have a positive increasing effect on the Maximum Recovery  $R_{\max}$  – calcite by 1 %.



**Figure 4.31:** Magnitude of pH, CS modification, and dosage effects on the Maximum Recovery  $R_{\max}$  – Calcite

## **5 Discussion of Experiments**

### **5.1 Effect of the colloidal silica concentration on the Zeta Potential**

In Figures 15, 16, and 17, it can be seen that concentration (w/w %) has a direct relationship with the zeta potential. At higher concentrations (w/w %) of CS, zeta potential is higher. In the case of non-functionalized colloidal silica, Std\_CS\_750 and Std\_CS\_500 have 2.79 w/w % and 2.82 w/w %. Aluminate modified CS modifications have the lowest zeta potential and highest zeta potential is being measured in silane modified CS modifications.

The research shows dilute colloidal silica suspensions were prepared at 0.5 % (w/w) solids, in 0.01 M KCl showing that zeta potential is the function of the SSA, zeta potential is low at the high specific surface area (Ben Said et al., 2024). In this work, the zeta potential increases at high concentration (w/w %). It shows the opposite effect to SSA. Maybe at high concentrations of suspension, electrolyte and particle-particle interactions in the suspension become more prominent, so the effect on the zeta potential may differ. Gu et al., 2014 shows that increasing the concentration of sodium aluminate increases the zeta potential.

### **5.2 Batch Flotation**

#### **5.2.1 Selectivity of Scheelite against Calcite and Hornblende**

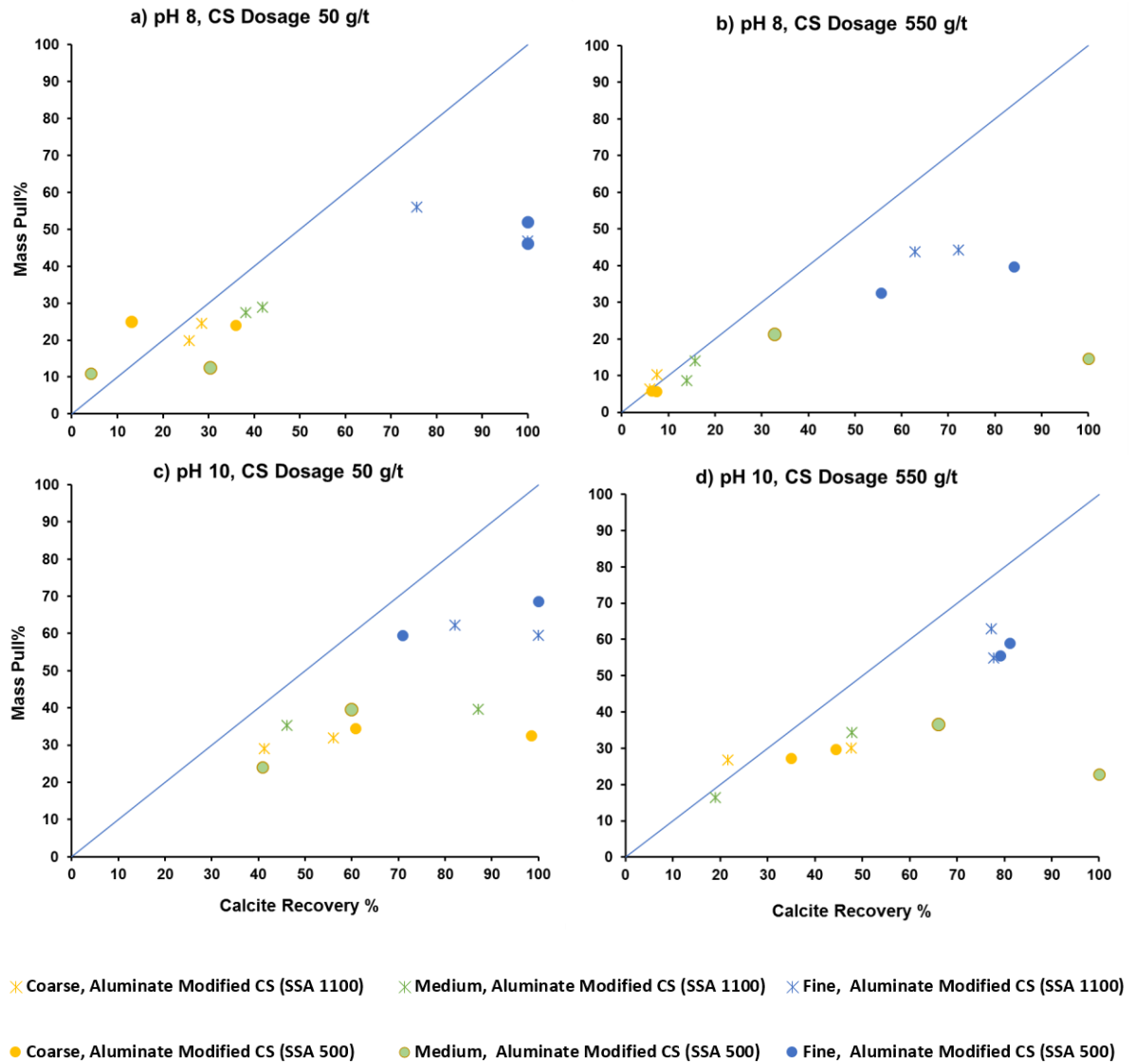
From Figure 4.10, it can be seen that there is a high recovery of scheelite and low depression of calcite for fine-shaking table products. Medium-size shaking products have higher scheelite recovery and relatively low calcite recovery than fine products at low pH but increased at pH 8. Coarse-size shaking table products have a similar trend to medium-size particles but relatively low calcite recovery and have highest scheelite selectivity against calcite.

The overall selectivity graph of scheelite and hornblende in Figure 4.12 shows that for the medium-sized shaking table products there is a good scheelite selectivity against hornblende.

It can be concluded that medium-size shaking table products have better scheelite-hornblende selectivity at pH 8, but Figure 4.14 upgradation curve of scheelite presents that the scheelite grade % in medium-sized products is comparable with fine-size products. The possible reason behind the lower grade of scheelite in medium-shaking table products could be the low scheelite grade % in the medium-sized feed for batch flotation.

The possible reasons for the high recovery of gangue minerals like calcite can be froth properties, hydrodynamic conditions, and bubble size.

Figure 5.1 shows that the higher mass pull of the fine-sized shaking table in batch flotation leads to a high calcite recovery. The higher mass pull and entrainments in the flotation of fine-sized shaking table products indicate towards high recovery of gangue minerals e.g. calcite.



**Figure 5.1:** Effect of mass pull and calcite recovery

Entrainment in the flotation is the non-selective flotation process in which particles are mechanically transferred into the froth (Smith & Warren, 1989). Fine particle and low-density particles are more prone to entrainments due to their tendency to suspend in the froth phase (Murhula et al., 2022). The reasons behind the entrainments in fine particle flotation could be froth stability, (Qiu et al., 2022) low settling velocity of fine-size particles.

This leads to higher recovery and grade of fine calcite particles in the froth phase (Kurşun, 2019). Froth stability is crucial for the flotation of the fine particles but the problem is that, it increases the entrainment which leads towards the low grade of scheelite in concentrate (Ling et al., 2020). Batch flotation tests of shaking table products were performed under the same hydrodynamic conditions, hydrodynamic conditions in the flotation cell are more advantageous for the flotation of fine particles because of low turbulence (Patil et al., 2010). The researcher studied that fine scheelite particles can aggregate with certain reagents, which can increase the flotation recovery and also compromise the grade of scheelite by recovery of the gangue mineral due to the formation of mixed mineral aggregates.

The coarse-size particles have a higher probability of collision with bubbles, but the low recovery of the coarse-size particles can be because of inability of the bubble to carry them from pulp zone to froth zone (Fuerstenau et al., 2007) because of the detachment of particles from the bubble, and instability between particle and bubble due to high turbulence in the flotation cell (De Gontijo et al., 2007; Jameson, 2010; Soto & Barbary, 1991). Along with turbulence, the detachment of particles from the bubble could be because of the mass and inertia (Tao, 2005). Coarse particles need high hydrodynamic conditions to stay suspended in the froth zone, which can cause the detachment of particles from the bubble. Coarse particles have the ability to rupture the froth to decrease the entrainment (Achaye et al., 2021).

Keeping in mind that medium-sized shaking table product is a bimodal system in Figure 4.9, the addition of fine-sized shaking table products could increase froth stability which can be a reason for the increased calcite recovery in batch flotation.

Larger bubble sizes have high buoyancy, ( $B = \rho \times V \times g$ ) where  $\rho$ ,  $V$  are the density and volume of the object respectively, and  $g$  is the gravity constant, forcing them to move out of the system quickly, causing the lesser interaction with particles. In Figure 4.22, it is seen that coarse-shaking table products have small bubble sizes, because of the hydrodynamic force breaks the big bubbles into small bubbles (Liu et al., 2018).

### **5.2.2 Effect of pH on the selectivity of scheelite**

Increasing the pH decreases the selectivity index of scheelite against calcite as shown in Figure 4.11, according to researchers, at higher pH formation of hydroxyl ions reduces the effectiveness of the collector like sodium oleate (Zhao et al., 2013).

### 5.2.3 Effect of the SSA on the Selectivity of Scheelite

The high specific surface area gives a more active site for adsorption, which can be beneficial for the scheelite selectivity against calcite of fine-sized shaking table product can be seen in Figure 4.11 and Figure 4.13, however, it can over-depress coarse particles to the selectivity of scheelite calcite selectivity (Yin et al., 2019).

### 5.2.4 Effect of the CS Dosage on the Selectivity of Scheelite

Figure 4.10 shows that increasing CS dosage decreases the scheelite recovery and decreases the selectivity of scheelite against calcite recovery for medium-sized shaking table products, the reason behind this can be the over-depression of the scheelite in batch flotation of medium-size shaking product (Jung et al., 2020).

## 5.3 Particle-Based Kinetic Model

A particle-based model was created to study how colloidal silica modification and dosage impact the flotation kinetics of the main minerals in scheelite batch flotation.

The model thoroughly explains how CS modification, dosage, and SSA affect the batch flotation of each shaking table product. Scheelite and calcite's modified flotation rate constants appear to respond to colloidal silica depending upon the pH, modifications and dosages, as shown in Figure 4.26.

At a high dosage of aluminate-modified CS (SSA 500) at pH 8 for coarse-size shaking table product, the lowest calcite-modified flotation rate constant is obtained, and the highest scheelite-modified flotation rate constant is obtained at 50 g/t dosage of aluminate-modified CS (SSA 500) for coarse-size shaking table.

Nevertheless, the lowest calcite maximum recovery  $R_{\max}$  is once more can be seen at a high dosage of aluminate-modified CS (SSA 500) and pH 8 for coarse-size shaking table products and also at a low CS dosage and pH 8 for medium-size shaking table products can be examined in the maximum recovery  $R_{\max}$  shown in Figure 4.29. The kinetic model of the batch flotation tests appears to indicate potential scheelite selectivity against calcite. Aluminate modification appears to enhance colloidal silica performance at high dosages.

The aluminate-modified colloidal silica exhibits the strongest effect on reducing calcite recovery, accompanied by a significant reduction in scheelite recovery. It also tends to form a coherent gel network in the presence of  $\text{Ca}^{2+}$  (Ben Said et al., 2024). Aluminate modification increases the negative zeta potential, which may improve the likelihood of adsorption (Gu et

al., 2014). For aluminate-modified CS, the precise mechanism underlying the observed higher selectivity between scheelite and calcite is still unknown.

## **6 Applications of Ultimate Tailing**

Worldwide mining industries and processing industries produce large quantities of tailings, approximately 7 billion tons of mine tailing waste till now, and are predicted to generate 19 billion tons of solid tailings by 2025. The buildup of hazardous waste has environmental risks, including land, sea, and air pollution. The history of environmental damage from inactive mines, with thousands of such sites across countries like Canada, Australia, South Africa, and China, highlights the importance of addressing mine waste management (Mporas et al., 2021).

Management of mine tailing has become an important approach to reduce environmental impacts. Numerous methods, e.g., oxygen barrier, bactericide, co-disposal, blending, and passivation of sulfide minerals, help to prevent acid mine drainage. Additionally, unhazardous mine tailings are progressively being reused as construction materials and in the production of geopolymers.

Reprocessing of mine tailings to obtain critical raw materials can lower the necessity for new mining activities and guarantee the cost-effective use of mine tailing. The environmental consequences of tailings can be acid mine drainage. However, recycling approaches and environmental remediation, e.g., metal recovery, fertilizer, and construction materials, can drastically decrease mine tailing stocks. The supervision of tailings waste is a global issue, as the mining industries generate large amounts of tailings that impact the environment and human health (Mporas et al., 2021).

### **6.1 Scheelite Tailing**

Scheelite tailings are the byproducts of tungsten mining and processing, have some special qualities, and show some potential applications in the ceramics industry. Some recent research presents that new ceramic formulations can be produced from scheelite tailing, e.g., producing stoneware, porcelain tile, and semi-stoneware.

These formulations are characterized based on their mineralogical phases, microstructure, and physio-mechanical properties, sintered at different temperature levels between 1150 and 1250 °C. These formulations have different content of scheelite tailings ranging between 0 – 8 %. Mullite is the main phase in all samples responsible for mechanical strength. The mechanical and physical properties i.e., linear shrinkage, water absorption, and porosity, are compliant with the ISO 13006 standards. The use of scheelite tailings in the ceramic industry is a sustainable solution for managing and recycling the tungsten mine waste.

Scheelite tailings can discharge unsafe substances into the environment when disposed of. By integrating scheelite tailings into the ceramic industry, waste disposal issues can be resolved and reduce the need for virgin raw materials, possibly lowering the cost of ceramic products by replacing expensive or scarce raw materials. This methodology contributes to the circular economy, lowers environmental impact, and possibly lowers the cost of ceramic products (Fernandes et al., 2020).

The scheelite ore beneficiation process includes pre-concentration, cleaning, and purification. Wolframite ores are high quality and easy to mine. Gravity and magnetic separation are common methods for enriching wolframite. These methods are not suitable for the recovery of ultra-fine wolframite, especially for particle sizes below 20  $\mu\text{m}$ . Tungsten tailings are mainly treated as waste, and limited experiments have been done on reprocessing. One experiment in Portugal showed that froth flotation was the only feasible approach to recovering wolframite from tailings. Recycling tailing yielded only a few kilograms of tungsten concentrate, making it uneconomical (Han et al., 2021).

## **6.2 Application of Scheelite Tailings**

Usually, tailings include compounds of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ , and  $\text{Fe}_2\text{O}_3$ , including a substantial part of other metals and metalloids e.g. Mn, K, Mg, Zn and  $\text{P}_2\text{O}_3$ , which is like the ultimate tailings obtained in this research (Wan et al., 2018). In this work, tailing mostly consists of 40 - 50 %  $\text{SiO}_2$ ,  $\text{CaO}$  is 10 - 15%,  $\text{Al}_2\text{O}_3$  is 7 - 10%, and  $\text{Fe}_2\text{O}_3$  is 10 - 15%, small quantity of other  $\text{P}_2\text{O}_5$ ,  $\text{MnO}$ , and  $\text{K}_2\text{O}$ . The obtained tailings are suitable for civil engineering applications, reducing pressure on natural resources (Mporas et al., 2021). They can be utilized in various areas.

### **6.2.1 Iron and Steel Production**

Scheelite tailing are rich of  $\text{Fe}_2\text{O}_3$ , iron can be extracted from tailings. Iron can be extracted from iron ores ( $\text{Fe}_3\text{O}_4$ ), reducing agent coke, limestone ( $\text{CaCO}_3$ ), and a carbon source react in this process, and the combination is then fed into a blast furnace. These reactants melt in the furnace at a higher operating temperature of about  $1500^\circ\text{C}$ . Carbon monoxide (CO) is produced in the furnace when oxygen from the iron ore combines with a reducing agent. Iron metal produced as  $\text{Fe}_2\text{O}_3$  get reduced by this carbon monoxide. Alongside, calcite  $\text{CaCO}_3$  breaks into calcium oxide ( $\text{CaO}$ ), which react with the impurities to generate slag. Slag comes on top of the molten iron because of low density. After removing molten iron from the slag, the molten iron, is also known as pig iron (Carmignano et al., 2021).

Steelmaking is part of refining pig iron, it contains almost 4% carbon which makes it brittle, by reducing carbon to enhance its properties. There are two processes: Basic Oxygen Furnace (BOF) and Electric Arc Furnace (EAF). In the BOF process, molten pig iron, scrap steel, and oxygen are combined to react (Pourya Khavari, 2018). The oxygen reacts with carbon to form carbon dioxide ( $\text{CO}_2$ ), which is vented out. The EAF process uses electricity to melt scrap steel or iron ore pellets. Tailings can be incorporated depending on the desired steel composition. Additional elements like carbon, manganese, or chromium to get the required properties in the steel product (Carmignano et al., 2021).

### **6.2.2 CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> (CAS) System Applications**

Depending on the ratio of each oxide, the mixture of these three compounds produces an adaptable system with a wide range of applications. Here are some important applications.

**Production of Cement:** Portland cement, the extensively used type of cement in buildings, is produced using the Calcium Aluminate Silicate (CAS) method, which the most significant use. The initial binding segments of cement are calcium silicates, and calcium aluminates, which are produced when CaO reacts with  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  at high temperatures. The CaO to  $\text{SiO}_2 + \text{Al}_2\text{O}_3$  ratio ( $\text{CaO}/(\text{SiO}_2 + \text{Al}_2\text{O}_3)$ ) is a basic element to define the cement's properties (Wang et al., 2022).

**Refractories:** CaO,  $\text{Al}_2\text{O}_3$ , and  $\text{SiO}_2$  are compounds with high melting points, which make them suitable to use as a refractory materials. They have applications in kilns and furnaces to line them. Depending on the operating conditions of kilns and furnaces qualities refractory brick can be produced using the CAS system (Aigbodion et al., 2010).

### **6.2.3 Hornblende**

Soil stability can be enhanced by using hornblende. Goethite is ferruginous compounds produced which produce by weathering of hornblende. It improves soil structure and control erosion (Velbel, 1989). Nepheline syenite can be found in hornblende, is a dimension stone, and has applications in both construction and decoration. It contains hornblende as one of its components. It has a wide arrange of applications for construction, decoration, facades, monuments, and other decorative applications. It can be used as a raw material for the manufacturing of the glass and ceramics (Chunyn, 2014; Jimoh & Raji, 2011). The hornblende from tailing waste can be beneficial for  $\text{CO}_2$  adsorption. This application achieves carbon capture and has potential for a sustainable waste recycling (Igalavithana et al., 2020).

## Conclusion

The objective of this work was to investigate the effect of aluminate-modified colloidal silica (SSA 1100 and 500 m<sup>2</sup>/g) on the separation of calcite minerals from fine, medium, and coarse-sized scheelite ores obtained by gravity separation (shaking table) and further processed with froth flotation method. Low-grade scheelite ores originated from European Mine. It's a challenge to separate scheelite from calcite because of having similar surface properties. The design of experiments for gravity separation and batch flotation was obtained using the full-factorial design of the experiment method. Particle surface charge was measured for different colloidal silica modifications based on the specific surface area with different concentrations of colloidal silica.

It was observed that zeta potential is related to the concentration of colloidal silica reagents in suspension. The effect of operating parameters, i.e., pH, colloidal silica dosage, and SSA on the selectivity of scheelite. Increase in pH reduces the selectivity of the scheelite against calcite. High colloidal silica dosage decreases the scheelite recovery for all sizes of shaking table products and decreases the selectivity of scheelite against calcite for medium-sized products. The high specific surface area of the depressant can over-depress the scheelite. It is observed that coarse-sized shaking table products showed better scheelite selectivity against calcite, and the overall grade of the scheelite is also higher for coarse-sized shaking table products.

However, the particle-based kinetic model shows that aluminate-modified CS (SSA 500) at pH 8 and CS dosage of 50 g/t shows the lowest calcite-modified-flotation rate constant for coarse size shaking table products, and the highest scheelite-modified flotation rate constant is obtained at CS dosage of 50 g/t and pH 8 with aluminate-modified CS (SSA 500) for coarse-size shaking table product. Ultimate tailings of the froth flotation can be used in iron and steel production facilities, CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> (CAS) System has applications in the cement industry and refractories and raw material for industries e.g. ceramics, glass making, and plastic fillers.

## Recommendations

It is observed that high colloidal silica dosage decrease the scheelite calcite selectivity, in future investigation of the lower dosage range around 50 g/t to optimize the selectivity against the calcite specially for medium sized fraction can be carried out. In addition, kinetic model shows aluminate modified colloidal silica SSA 500 m<sup>2</sup>/g has higher scheelite-modified-flotation-rate constant and it is dependent on the colloidal silica dosage. There is a particle size dependency on the scheelite recovery, grade and selectivity against calcite. There is a need to develop a comprehensive kinetic model that take care of particle size distribution in the feed. Aluminate modified colloidal silica (SSA 250 m<sup>2</sup>/g) can be a potential depressant reagent to increase the selectivity of scheelite against calcite, because the low zeta potential measured in this work, is dependent on the concentration of silica in the CS.

Appendix

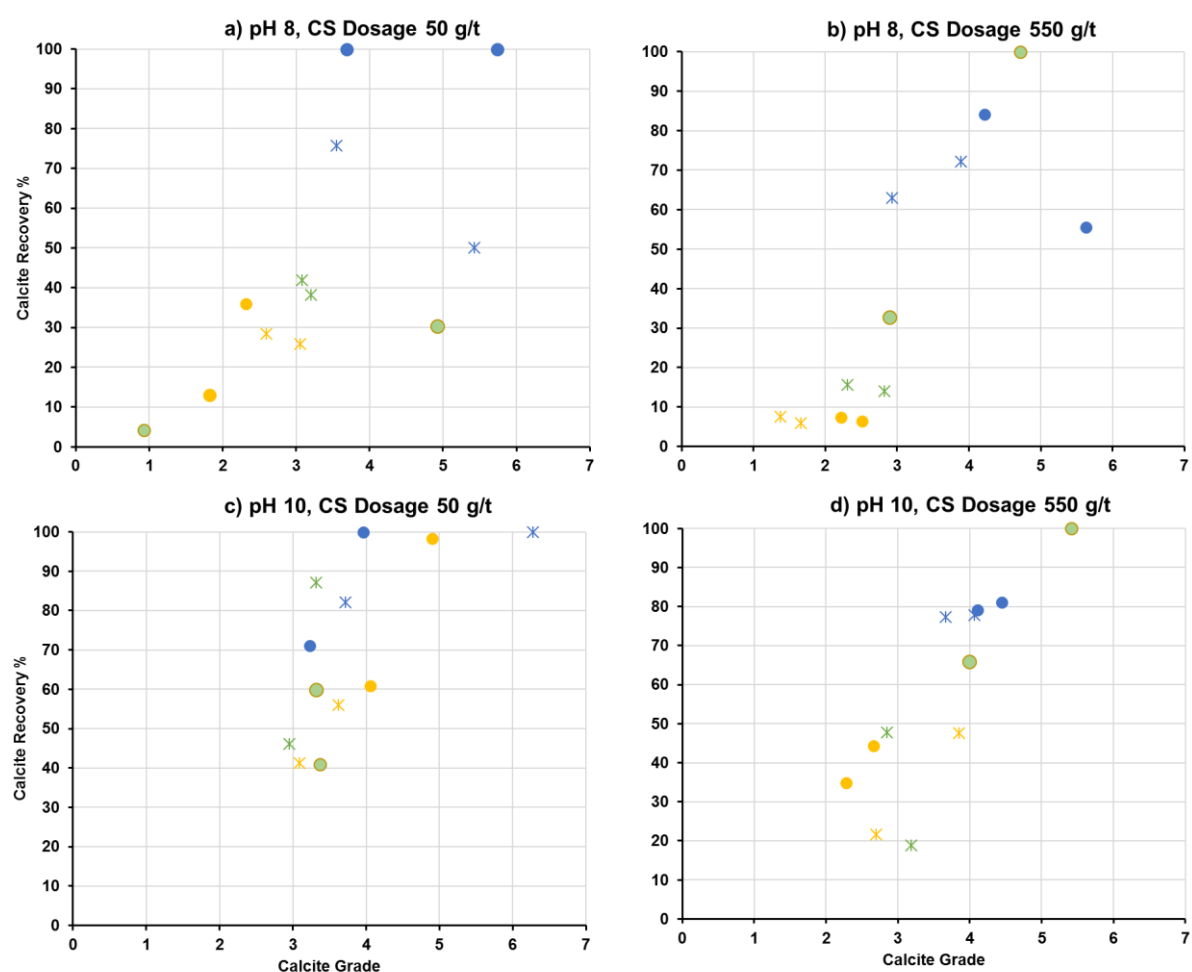
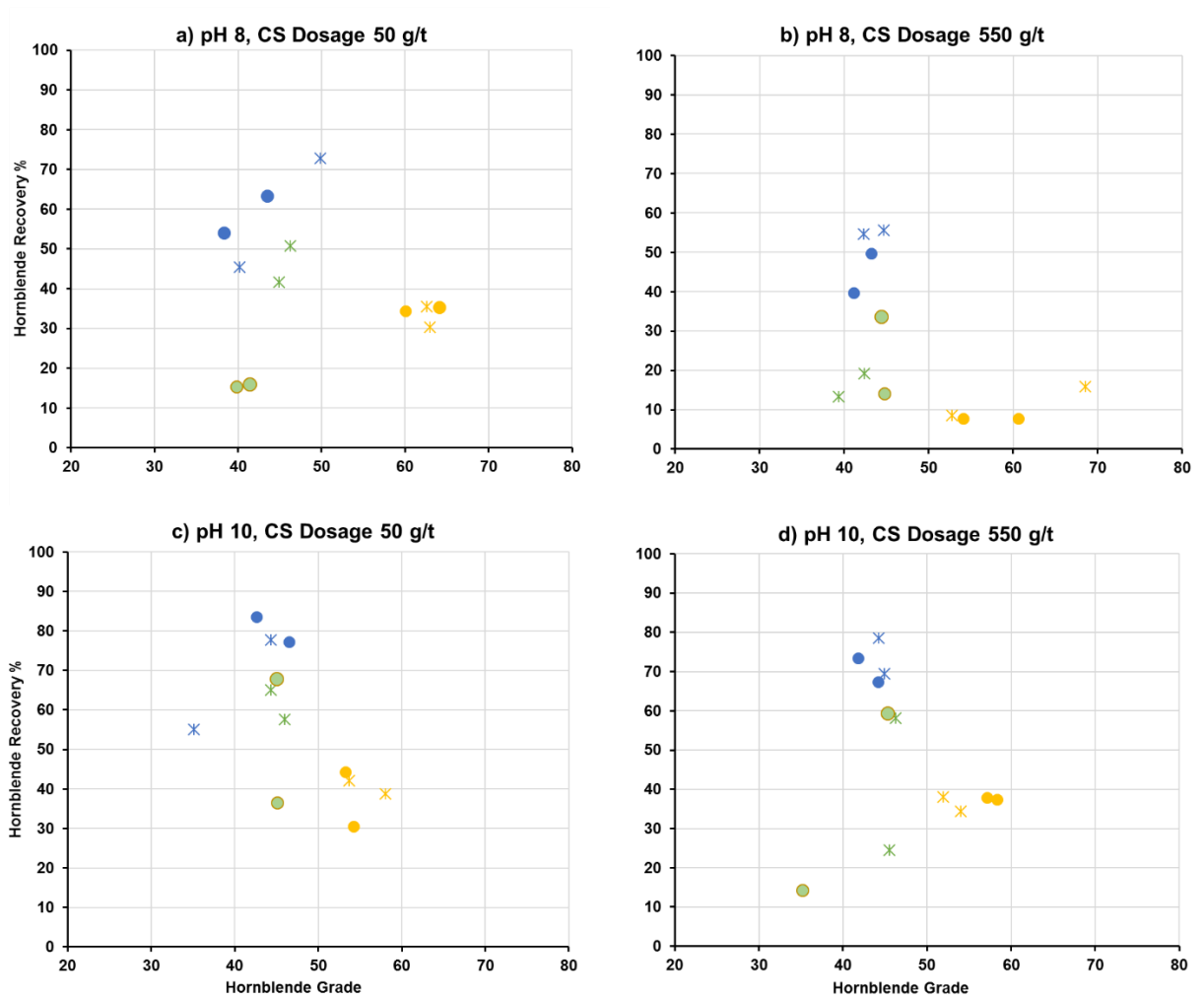
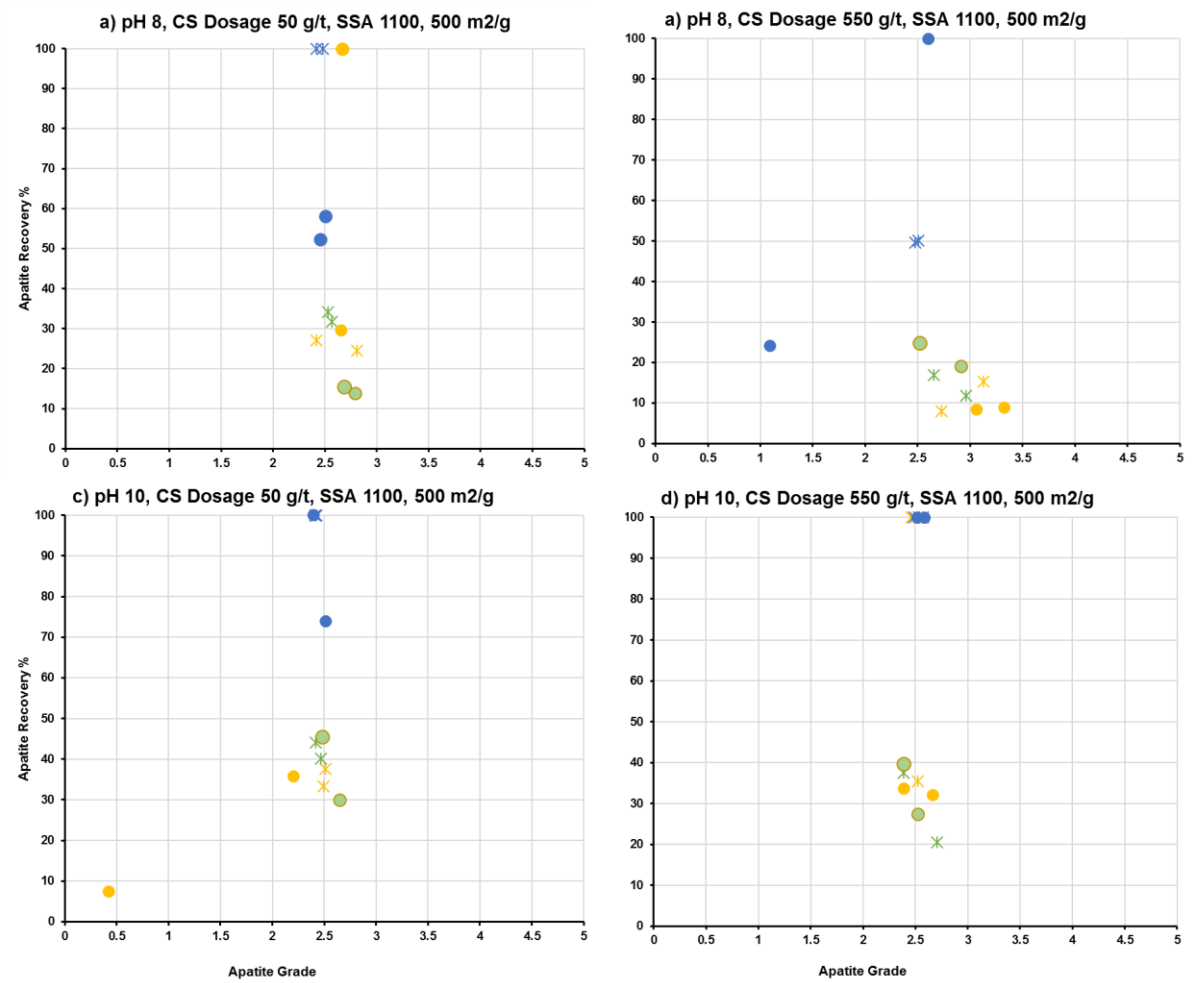


Figure A. 1: Upgrading Curve for Calcite



**Figure A. 2:** Upgrading curve for Hornblende



**Figure A. 3:** Upgrading curve for Apatite

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