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Freiberg, 29.08.2022

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1. General Introduction

1.1 Motivation

Barite (BaSO_4) and fluorite (CaF_2) have found wide application in industrial processes. The former is primarily used as a weighting agent in the drilling industry due to its high density ($4.3 - 4.5 \text{ g/cm}^3$), as a filler in paint and plastics (due to its high brightness and whiteness), and as a flux in glass production to increase the brightness of the glass. The latter is the primary raw material used in the production of hydrofluoric acid, and as a metallurgical flux in steel and aluminium making (Gao et al., 2020; Wang et al., 2006; Zhu et al., 2018). Both minerals co-exist in nature, together with other gangue minerals such as calcite and quartz, and are often beneficiated through gravity separation, flotation, or both to increase the mineral grade for a particular industrial use. Barite concentrates grade for industrial application are generally classified as drilling mud grade (92 % BaSO_4), chemical grade (96-98 % BaSO_4) and filler grade (85-95 % BaSO_4). For fluorite, an acid grade (98-99 % CaF_2), ceramic grade (85-96 % CaF_2) and metallurgical grade (60-85 % CaF_2) are required (Bonel, 2005; Bulatovic, 2015a).

Flotation is currently the most common and effective beneficiation process for producing high-quality barite/fluorite concentrate. However, due to the similar surface properties (i.e., solubility, crystal structure, hydrophobicity, and zeta potential) of barite, fluorite, and the associated gangue minerals as well as similar flotation response to conventional fatty acid collectors, the process remains difficult as it is nearly impossible to achieve a high selectivity for one mineral over the other (Gao et al., 2020; Liu et al., 2019). Fluorite and barite are classified as critical raw materials (since 2011 and 2017, respectively) due to their high economic potential and supply risks, resulting in a global resurgence of interest for their ores (Blengini et al., 2020). Since high-grade resources have been depleted in recent years, processing of low-grade barite/fluorite ores has become necessary not only to meet current demand but also for environmental reasons (Naseem et al., 2011).

A massive pile of mine tailing is located near the Hammam Jedidi barite mine and the Hammam Zriba fluorite mine in the Zaghouan district of northern Tunisia (see location map in **Figure 1**). Between 1970 and 1992, these mine sites operated flotation plants producing an estimated 732,000 tons of high-grade fluorspar and 18,000 tons of barite (ONM, 2008). The production

ceased in 1992, and a total of 260,374 m³ of waste has been concentrated in three flat top tailings spread across an area of 96,658 m² with an average height of 2 to 14 m. The waste was dumped close to the treatment plants and olive groves, with no reclamation or protection against water and/or wind erosion (Mezned, 2010).

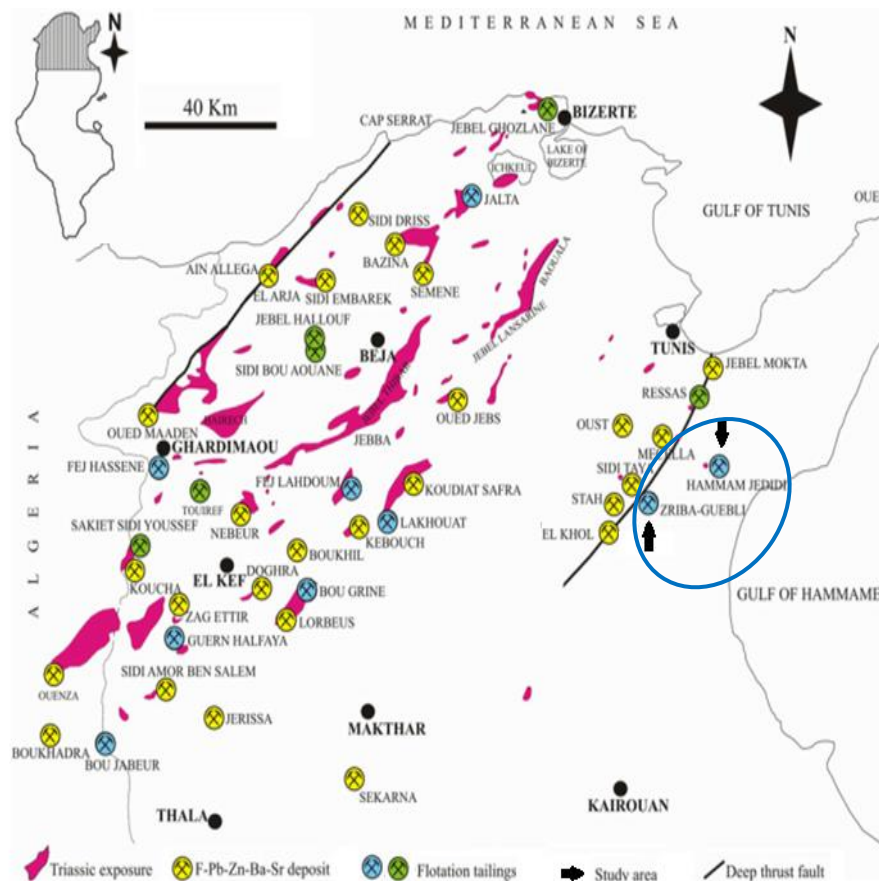


Figure 1. Location map of Hammam Zriba and Hammam Jedidi mines (Djebbi et al., 2017)

According to the chemical and mineralogical analysis, these wastes still contain significant amounts of barite (BaSO_4), celestine (SrSO_4), and galena (PbS), as well as other potentially toxic elements (PTEs) of hydrothermal origin, such as Cr, As, Cd, Sb, Hg, and Pb. As a result, appropriate mine waste isolation measures are required for future environmental protection (Yoshida et al., 2002).

According to Wills & Napier-Munn (2006) mine tailings that still contain valuable components have the potential to be a future resource since new or improved technologies may enable the recovery of the valuables that were lost in the previous process. Tailings reprocessing is aimed at reducing the waste's environmental impact. Also, the cost involved is sometimes less than

that of processing a virgin material since much of the expenses, particularly in mining and comminution has already been incurred.

1.2 Aims and expected outcomes

The work seeks to:

- i. Ascertain the technological feasibility of recovering barite and fluorite present in the said mine tailings
- ii. Investigate potential applications for the ultimate tailing generated after the recovery of the target minerals

1.3 Methods used

The following methods would be used in this work:

- i. Review of relevant literature concerning the study area
- ii. Sample and reagent preparation
- iii. Microflotation of barite, fluorite, and calcite
- iv. Batch flotation of barite and reverse flotation of fluorite
- v. Characterisation of flotation products
- vi. Critical analysis, interpretation, and reporting of results

2. Theoretical Background

2.1 Froth Flotation

Mineral processing involves two fundamental operations, namely, comminution and concentration (Wills & Napier-Munn, 2006). Froth flotation has remained the most significant and adaptable concentration technique in mineral processing, and its application and use are constantly being expanded to handle high volumes of material and cover new areas. The process was first patented in 1906 and has made it possible for low-grade and complex ores that would otherwise be considered waste, to be economically viable (Wills & Napier-Munn, 2006). A schematic illustration of the froth flotation process is shown in **Figure 2**.

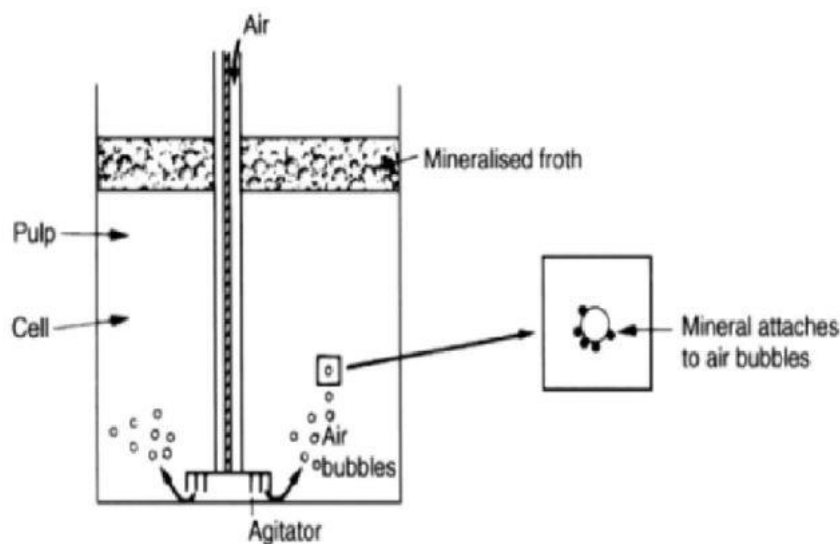


Figure 2. Schematic illustration of froth flotation process (Wills & Napier-Munn, 2006)

2.1.1 Principles of flotation

Flotation is a physico-chemical separation process based on the separation characteristics of different particle surfaces' wettabilities. The surface properties of the mineral influences the wettability of solid particles, though it can also be modified using auxiliary reagents (Lauth & Kowalczyk, 2016). The separation of target mineral from gangue is carried out on the basis that hydrophobic particles (water-repellent) adhere to air bubbles in the suspension zone and are released as particle-bubble aggregates as a foam (foam product/concentrate) above the slurry.

The hydrophilic particles (water-wetted), on the other hand, sink and enrich the bottom product (Derhy et al., 2020).

As illustrated (**Figure 2**), the agitator provides enough turbulence in the pulp to promote suspension and collision of particles. Air is introduced at the bottom of the cell, and a rising current of air bubbles are created in the pulp with the intention of providing attachment of selected kind of particles to the air bubbles. The collision of hydrophobic particles with the bubbles results in the solids adhering to the air bubbles and forming a particle-bubble aggregate, enabling them to float and exit through the froth phase at the slurry surface due to their buoyancy. Water-wetted hydrophilic particles remain in the pulp phase and eventually sink to the bottom as tailings. The process is only feasible when particles are of fine grain sizes (e.g., 40 -120 μm). This is because if they are too large, the adhesion between the particle and the air bubble will be less than the weight of the particle, hence, the bubble will drop the load (Trahar & Warren, 1976). Flotation can either be **direct**, where the mineral of interest is usually transported to the froth phase with the gangue remaining in the pulp phase, or **indirect**, where mineral of interest is inhibited from floating, thereby remaining in the pulp phase and the gangue transported to the froth phase, (Wills & Napier-Munn, 2006).

The theory of froth flotation is complicated, and involves three phases (solids, water, froth) and several subprocesses and interactions which are not understood entirely. The recovery of material via froth flotation involves three mechanisms: (i) Selective attachment to air bubbles (or "true flotation"), ii) entrainment in the water which passes through the froth, iii) physical entrapment between particles in the froth attached to air bubbles (often referred to as "aggregation"). The most essential mechanism in froth flotation is the selective attachment of valuable minerals to air bubbles, which relies on the difference in the physico-chemical surface characteristics of the mineral surfaces and accounts for the bulk of particles recovered to the concentrate (Wills & Napier-Munn, 2006). Entrainment is a phenomenon whereby particles are mechanically transferred from the pulp phase to the froth in the flow of water which allows for a fraction of the hydrophilic minerals to report to the concentrate (Wiese & O'Connor, 2016). Although true flotation is the major process for valuable mineral recovery, the separation efficiency between valuable mineral and gangue is also affected by entrainment and physical entrapment, making it impossible to achieve a perfect separation between hydrophobic and hydrophilic minerals.

The degree to which a particle's surface is wetted by water determines whether particle-bubble attachment occurs. When a solid surface has minimal attraction for water, it is described as hydrophobic, and air bubbles adhere to it. When a solid surface has a strong affinity for water, it is called hydrophilic, and air bubbles are less likely to adhere to it (Wills & Napier-Munn, 2006). Thus, during flotation, particles that are to be floated must be hydrophobic to be selectively attached to air bubbles. Minerals such as sulfur, graphite, coal, diamond, talc, are naturally hydrophobic, and thus, can be floated directly. Most minerals are, however, hydrophilic and must be made hydrophobic through the addition of selected surface-active reagents called collectors, which adsorb onto the mineral surface. The wettability of mineral particles to be separated as well as the changes in their wettabilities achieved through the adsorption of reagents are usually expressed in terms of contact angle, which is defined as the angle (θ), subtended by a bubble on a solid submerged in liquid and measured through the liquid as shown in **Figure 3** (Fuerstenau & Han, 2009).

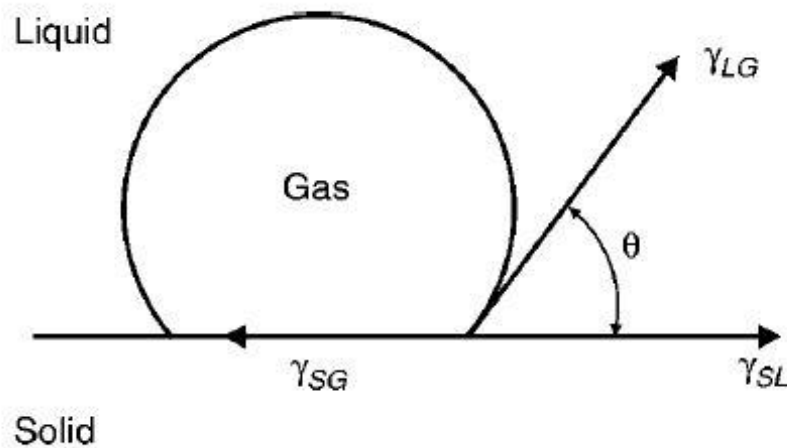


Figure 3. Schematic of the equilibrium contact between air bubble and solid immersed in a liquid (Fuerstenau & Han, 2009)

The Young–Dupre equation relates contact angle to the interfacial tension, γ , between solid (S), liquid (L) and gas (G) as shown in [Eq.1].

$$\gamma_{SG} = \gamma_{SL} + \gamma_{LG} \cos \theta$$

1

where SG = solid-gas interface, SL = solid-liquid interface, and LG = liquid-gas interface.

Particle-bubble attachment can be established if θ is greater than zero, with hydrophobicity increasing with increasing contact angle. The addition of collector can adsorb on all the three interfaces (SG, SL, LG) to reduce the surface tension. The amount of collector adsorption and the decrease in surface tension required is determined by the type of the solid and its original surface tension in the liquid. For effective flotation, a very hydrophilic solid (having a low γ_{SL}) also requires a low γ_{SG} which is attainable through high collector adsorption. A less hydrophilic material, on the other hand, requires less collector adsorption for particle-bubble attachment to occur. Thus, particles can be rendered selectively hydrophobic by modifying the appropriate solid interfacial tensions through collector addition (Fuerstenau & Han, 2009).

Although the wettability of mineral particles is determined based on their contact angles, with a hydrophilic particle having $\theta < 90^\circ$, and hydrophobic if $\theta > 90^\circ$, whether a solid particle is floatable largely depends on a variety of other parameters, including particle size and surface structure or roughness. Thus, in flotation, contact angle larger than 90° does not put permanent boundaries on whether a material may float. Materials with contact angles between 60° and 90° , for example, are regarded naturally hydrophobic and are amenable to flotation (Wills & Finch, 2015). Drelich & Marmur, (2018) classified the floatability of solid particles based on contact angles and is summarised in **Table 1**.

Table 1. Classification of floatability of solid particles based on contact angles (Modified after Drelich & Marmur, 2018)

Contact angle, θ	Floatability of particle
< 10	Not floatable particles
10-25	Poorly floatable
25-50	Low-rate floatable
50-70	High-rate floatable
>70	Spontaneously floating

2.1.2 Flotation reagents

To increase the hydrophobicity of mineral particles and as well achieve a good selectivity during flotation, several organic and inorganic reagents are used and are generally classified as collectors, regulators, frothers (Fuerstenau & Han, 2009).

2.1.2.1 Collectors

These are organic compounds that render minerals of interest water-repellent by adsorption of molecules or ions on the mineral surface. This reduces the stability of the hydrated layer separating the mineral surface from the air bubble to the point where particle-bubble attachment is possible (Wills & Napier-Munn, 2006). They contain at least two functional groups: a nonpolar part with appropriate hydrophobicity and a polar or ionic part that will be electrostatically or chemically reactive toward species on the mineral surface. Typical collectors used in oxides and sulfides flotation usually contain nonpolar parts made up of long-chained hydrocarbons (10 to 18 CH, CH₂, and CH₃ groups) and short-chained hydrocarbons (2 to 5 CH₂ or CH₃ groups), respectively. An anionic sulfate, sulfonate, phosphate, carboxylate, oxime or thiocarbonate (xanthate), cationic amine, or non-ionic oximes are the common polar parts (Fuerstenau & Han, 2009).

Collectors' molecules are classified depending on their ionic charge as ionising or non-ionising as shown in **Figure 4**.

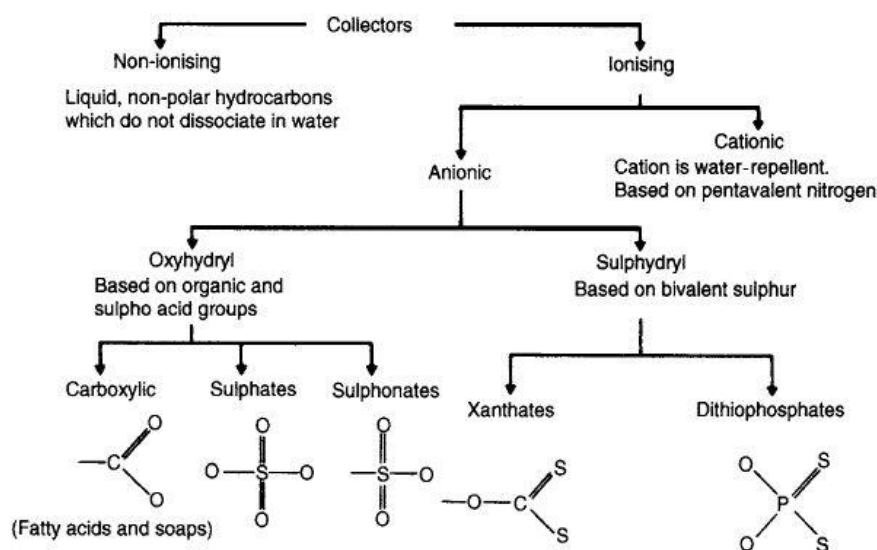


Figure 4. Classification of collectors (Glembotskii et al., 1972)

The ionising collector molecules, easily disintegrate into ions in water. They have a polar part that preferentially adhere to the mineral surface due to chemical, electrical or physical attraction between the polar part and the sites on the mineral surface, leaving the non-polar end oriented toward the surrounding water molecules, making the mineral hydrophobic. The collectors used

in this project, i.e., sodium dodecyl sulfate and sodium oleate are examples of ionising collectors, specifically anionic collectors. The non-ionising collector compounds on the other hand are simple non-polar hydrocarbon oils that cannot dissociate into ions, hence, render minerals hydrophobic by coating the surface with a thin film (Nguyen & Schulze, 2003; Wills & Napier-Munn, 2006). The mechanism of collector adsorption is shown in **Figure 5**.

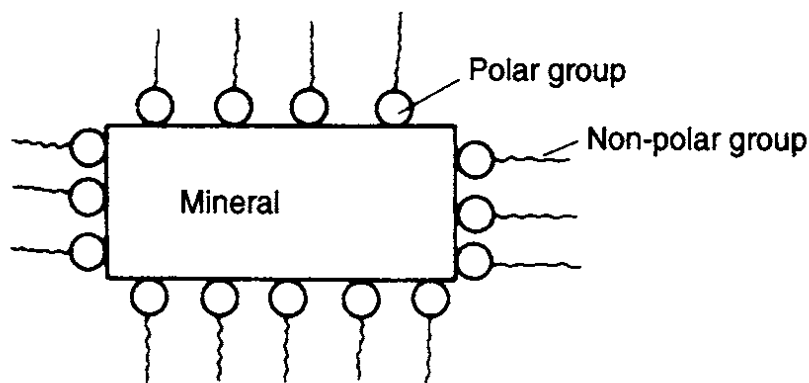


Figure 5. Collector adsorption on mineral surface (Wills & Napier-Munn, 2006)

The performance of collectors depends on their ionization constant, solubility, critical micelle concentration, and emulsifying power. Collectors must be easily distributed in the pulp so that contact with the mineral surface is achieved with minimum use of mechanical energy (Fuerstenau & Han, 2009).

2.1.2.2 Frothers

When mineral-bubble couple reach the surface of a flotation cell, the bubbles can break, and the collected mineral can fall back into the pulp. A frother is introduced to the pulp to stabilize air bubble formation and produce a stable froth layer that can be recovered before the bubbles rupture (Young & Luttrell, 2012). Frothers consist of organic, non-ionic compounds with a polar head group and a non-polar residual group which makes it possible to be adsorbed at the gas/liquid interface as shown in **Figure 6**. They function by reducing bubble coalescence, ensuring smaller bubbles for improved flotation kinetics and, also promote the formation of froth by decreasing the surface tension at the air-water interface, leading to the formation of stable foams (Fuerstenau & Han, 2009). Frothers are chemically similar to ionic collectors in many ways, and many collectors, such as oleates, are powerful frothers. A good frother should

have negligible collecting power and produce froth that is just stable enough to allow floating mineral to be transferred from the cell surface to the collecting launder (Wills & Napier-Munn, 2006). Most common used frothers belong to the group of alcohol, such as Methyl isobutyl carbinol (MICB), and polyglycols, such as polypropylene glycol.

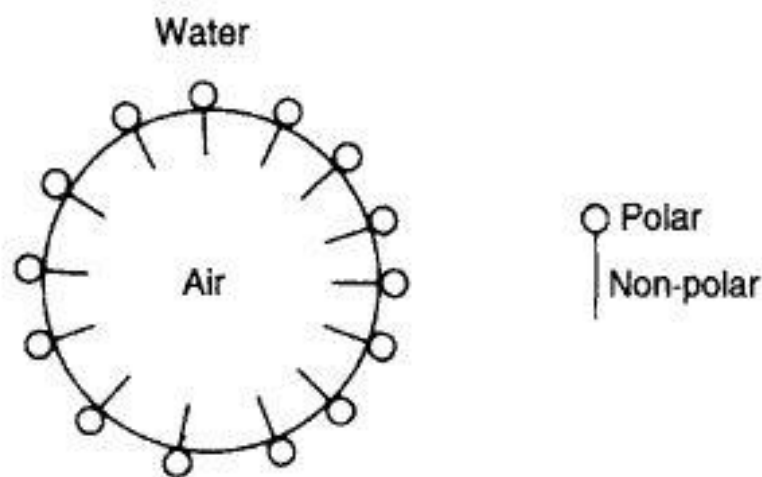


Figure 6. Action of Frother (Wills & Napier-Munn, 2006)

2.1.2.3 Regulators

These are a variety of other compounds added to optimize the separation process. Such species do not interact directly with the mineral but modify the physical properties of the solution. They can either increase the adsorption of collector onto a given mineral (activators) or prevent collector from adsorbing onto a mineral (depressants) (Wills & Napier-Munn, 2006).

Activators alter the chemical nature of mineral surface by ionising in solution and adsorbing on the mineral, providing sites for collector species to be adsorbed. **Depressants** slow or prevent the floating of undesired minerals. The adsorption of a depressing agent on the mineral surface often covers the mineral, thereby, preventing the collector from adsorbing on the surface to render it hydrophobic. To enhance recovery and selectivity, the pH of the pulp must be properly regulated using suitable **pH modifiers**. Alkalinity in a solution is achieved by the addition of lime, sodium carbonate, and to a lesser extent NaOH and ammonia while hydrochloric acid, and sulfuric acid are used to maintain acidity (Fuerstenau & Han, 2009).

2.1.3 Grade recovery curve

One essential characteristic in industrial flotation is the grade–recovery relationship which is the most common measure of separation performance. They are both expressed in terms of the valuable content in the ore. Recovery is the percentage of the valuable constituent (by mass) in the concentrate recovered from the feed while grade denotes the purity of the obtained product. **Figure 7a** shows a conventional grade-recovery curve, where higher-grade concentrate corresponds to lower recovery. However, certain operational adjustments might create a shift in the grade–recovery curve, resulting in higher recovery and higher grade at the same time (**Figure 7b**). Changing comminution practices to promote better liberation of the target mineral is one technique to achieve this shift. Another technique is to improve the reagent scheme, increase residence time, etc (Kawatra & Young, 2019).

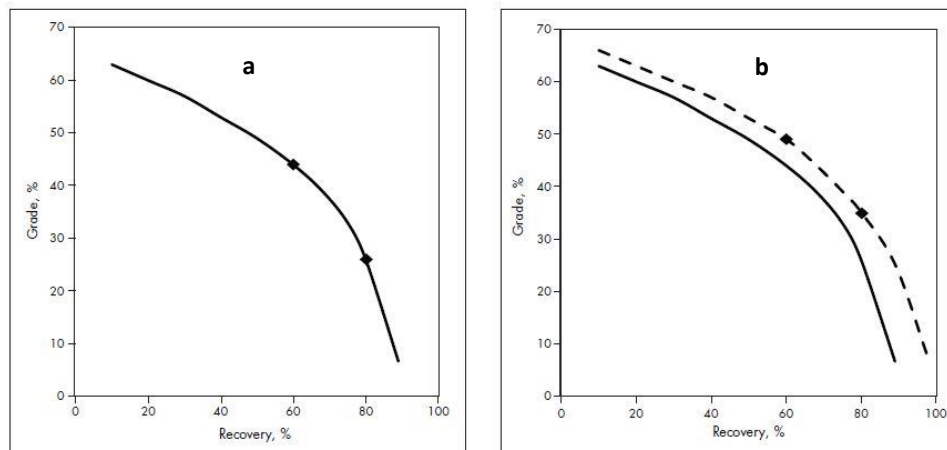


Figure 7. (a) Example of grade-recovery curve, (b) Grade-recovery curve shifted by a change in operational adjustment (Kawatra & Young, 2019)

2.1.4 Flotation stages

The grade and recovery in flotation processes are often not achieved in a single stage. As a result, the operation is done in stages, each with its own function. The common flotation stages are rougher, cleaner and scavenger, and are all connected to form a "circuit. **Roughers** are typically the first stage designed and operated to achieve high recovery with acceptable selectivity. This stage removes a major amount of the undesired tailings, resulting in a significant reduction in the volume of slurry that reports to the next step. **Cleaners** are used to treat concentrate from rougher. They are used to increase concentrate grade to meet downstream

requirement and avoid penalties for undesired constituents. This stage ensures the removal of entrained particles recovered in the rougher. **Scavengers** clean up tailings from earlier stages. The goal is to extract as much valuable material as possible and produce a final tailing. Concentrates obtained from scavengers is often rich in trapped middling particles and must be regrind to fully liberate the target minerals (Kawatra & Young, 2019; Rao, 2004).

2.2 Flotation of Barite and Fluorite

2.2.1 Barite

Barite (BaSO_4) and witherite (BaCO_3) are the only commercially available barium minerals for industrial applications. Witherite is mostly preferred in the chemical industry as it can easily be dissolved, however, it is less common and occurs in minor amounts in some barite deposits, making barite the main industrial source of barium. Barite can naturally exist as barium sulphate (BaSO_4 in the proportion 66 % BaO and 34 % SO_3), however, it is usually associated with secondary minerals or gangue such as calcite, fluorite, quartz, etc (Deng et al., 2019; Grigorova et al., 2015; Ren et al., 2017). The mineral has found wide application in the chemical, petroleum, paint, and other industries due to its properties such as high density ($4.3 - 4.5 \text{ g/cm}^3$), high brightness and whiteness, low solubility in water and acid, ability to absorb X-rays and gamma rays, etc (Abdou et al., 2018; Wang et al., 2006). It is used as a weighting agent for drilling mud such as oil and natural gas, as a filler in paint and plastics, flux in glass manufacturing and to add brilliance and clarity, as the main source of barium for the chemical industry, among other minor applications (Wang et al., 2014; Zhang et al., 2014). The major industrial applications of barite are presented in **Figure 8**.

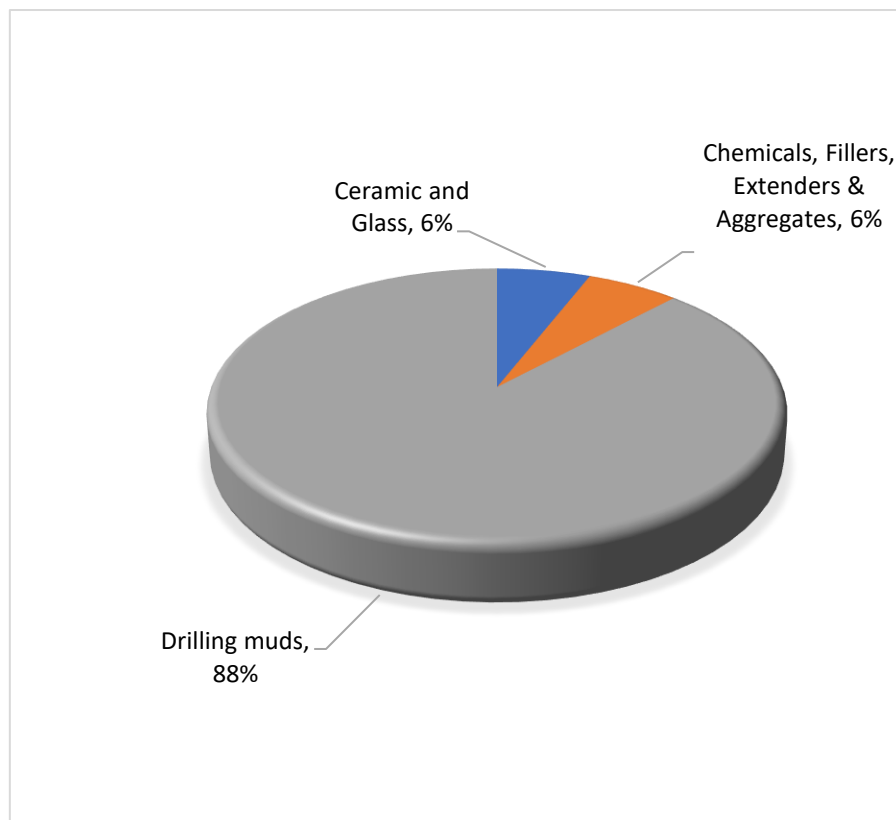


Figure 8. Major end-uses of barite (modified after Bonel, 2005)

The requirements for each of these applications determines the composition of the commercial barite product as explained in **Table 2**.

Table 2. Typical specification of commercial barite product (Modified after Bulatovic, 2015a)

Drilling Mud Grade	Chemical Grade	Filler Grade
Grade of BaSO ₄ = 92 %	Grade of BaSO ₄ = 96 – 98 %	Grade of BaSO ₄ = 85 – 95 %
Specific gravity = 4.2 g/cm ³	CaF ₂ = < 0.5 %	Brightness = 70 – 95 %
% 0.075 mm = < 98.9 %	SiO ₂ = < 1.0 %	100 % < 0.045 m
% 0.006 mm = > 70 %	F ₂ O ₃ = 0.5 %	
	SrSO ₄ = < 2 %	
	Sr/Bo = < 0.017	
	100 % < 0.04 mm	

2.2.1.1 Beneficiation technology of barite ore

Barite ore can be beneficiated through either of these methods, or a combination of two or more, i.e., hand sorting, magnetic and gravity separation, flotation, etc (Bonel, 2005). Hand sorting relies heavily on the colour and density difference between the minerals from which majority of the target mineral is removed. It can ensure a high-grade product without the need for large scale equipment and reagents; however, it is less efficient and requires intensive human labour. Based on density or particle size, gravity separation can be employed to recover barite from other gangue minerals with the aid of fluid power and all kinds of mechanical force. Though the method is less costly, the concentrate recoveries are often low. Barite ores containing magnetic minerals (such as iron minerals) can be sorted through magnetic separation to improve the grade of the concentrate. However, this method is less applicable in mineral processing.

Flotation relies on the chemical and physical properties difference between barite and the associated gangue minerals surfaces to obtain high grade products for commercial purposes. It is often employed in depositional barite ores, hydrothermal barite ores associated with fluorite, finely disseminated ore as well as tailings of gravity separation (Grigorova et al., 2015; Wang et al., 2014). Several studies on various barite ore types have been conducted using flotation, gravity preconcentration, and magnetic separation, with most operating plants employing flotation to recover barite from complex ores. The process is heavily influenced by the type of ore and gangue composition as well as the liberation size of barite. Barite flotation can either be direct or indirect, where the former is used to concentrate barite ore using fatty acid collectors usually at pH 8.5-9. The latter is to remove base metal sulfides or pyrite, leaving a concentrated barite in the tailing that is later recovered (Bulatovic, 2015a). For a barite ore containing fluorite, two possible recovery methods exist, i.e., flotation of fluorite ahead of barite while depressing barite or flotation of barite ahead of fluorite while depressing fluorite. Bulatovic (1987) conducted test works on barite/fluorite flotation by floating fluorite ahead of barite. Although a reasonably good CaF_2 grade was obtained (75 %), the barite concentrate was contaminated with a large portion of fluorite (15 %). However, when barite was floated ahead of fluorite, a BaSO_4 grade of 94.6 % (containing 1.2 % fluorite) was achieved, showing a significant improvement in the results. It is therefore, recommended to float barite ahead of fluorite for good selectivity.

2.2.2 Fluorite

Fluorite (CaF_2), a scarce non-metallic mineral resource, is widely used for various industrial productions. It is the primary raw material used in fluorine products applicable in the production of hydrofluoric acid, manufacture of glass, as a flux in steel making, aluminium industry, aviation, medicine, refrigeration, etc as shown in **Figure 9** (Gao et al., 2018; Zhu et al., 2018).

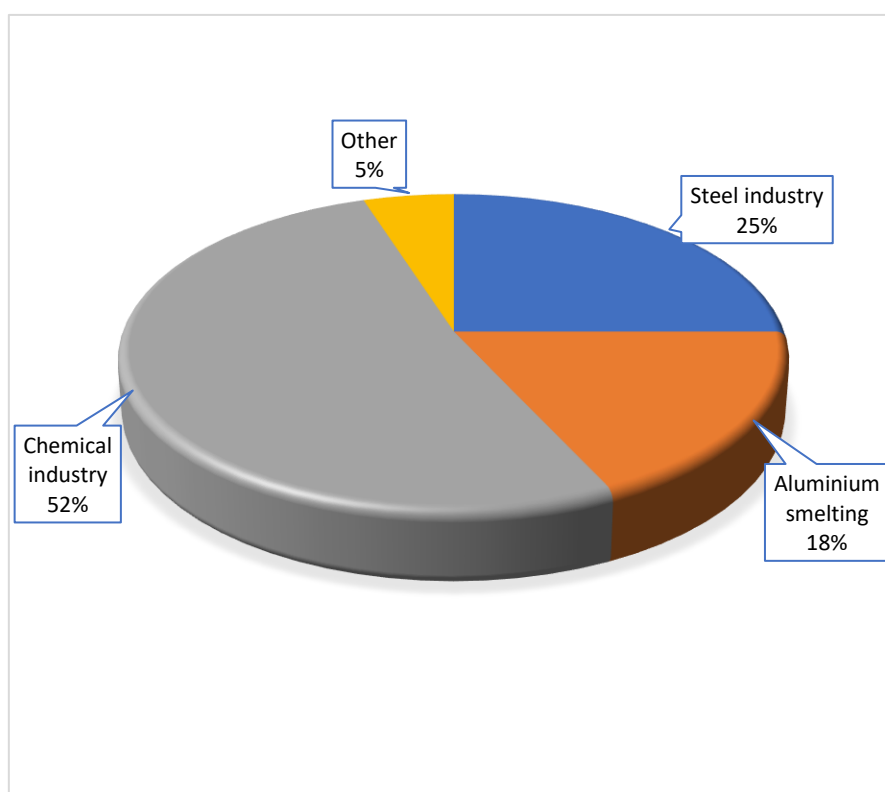


Figure 9. End-use of fluorite (modified after Masoudi et al., 2017)

Fluorite is considered as a strategic reserve supply by many countries, and the demand for high-quality fluorite concentrate has increased due to the increasing development in the relevant fields (Fa et al., 2006; Li & Gao, 2018; Zhang & Song, 2003). The commercial name for the naturally occurring fluorite-containing mineral is fluorspar, CaF_2 , which contains 51.5 % calcium and 48.9 % fluorine in its pure form, with a specific gravity of 3.18 g/cm^3 . Fluorspar commonly exists as glassy, colourless, white, greyish, pink, purple, blue or yellow, and appears in massive forms with interlocking crystals in most ore types (Bulatovic, 2015a; Cairncross, 2011). However, in most deposits, fluorspar is often associated with gangue minerals such as barite, calcite, quartz, all of which have similar surface properties (i.e., solubility, crystal structure, hydrophobicity, and zeta potential) (Gao et al., 2020; Wang et al., 2020). Fluorite

ores, therefore, need to be upgraded to various grades to fit a particular industrial use. For instance, fluorite concentrate grade of 98-99 % CaF_2 is required for the acid grade fluorite in the production of hydrofluoric acid, 85-96 % CaF_2 for the ceramic grade used in the manufacture of specialty glass, ceramics, and enamelware, and 60-85 % CaF_2 for the metallurgical grade used as fluxing agent (Bulatovic, 2015a).

Several attempts such as flotation techniques, gravity separation, or a combination of both have been made to enhance the beneficiation of fluorite from relatively low-grade ores. In practice, flotation is currently the most common and effective beneficiation process to achieve high-grade fluorite concentrate (Bulatovic, 2015a; Dill et al., 2011). Froth flotation of fluorite, especially carbonaceous ores, disseminated fluorite-silicate ores and ores that contain barite are difficult to treat due to the similar surface properties possessed by fluorite and the associated gangue minerals. The process is, therefore, complex and requires the application of selective reagent schemes coupled with multiple stages of roughing, scavenging and cleaning to obtain a high-grade fluorite concentrate (Liu et al., 2019). The development of an efficient flotation technique for selective separation of fluorite has, therefore, received a lot of attention in recent years.

2.2.2.1 Floatability of Fluorite

Extensive research works have been conducted on the various fluorite containing ores over the past 30 years from which alternative reagent schemes including various collectors and depressants have been tested (Bulatovic, 2015b). Fluorite can be considered as a hydrophobic mineral in one case, and as hydrophilic in another case. This is because the degree of hydrophobicity, expressed by a water contact angle varies with the crystal structure and the colour of the mineral (Gao et al., 2012; Zawala et al., 2007). The common crystal surfaces exhibited by fluorite after pulverisation are {111}, {110}, {100}, and {310}, which influence its unique properties (Gao et al., 2019). When a crystal surface of {111} is exhibited, fluorite is moderately hydrophobic, having a water contact angle of almost 20° while {110} and {100} surfaces give fluorite a zero-water contact angle making it hydrophilic (Zhang et al., 2015).

Li & Gao, (2018) stipulated that after grinding of fluorite, the highest degree of exposure (> 60 %) exhibits the {111} crystal surface. Schultz et al. (1994) also concluded that the perfect cleaving plane of fluorite is the {111} surface, and a natural piece of fluorite is likely to cleave along this hydrophobic surface. As a result, fluorite can be said to be mildly hydrophobic in

nature and can be floated by air bubbles in small devices such as the monobubble Hallimond tube without any surfactant. It is worth mentioning, however, that the floatability of fluorite is highly dependent on the pH of the slurry (Kowalczyk & Zawala, 2016). The pH for fluorite flotation ranges from 7-11 in either pure water (without collector) or in the presence of surfactants (froth flotation) (Filippova et al., 2014b; Gao et al., 2015). Some studies have also shown that regardless of the flotation reagents used, pH 9 is often chosen as the best pH as it is quite close to fluorite's zero charge point (Gao et al., 2016; Song et al., 2006). Fluorite is positively charged in water at these pH range and can be electrostatically bonded to a negatively charged bubble surface (Kowalczyk & Zawala, 2016). In the absence of collectors, fluorite may display its inherent floatability in single bubble tests with satisfactory results, according to several research. However, laboratory and pilot-scale flotation tests have shown that efficient flotation reagents are still required to separate fluorite from associated gangue minerals (Gao, 2016; Gao et al., 2012; Kowalczyk & Zawala, 2016).

2.3 Flotation reagents of Barite and Fluorite

Barite and fluorite are generally closely associated with each other, thus, require efficient separation mechanism to obtain high grade concentrate for further usage (Wang et al., 2020; Zou et al., 2017). The most widely used method in practice for the separation of barite or fluorite from other associated non-metallic minerals (such as calcite, quartz) is froth flotation, using fatty acids and other derivatives as collector (Huang et al., 2020; Liu, et al., 2019). However, most of these collectors can actively interact with the Ba^{2+} , Ca^{2+} sites on the surface of barite and fluorite, making selective separation of either of these minerals difficult. Hence, it is nearly impossible to separate either of these minerals from the other without depressants (Chen et al., 2018; Gao et al., 2018; Ren et al., 2017).

2.3.1 Collector

The interaction between collectors and barite/fluorite minerals greatly influences the grade and recovery of each mineral type. Most collectors used in industrial processes have been found to contain certain bubbles, therefore, there is less research on foaming agents (frothers) in barite/fluorite flotation, with most research focusing on collectors and depressants (Kejun et al., 2015). The collectors used in barite/fluorite flotation can be broadly divided into four principal groups: i) anionic, ii) cationic; iii) amphoteric, and iv) microbial collectors (Gao et al., 2021; Wang et al., 2014).

2.3.1.1 Anionic collector

These collector type adsorb onto the mineral surface to effect separability according to the chemical adsorption manner. They are further classified according to the following.

2.3.1.1.1 Fatty acid

These collectors are known to allow flotation of many non-sulfide minerals while being relatively environmentally friendly (Wang et al., 2020). They include sodium oleate, oleic acid, tall oil, oxidized paraffin soap, naphthenic acid, etc. They are the most widely used barite/fluorite collectors, with sodium oleate (NaOl) and oleic acid being the most preferred for industrial application. These collectors are usually characterised by strong collecting capabilities, low cost, availability, non-toxicity (El-Hakim, 2003; Pugh & Stenius, 1985; Uçar & Özdag, 2002). Yue Chenglin (2001) studied the adsorption mechanism of oleic acid on the surface of barite and fluorite and proposed that the adsorption form of oleic acid on the two minerals is related to the zero electric point of the mineral surface, the pH of the pulp and the collector dosage. The barite surface was mainly dominated by chemical adsorption, and the optimum working pH range of oleic acid was 7-10. Despite the advantages associated with fatty acid collectors, they still have shortcomings such as poor selectivity, high dosage requirement, low solubility, and low flotation activity in low-temperature pulps (Kellar et al., 1992). Therefore, mineral processing plants often resort to the use of amphoteric collectors obtained through the modification of fatty acid by halogenation, emulsification, sulfate, sulfonation, and addition of nitrogen atoms (Gao et al., 2021).

2.3.1.1.2 Oxidized paraffin soap

Oxidized paraffin soap ($C_{12-16}COONa$) is also used in the selective separation of quartz-fluorite, barite-fluorite, and calcite-fluorite ores during flotation. This kind of collector is rich in raw materials, cheap, with better selectivity. Soap made from saponified waste oil can be used to obtain a fluorite concentrate grade of around 98 % and a recovery of 86 %. However, it has a weak collecting ability compared to oleic acid, making it a less preferred collector choice for barite/fluorite flotation (Zhu et al., 2019).

2.3.1.1.3 *Alkyl sulfonates and alkyl aminates*

Like sodium oleate, sodium hexadecyl sulfate and dodecyl sulfate are also mostly used as collectors in barite/fluorite flotation. They are less toxic, highly selective, soluble in water, have strong collecting power with certain bubble performance (Gao, 2016). These collector type mainly absorb on the mineral surface through electrostatic adsorption. The use of sodium hexadecyl sulfate ensures effective separation of barite/fluorite from gangue minerals such as calcite, quartz at low temperatures. Sodium dodecyl sulfate on the other hand can spontaneously decompose and release dodecanol, which will increase the recovery of quartz alongside the target mineral. The addition of depressants is therefore necessary to obtain exceedingly good concentrate index (Asadi et al., 2018; Wang et al., 2006). Wang Yuting et al. (2008) studied the recovery of barite from Pingshui copper mine tailings using sodium dodecyl sulfate as collector and obtained a barite concentrate grade of 91.68 % and a recovery of 80.43 %. St. Ślęczka (1987) also used sodium dodecyl sulfate as a collector to selectively recover barite from a mixed ore of barite-fluorite-quartz, and achieved a barite concentrate grade of 96.4 % and a recovery of 76.2 % without ultrasonic treatment.

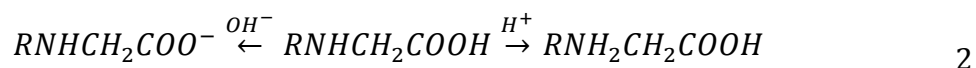
2.3.1.2 *Cationic collector*

They are mainly fatty amine collectors which interact with minerals based on physical adsorption. They react rapidly with minerals compared to other collector types, giving satisfactory flotation (Filippov et al., 2014a; Uçar & Özdag, 2002). Their collecting efficiency on barite is low and are sensitive to slime. The positively charged mineral surface of barite/fluorite ($\text{Ba}^{2+}/\text{Ca}^{2+}$) is again unfavourable for physical adsorption, hence, few studies exist on this collector type including their usage (Wang et al., 2014). Hu Yuehua et al. (1990) studied the solution chemistry characteristics of alkylamines on the collection performance of salt minerals and observed that they had the strongest collection ability on scheelite, followed by barite and apatite, with fluorite and calcite being the lowest. Cationic collectors usually require the presence of acid to fully dissolve in water. Various researchers have attempted to introduce an ether group on the amine alkyl group to reduce the melting point and form a liquid ether amine, resulting in a modified amine which is easily soluble in water with significant improvement in flotation (Papini et al., 2001). However, high dosages are required which is usually more extensive than that required when using anionic collectors (Gao et al., 2021). Considering that amine collectors are easily affected by fine particles (such as fine mud) and

have low collection efficiency, they are only limited to laboratory test stage, and their application in industrial processes is not promoted (Kejun et al., 2015).

2.3.1.3 *Amphoteric collectors*

These are collectors with both anionic and cationic hydrophilic groups in their molecules. They are characterised by a general formula $R_1X_1R_2X_2$, where R_1 is either an alkyl/aromatic group with a strong collecting capability; X_1 is a cationic group; R_2 can be an aromatic group, an aliphatic group, or a cycloalkyl group; and X_2 is an anionic group. Amphoteric collectors are known to pose several technological problems, including high operating costs and complex flotation flowsheets (Fa et al., 2006). The collecting ability of amphoteric collectors on each mineral varies according to the pH of the pulp (El-Reheim, et al., 2008). The reaction mechanism under either acidic or alkaline medium is shown in [Eq.2].



2.3.1.4 *Microbial collectors*

This involves controlling the surface properties of minerals with microorganisms due to the interaction between them, for instance, atomic or electronic structure, acid-base, charge, wettability, etc. Again, some metabolites such as polypeptides, polysaccharides and proteins produced by microorganisms can react with the mineral surface, modifying its properties. Biologically extracted lipid compounds from fungi, bacteria, yeast are used as flotation collectors during flotation of fluorite to improve the recovery and concentrate grade, which are potential replacements for oleic acid (Mahmood et al., 2009; Rao et al., 2010; Sharma & Hanumantha Rao, 2002).

2.3.1.5 *Combined collectors*

A recent industrial practice is the use of combined collectors according to the principle of synergy between the reagents. Here, two or more collectors are used together according to a certain ratio to improve the mixed reagents. The collection ability as well as the selectivity of the obtained reagent can somewhat improve the flotation efficiency as evident in the study conducted by Wang Yuting et al. (2008). In this study, a mixed collector of sodium oleate and sodium dodecyl sulfate were used to increase barite concentrate grade and recovery from 91.68

% to 95.2 %, and 80.43 % to 83.1 %, respectively. Mixture of fatty acid collectors has been extensively used in the flotation separation of fluorite from calcite resulting in lower dosage requirement. For instance, in India, a collector named AK-2 which is a mixture of oleic acid, phosphate ester, and ethylene diamine was used in fluorite flotation. The results showed significant improvement compared to using only oleic acid (Mao et al., 1995).

2.3.2 Depressants

The attempt to selectively recover barite or fluorite from associated Ca-bearing minerals and silicates has resulted in the discovery of various depressants such as sodium silicate (SS), modified SS, sodium fluorosilicate, sodium alginate, calcium lignosulphonate, etc (Bo et al., 2015; Chen et al., 2017). The type of depressant to be chosen in barite/fluorite flotation depends on the target mineral since no one depressant is all size fits all. Depressants can either be organic, inorganic, or a mixture of both (Gao et al., 2021).

2.3.2.1 Organic depressants

Inorganic depressants, although are effective and widely used, they are harmful to the environment with tailing handling requiring extra cost. Organic depressants on the other hand are biodegradable and relatively cheaper, receiving attention from various researchers (Lopez et al., 2007). The most used organic depressants in barite/fluorite flotation are starch, citric acid, tannins, sodium carboxymethyl cellulose, dextrin, etc (Song et al., 2006). These group of depressants have similar structural features such as: i) presence of hydrocarbon segment adsorbing on hydrophobic mineral surfaces; ii) strongly hydrated polar groups, such as SO_3^{2-} , COO^- , iii) availability of numerous hydroxyl group which undergo ionization or hydrogen bonding (Mu et al., 2016).

The interaction between organic depressants and the mineral surface is complex, with most researchers suggesting that a possible interaction may account for either the adsorption or association of the reagent with the surface of the mineral as shown in **Figure 10**. An electrostatic adsorption between oppositely charged polymers and the mineral surface may exist at first. Then, an interaction between the hydrophobic nonpolar molecules of the depressant and the mineral surface contributes to aggregation. A formation of hydrogen bonds, specifically at basic pH, plays a critical role in this process. The final stage is the formation of chemical bond between the anionic functional groups (such as carboxylate or sulfuric groups) and the metallic

cations of the mineral surface which may drive the binding of polymers (Boulton et al., 2001; Gregory & Barany, 2011). The suppression effect of organic depressants is greatly related to the chemical features of the polymers, such as charge density, polymer functionality, and molecular weight. Again, the operating parameters during flotation (i.e., pH, composition of the ore, dissolved ions, ionic strength of aqueous phase) all influence the effectiveness of the depressants (Bulatovic, 2015c).

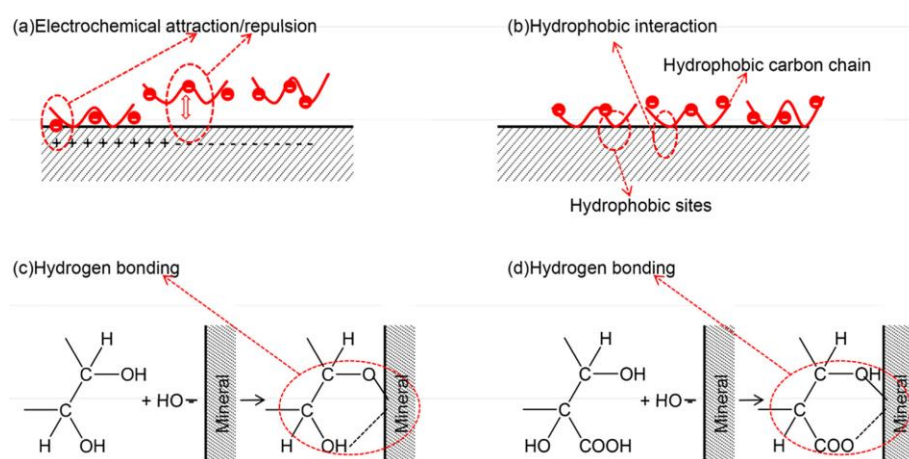


Figure 10. Possible interaction mechanism of organic depressants with a mineral surface: (a) electrochemical attraction, (b) hydrophobic interaction, (c) hydrogen bonding, (d) chemical interaction (Mu et al., 2015)

2.3.2.2 Combined depressants

Complex ores sometimes require the use of a mixed depressant to depress gangue minerals rather than using single depressant. In general, the two reagents are added at the same time during flotation, rather than being premixed prior to flotation (Cao et al., 2012). For instance, a mixture of sodium silicate and aluminium sulfate was used as the depressant in fluorite flotation to depress sulfate minerals and calcite. The grade and recovery of fluorite concentrate increased by 10 % and 3 %, respectively, compared to using only sodium silicate (Tian et al., 2019).

2.3.2.3 Calcite/Quartz depressants

2.3.2.3.1 Water Glass

Sodium silicate, commonly known as water glass is undoubtedly the most used inorganic depressant due its low cost, including compounds made of different proportions of SiO_2 and Na_2O . It is good in depressing calcite and silicate gangue minerals associated with barite and

fluorite, and also acts as a dispersants of slime by weakening the negative effects of micro-sized particles on flotation process. (Song et al., 2006; Zhang et al., 2017; Zhou & Lu, 1992). Though sodium silicate has a depressive effect on both calcite and fluorite, increasing the dosage in substantial amount (kg/t) reduces the suppression effect on fluorite due to the changing proportion of SiO_2 and Na_2O (Yongxin & Changgen, 1983). According to (Deng et al., 2019), alkaline sodium silicate in solution produces silicic acid $\text{Si}(\text{OH})_4$ as the main specie at pH below 9.4, $\text{SiO}(\text{OH})_3^-$ at pH above 9.4, and $\text{SiO}_2(\text{OH})_2^{2-}$ at pH above 12.6, with various authors stipulating that these low molecular weight of silica species are responsible for the depressive effect of sodium silicate (Azizi & Larachi, 2018; Bo et al., 2015). However, Fuerstenau et al., (1968) argued that colloidal silica would be the main species responsible for the depressive effect.

2.3.2.3.2 *Acidified water glass*

Common water glass can be acidified to enhance its depressive effect on gangue minerals such as calcite and quartz with the following advantages: i) improve the grade and recovery of fluorite and barite concentrates, ii) reduced reagent dosage, iii) acceleration of the rate at which tailings particles settle, iv) high polymerization ability. The mechanism of acidified sodium silicate is the same as that of ordinary sodium silicate, however, the presence of acid increases the formation of colloidal silica (Zhou et al., 2013; Fuerstenau et al., 1968). The main challenge associated with acidified water glass is its preparation, specifically the type of acid to be used, acid to sodium silicate ratio, which significantly affect the reagent's separation efficiency (Gao et al., 2021).

2.3.2.3.3 *Polyphosphate*

Sodium hexametaphosphate (SHMP, $(\text{NaPO}_3)_6$), sodium pyrophosphate (SP, $\text{Na}_4\text{P}_2\text{O}_7$), trisodium phosphate (TSP, Na_3PO_4), and sodium tripolyphosphate (STPP) are known to have depressive effect on both calcite and barite (Gao et al., 2021). Liu et al., (2019) studied the selective flotation of fluorite from barite and found that trisodium phosphate could not prevent the adsorption of sodium oleate on the surface of fluorite but could effectively block the adsorption of sodium oleate on the barite surface.

2.3.2.3.4 Tannin

Tannin (tannin extract), a macromolecular amorphous substance obtained from the roots and shells of some plants is known to have depressive effect on calcite and quartz during fluorite flotation. The carboxyl group of tannin acid adsorbs on the surface of calcite/quartz while the polar group points outward. The water molecules then form a hydration layer by a hydrogen bond, making the surface of the mineral hydrophilic as shown in **Figure 11** (Zhang et al., 2018; Kupka & Rudolph, 2018). When using tannin, the equilibrium concentration of tannin and collector is critical for selective separation of fluorite and gangue minerals. Tannin in the right amount can effectively improve the concentrate grade, but when used in excess affects the recovery especially in the cleaning stage (Bulatovic, 2015c; Zhang et al., 2018).

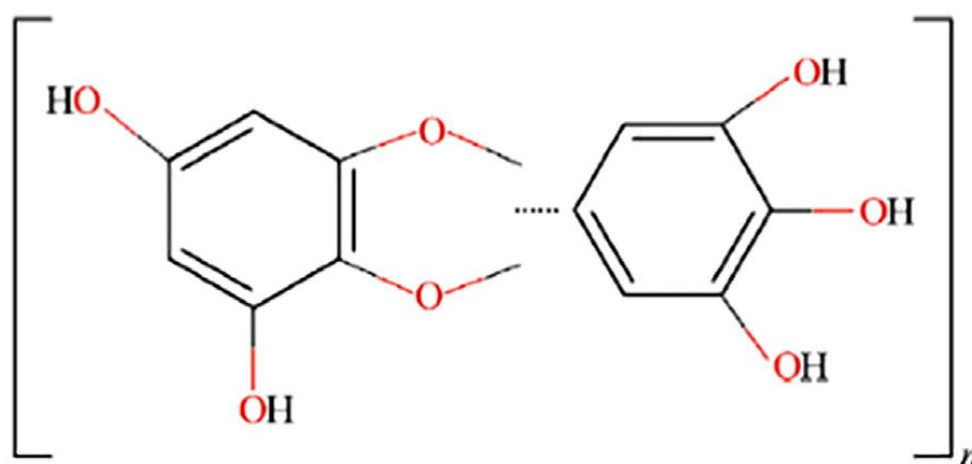


Figure 11. Structure of Tannin (Gao et al., 2021)

2.3.2.4 Fluorite depressant

For barite ores with low fluorite contents, it is necessary to depress fluorite rather than barite due to reagent consumption. Citric acid (CA) functions as a chelating agent by forming a loosely bound, soluble complex with metal ions. This causes the mineral surface to become hydrophilic (Zeng et al., 2017). Citric acid was found to partially create aqueous soluble metal-ligand complexes, which led to the removal of Al^{3+} ions from the mineral surface, according to Xia et al. (2015). It was discovered that adding citric acid increased the recovery of copper by removing Ca^{2+} ions from chalcopryrite surfaces (Liu & Zhang, 2000). An earlier investigation discovered that citric acid might prevent the coagulation of hexadecane-quartz in aqueous solutions containing the ions Ca^{2+} , Mg^{2+} , and Fe^{3+} (Gan et al., 2009).

A study by Gao et al., (2016) using CA to selectively separate calcite from fluorite gave a calcite concentrate recovery of 85.2 % from a feed containing 39.97 % fluorite and 17.87 % calcite. Liu et al., (2017) studied the performance of combined depressant in flotation and found that CA had a depressing effect on apatite, though a mixture of CA and sulfuric acid had a stronger effect. Wang et al., (2019) also used CA as a depressant to reduce the flotation recovery of Ca^{2+} activated quartz. Based on these findings, it is evident that CA could interact with calcium ions present on Ca-minerals surfaces, and thus, has the potential to be used in separating barite from fluorite during flotation (Liu et al., 2020).

2.3.2.5 Barite depressants

Barite depressants such as starch, dextrin, cellulose and their derivatives have been used in mineral processing industry for over 50 years. It is believed that the adsorption of these depressants on the mineral surface includes hydrogen bonding, electrostatic interaction, chemical bonding, and hydrophobic bonding, with active groups such as HCOOH existing on the mineral surface (Kejun et al., 2015). The type of starch and dextrin and their preparation method play an important role in their efficiency. For example, causticized and boiled starches are known to have better depressing ability than ordinary prepared starch due to their significantly improved solubility, though their adsorption is still based on the active groups such as $-\text{OH}$ and $-\text{O}-$. Branched dextrin are also known to be more efficient than standard unbranched dextrin (Bulatovic, 2015b). Wu Yongyun (1999) studied the flotation effect of various starches on barite and fluorite and observed that caustic starch had a stronger depressing ability on barite than on fluorite. Li Ye et al (1997) found that dextrin is capable of depressing barite than fluorite by analysing the Langmuir-type adsorption characteristic on the mineral surfaces using X-ray Photoelectron Spectroscopy (XPS). The results indicated that the Auger parameter change of barite was significantly higher than that of fluorite, confirming the stronger depressing effect of dextrin on barite.

Other secondary depressants are also used in fluorite flotation to depress barite, such as i) sodium fluorosilicate (Na_2SiF_6), which is used as a barite depressant and also to improve silica rejection, ii) lignin sulfonate to improve barite suppression, iii) sodium and ammonium fluoride used as barite depressant and also as an activator when floating fluorite with diamine collectors (Bulatovic, 2015b).

2.3.3 Modifiers

To obtain the desired pH, different pH modifiers such as sodium hydroxide (NaOH), sodium carbonate (NaCO₃), calcium oxide (CaO), hydrochloric acid, (HCl), nitric acid (HNO₃), sulfuric acid (H₂SO₄) etc, can be used (Zhang et al., 2017). However, some studies have found that sodium carbonate was more effective than sodium hydroxide because NaCO₃ increases the content of CO₃²⁻, thereby, limiting the content of Ca²⁺/Mg²⁺ in the pulp, whose concentrations if higher, will significantly reduce the recovery of valuable minerals. Lime is, therefore, not recommended in barite/fluorite flotation (Hernández-Bermúdez De Castro et al., 1996). Because HCl is highly volatile and HNO₃ is a strong oxidizer, they are both not suitable for pH regulating, with H₂SO₄ being the preferred option (Zhao et al., 2013).

2.3.4 Activating reagents

A number of activators have been suggested to be used in barite/fluorite flotation including NaCl, MgCl₂, NaF, Pb(NO₃)₂, and BaCl₂. However, NaCl and MgCl₂ have depressing effect on both barite and fluorite, leaving BaCl₂, NaF and Pb(NO₃)₂ (Bulatovic, 2015a).

2.4 Stoke's law

Stoke's law is concerned with the movement of small spherical objects through a fluid at slow velocities. The object needs to move at slow speeds for the flow to be laminar rather than turbulent. The velocity, mass, and volume of the sphere can all be used to calculate the viscosity. The force of gravity acts on the moving object in a downward direction while the forces of buoyancy and drag act on the opposite direction as the object moves through the fluid. The net force acting on the sphere is zero at terminal velocity (V_T). The weight of the sphere becomes equal to the buoyancy force plus the drag force (Cartwright, 2020). The sphere's drag force is given as follows:

$$F=6\pi\eta rv \quad 3$$

This is called the Stoke's law, where η is the viscosity of the fluid, r is the radius of the sphere, and V is the terminal velocity of the sphere in that fluid.

2.5 Statistical Design of Experiments (DoE)

2.5.1 Fundamental concepts of statistics

To analyse statistical data, the arithmetic mean value remains the important parameter for characterising measured or observed values. A sample's arithmetic mean, denoted by $\bar{x}$ is the mean value of the measured values x_i while the arithmetic mean of the entire population is represented by μ (Schiefer & Schiefer, 2021). The arithmetic mean of a sample is calculated as

$$\bar{x} = \frac{1}{n} \sum_{i=1}^n x_i \quad 4$$

where n represents the number of observations in the sample.

For a given dataset, the central value x_z , often referred to as the median, is the value that divides an ordered series of values into two. For instance, if a dataset has an odd number of values $(2k+1)$, the median is the $(k+1)$ -th value from the start or end of the series. For an even number of values $(2k)$, the average of the two k -th values from the beginning or end of the series is the median value. The median value, unlike the arithmetic mean is rigid, hence, is not affected by extreme values such as outliers. For a given ordered series, the mean is also referred to as the 50th percentile (0.5 quartile) (Schiefer & Schiefer, 2021).

2.5.2 Measure of dispersion

Dispersion exists in measured or observed values, with standard deviation being the most significant descriptive variable for dispersion in technical field.

2.5.2.1 Range (R)

The simplest value used to describe dispersion is the range. This is the difference between the highest and lowest values in a dataset, Mathematically, range is given as:

$$R = x_{max} - x_{min} \quad 5$$

The range provides only a limited information on the dispersion when the volume of dataset is enormous, hence, it is only appropriate for small series of dataset (Schiefer & Schiefer, 2021).

2.5.2.2 Variance and Standard deviation

The most important descriptive variables for random deviations from the mean value are variance and standard deviation. For a given sample, variance and standard deviation are denoted by S^2 and S , respectively. The variance or standard deviation is appropriate for defining single-peak distributions but not asymmetrical distributions, as they are susceptible to outliers (Schiefer & Schiefer, 2021). A sample's variance is defined as:

$$s^2 = \frac{1}{n-1} \sum_{i=1}^n (x_i - \bar{x})^2 \quad 6$$

The positive root of the variance is the standard deviation s , which is also called the dispersion or mean deviation.

$$s = \sqrt{\frac{1}{n-1} \sum_{i=1}^n (x_i - \bar{x})^2} \quad 7$$

2.5.2.3 Confidence Interval

The confidence interval denotes the boundaries within which the population mean value (μ) lies. The arithmetic mean value ($\bar{x}$) has a given degree of confidence within the confidence bounds and the population's unknown mean value is also found in this area, with a specified confidence level (Schiefer & Schiefer, 2021). The unknown population mean is defined as:

$$\mu = \bar{x} \pm f_{\bar{x}} \quad 8$$

where $f_{\bar{x}}$ = confidence region

Using the rule of dispersion transfer, the confidence region is calculated as:

$$f_{\bar{x}} = \pm \frac{t \cdot s}{\sqrt{n}} \quad 9$$

Combining [Eq. 8] and [Eq. 9] results in the following:

$$\mu = \bar{x} \pm \frac{t \cdot s}{\sqrt{n}} \quad 10$$

where, t = Student's factor, s = standard deviation, n = sample size

2.5.3 Statistical tests

2.5.3.1 Statistical test hypotheses

Statistical tests such as the t-test, F-test, and Chi-squared test allow for comparisons to be made with a particular level of statistical confidence. The results of the sample are used to validate assumptions made about the population. They are carried out through the development of hypotheses. The tests include the null hypothesis, H_0 and the alternative hypothesis, H_1 , with the alternative hypothesis contradicting the null hypothesis. The null hypothesis is always tested, but only one of the two hypotheses can be true. Even though H_0 is correct, the more serious error is chosen as an error of the first kind (α -error) which is in favour of H_1 . The error of 2nd kind (β -error) is the decision in favour of H_0 although H_1 is true (Montgomery, 2013; Schiefer & Schiefer, 2021).

The probability of an error of the 2nd kind is determined by setting the probability of error. An increase in β causes a decrease in α . The α -error should be maintained as small as possible to avoid rejecting the correct hypothesis. When there is a substantial difference between the sample mean value and the true population mean value, a small β -value arises, and vice versa. To increase the β -value which will result in a small α -value, the sample size should be increased as much as possible to get the sample mean closer to the population mean. A distinction must be established between one-sided and two-sided tests when testing null and alternative hypotheses. In the case of two-sided testing, the null hypothesis is a point hypothesis, as in the case of the t-test for population mean value. The hypothesis is thus, stated as follows:

$$\begin{aligned} H_0: \bar{x} &= \mu & 11 \\ H_1: \bar{x} &\neq \mu \end{aligned}$$

For a normal distribution, the probability error (α -error) and confidence level (S) add up to 1, where $S + \alpha$ correspond to the region below the Gaussian distribution curve (Schiefer & Schiefer, 2021).

2.5.3.1.1 *t* - test

The t-test or “Student’s test” is a statistical method for testing hypothesis. The mean value and the dispersion are used for this purpose. The test is used to determine whether there is a disparity between the mean values of two samples, or the mean value of a sample and a population mean. To apply this test, the samples must be taken randomly and must be independent of each other.

The must also be equal variances of the characteristics to be compared. The test value t_p is calculated as:

$$t_p = \pm \frac{\bar{x} * \mu}{s} * \sqrt{n} \quad 12$$

where μ is the value that is tested against.

The empirical t-value (t_p) is then compared to the critical t-values (table value). If t_p is more than or equal to the table value at $S = 99 \%$, then the conclusion is that the two mean values are different, hence, the null hypothesis would be rejected (Schiefer & Schiefer, 2021).

2.5.4 Design of Experiment (DoE)

This is a systematic approach to experiment planning and evaluation that aims to obtain the most precise possible statements about the cause-effect relationships of input parameters, disturbance variables (stochastic inputs), and target variables (outputs) with the least amount of experiment or expenditure in terms of material, time, etc. It involves making deliberate adjustments to the input parameters of a process in order to observe the consequences on the output (Mäkelä, 2017).

When performing experiments, it is critical to understand the magnitude and type of impact the input variable(s) have on the outcome or output variable(s). To accomplish this, the input variable(s) must be varied to determine their effect on the result, which is typically expressed as a "black box" (see **Figure 12**) where the input variable(s), output variable(s) and the testing range are well-defined (Schiefer & Schiefer, 2021).

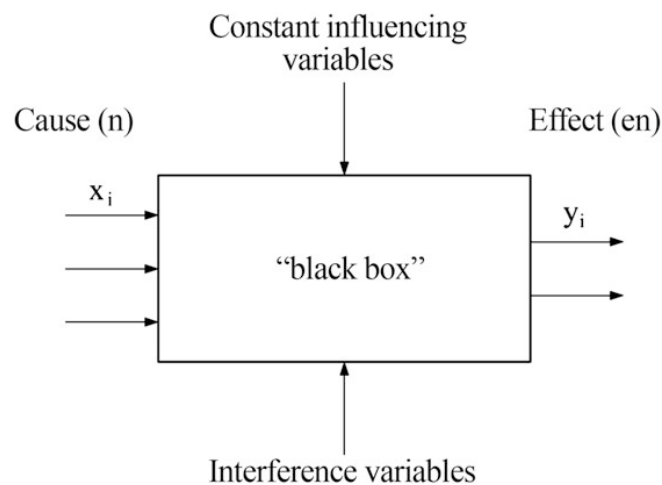


Figure 12. The cause-effect relationship as a "black box" (Schiefer & Schiefer, 2021)

2.5.4.1 Fundamentals of experimental design

The following are the general guidelines to follow when designing, performing, and evaluating tests: (i) **Repeating tests:** It is always necessary to conduct several tests for each experiment point to evaluate the dispersion and allow for claims about the confidence interval to be made. For an optimal test plan, at least two tests per each experimental point are suitable. This is because as the number of experiments per point increases, the sample mean ($\bar{x}$) approaches the mean of the entire population (μ), thereby, reducing the confidence interval. (ii) **Randomization:** In the case of extensive tests, the tests must be randomly assigned to eliminate gradients (e.g., a change in test conditions over time). This ensures that patterns within the experiment range, such as temperature, humidity, or geography, do not influence the outcomes. If the patterns, on the other hand, are known, they might be considered as further influencing variables to reduce the dispersion in the achieved outcome. (iii) **Blocking:** A block is a collection of tests that correspond to a fundamental attribute or factor. Within the blocks, the effect of the influencing variable(s) can be evaluated. If the trait that distinguishes the blocks can be quantified, its influence in the testing range can also be calculated. As a result, the dispersion in the description of the cause-effect relationship is reduced (Schiefer & Schiefer, 2021).

2.5.4.2 Experimental Design

2.5.4.2.1 One-Factor-At-A-Time Method

The traditional one-factor-at-a-time (OFAT) method is a fundamental concept that has had widespread application in scientific and engineering experiments. The OFAT approach is carried out by altering one factor level at a time while holding the other factor levels constant. The experimenter then decides which level produces the greatest results, keeping that factor level fixed while varying the other factor levels successively. While methodical, this method cannot evaluate interaction effects between components. Furthermore, there is no guarantee that the level combination will produce the best outcomes, making this approach inefficient and frequently producing erroneous findings (Giesbrecht & Gumpertz, 2004; Ryan, 2007).

2.5.4.2.2 Factorial experiment design

The term factorial design, also known as combination or crossed design, refers to the execution of all combinations of factor levels. In this case, all the factors influencing the process are fully mixed and modified at the same time. Factorial design, however, can be quite time-consuming because it needs the experimenter to conduct all conceivable combinations of all factor levels (Anderson et al., 2017; Montgomery, 2013). In most circumstances, the experiment designs can be expanded in an unexpected manner in one or more directions. This necessitates varying the extended parameters on two levels in the linear situation and at least three levels in the nonlinear scenario (Schiefer & Schiefer, 2021).

2.5.4.2.3 Full factorial experiment design

The two-level factorial design (see **Table 3**) is the simplest form of this design, which involves two influencing variables (A and B) varied on two levels (+, -). This results in four experiments which can be seen as the four corners of a square (see **Figure 13**). This design is useful at the start of an experimental attempt to pick only the potentially significant components, especially if the experimenter has limited knowledge of the experiment (Schiefer & Schiefer, 2021; Yuangyai & Nembhard, 2010).

Table 3. Experiment design with two factors (modified after Schiefer & Schiefer, 2021)

Experiment number	Level combination	
	A	B
1	-	-
2	+	-
3	-	+
4	+	+

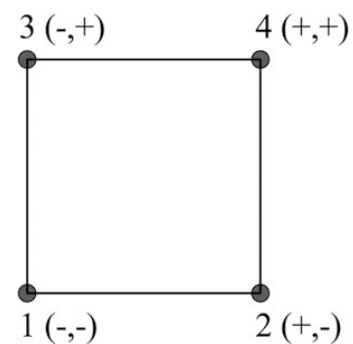


Figure 13. Factorial experiment design with four experiments (Schiefer & Schiefer, 2021)

In general, the number of experiments to be performed in a full factorial experiment designs with two levels and k influencing variables can be determined as:

$$Z = 2^k \quad 13$$

where Z = number of experiments, k = influencing variables

For a two-level factorial design, because the variation occurs only at two levels, there is a linear dependency between the variables. The main effects can, therefore, be calculated using [Eq. 14] or [Eq. 15] for a process with two or three influencing variables, respectively. The calculation generates a residual dispersion, S_R , which cannot be ascribed to the influencing factors.

$$y = a_0 + \underbrace{a_1x_1 + a_2x_2}_{\text{Main linear effect}} + \underbrace{a_{12}x_1x_2}_{\text{Reciprocal effect}} + S_R \quad 14$$

$$y = a_0 + a_1x_1 + a_2x_2 + a_3x_3 + a_{12}x_1x_2 + a_{13}x_1x_3 + a_{23}x_2x_3 + a_{123}x_1x_2x_3 + S_R \quad 15$$

For a process with two or more parameters together, the main effects and the interactions between the parameters can be calculated independently of one another without mixing of the parameters. This can be achieved using the equations below.

$$y_1 = a_{11}x_1 + a_{12}x_2 + \cdots + a_{1n}x_n \quad 16$$

$$y_2 = a_{21}x_1 + a_{22}x_2 + \cdots + a_{2n}x_n \quad 17$$

⋮

$$y_m = a_{m1}x_1 + a_{m2}x_2 + \cdots + a_{mn}x_n \quad 18$$

Because there is no solution matrix that fulfills all equations, the solution is derived using Gaussian normal equations, where the deviation squares are minimized (Schiefer & Schiefer, 2021).

2.5.4.2.4 Fractional Factorial Experiment Designs

In an event where the complete effect and interaction of the influencing variable(s) on the target variable is not of interest for the task at hand, adjustments can be made to improve the cost and time of experimentation by reducing the number of tests by half, quarter, or eighth of the original design. This is known as factorial experiment designs. For instance, considering a full factorial experiment design with two levels with three influencing variables, eight experiments

are required, making up the eight corners of the cube (Schiefer & Schiefer, 2021). These experiments can, however, be reduced to four in fractional factorial experiment design as shown in **Figure 14**.

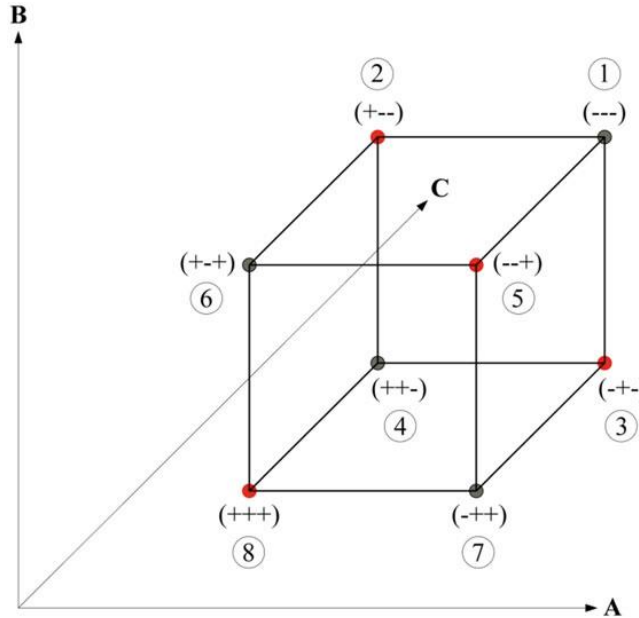


Figure 14. Fractional factorial design with three influencing variables compared to the full factorial design (Schiefer & Schiefer, 2021)

It should be emphasized that in the case of fractional factorial designs, each parameter is also altered in the design; else, the effect cannot be estimated. This yields two fractional factorial designs. The fractional factorial experiment design (**Figure 14**) appears as four experiments with the numbers 2, 3, 5, 8 (red experiment points) or the alternate experiments 1, 4, 6, 7. (black experiment points). In this case, each factor A, B, and C must have measured values of the target variable y at both the first and second tests limits, i.e., (plus) and (minus), respectively (Schiefer & Schiefer, 2021). Here, the main effects of the three influencing variables is calculated as:

$$y = a_0 + a_1A + a_2B + a_3C \quad 19$$

2.5.4.2.5 Factorial Experiment design with a center point

Full factorial experiment designs, as well as fractional factorial experiment designs are generally generated based on the assumption that cause-and-effect relationship are linear. However, in process engineering, nonlinearity generally exists between influencing variables

and their effects. To determine this, tests are carried out in the central point (see **Figure 15**) and the measured value is compared to the calculated value of the linear regression model in the central point. The distance between the center point and the other experiment points is the same. When the tests in the center point are repeated severally, information about the dispersion is obtained. For a process with two or three influencing variables, at least one repetition is recommended for each experimental point. However, when there are four or more influencing variables, the center point is repeated between 3 to 10 (Schiefer & Schiefer, 2021).

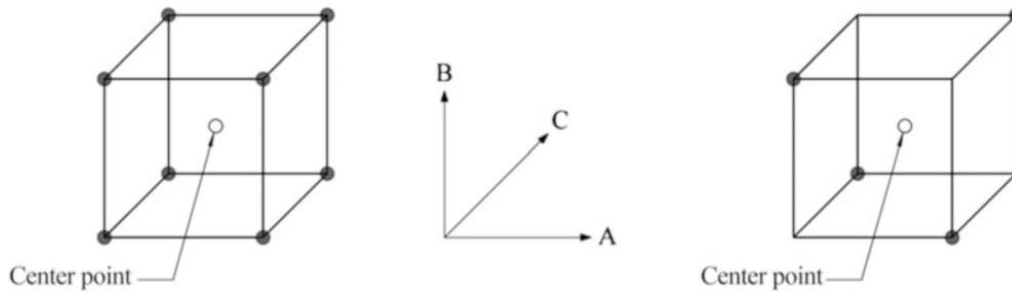


Figure 15. Factorial experiment design with center point

2.5.4.3 Response Surface Methodology (RSM)

After determining a few critical factors, the experimenter may desire to improve the process by attempting to optimize the process output using response surface methodology (Yuangyai & Nembhard, 2010). RSM was first proposed in the early 1930s, but it was not widely accepted until the work of Box and Wilson in 1951 (Mead & Pike, 1975). RSM is defined as a set of statistical design and numerical optimization techniques for empirical model construction and model exploitation that are used to optimize processes and product design. This method enables researchers to evaluate the second-order effect of components that cannot be calculated using two-level factorial designs (Box & Draper, 2007; Myers et al., 2004). RSM is a three-step procedure that includes screening, region seeking, and product/process characterization. **Screening** determines which factors of interest are important. It should be noted that the strategy utilized at this step can be a two-level (fractional) factorial design. The surface can be calculated using the first-order model:

$$y = \beta_0 + \beta_1x_1 + \beta_2x_2 + \cdots + \beta_kx_k + \epsilon \quad 20$$

where y is the response, the β 's represent the unknown parameters that will be estimated from the data in the experiment, x 's are the interaction between the design factors, and ε is a random error term.

This is followed by determining whether the current response situation lies within the optimal region. Otherwise, the **region seeking** procedure is employed to identify a path to an optimal region. Once determined, a second order model [Eq.21] can be used to estimate the process phenomena.

21

$$y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum_{i < j} \beta_{ij} x_i x_j + \varepsilon$$

In general, the response surface is depicted graphically, as shown in **Figure 16**, and is frequently useful to trace the contours of the reaction to aid in understanding (Yuangyai & Nembhard, 2010).

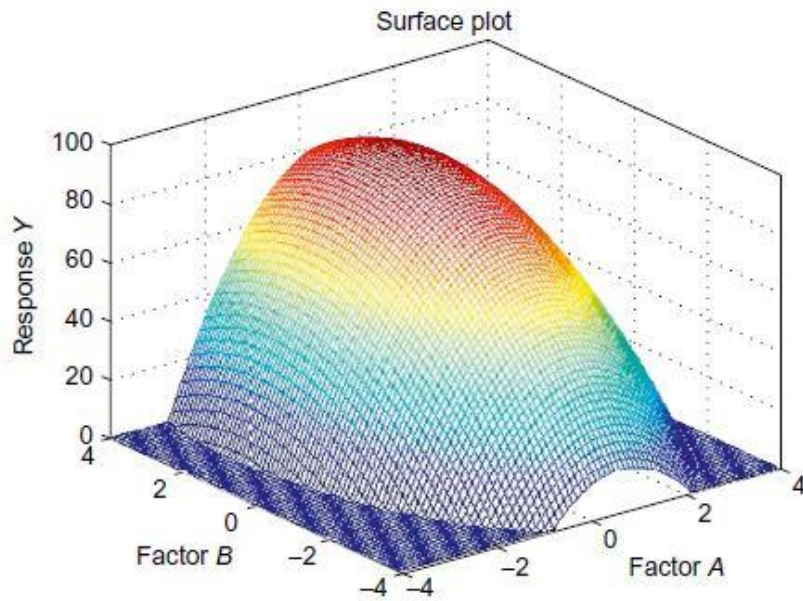


Figure 16. 3D surface response (Yuangyai & Nembhard, 2010)

2.5.4.4 Interactions in experimental design

In statistical experimental design, two-factor interactions are shown in interaction diagrams. In each instance, the two factors are configured in dependence. Two diagrams are produced as a result, one for each two-way interaction. Both factors can be interpreted globally if the factor lines in the two diagrams do not overlap. This is referred to as ordinal interaction (Widaman et al., 2012). **Figure 17** illustrates an ordinal interaction, where a1 and a2 represent the amounts of factor A and b1 and b2 represent the levels of factor B.

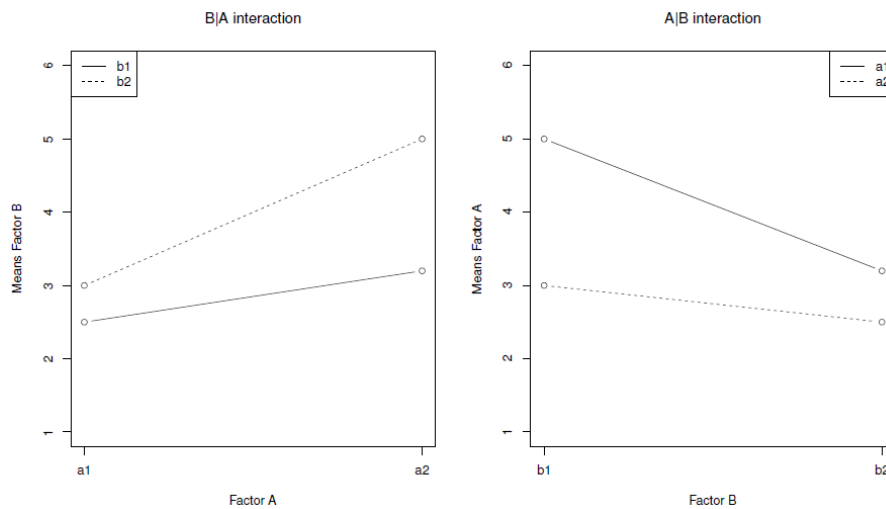


Figure 17. Ordinal interaction between factor A and B (Widaman et al., 2012)

Disordinal interaction on the other hand refers to the interaction that has an intersects in both diagrams. In this situation, it is impossible to interpret the impacts of both components globally, hence the only way to describe the impact on the target variable is through the interaction. An interaction which has only one intersect one of the diagrams is called hybrid or semi-ordinal interaction. In this case, only the effect whose lines do not overlap can be interpreted globally (Widaman et al., 2012). As can be seen in **Figure 18**, factor B can be globally interpreted, whereas factor A can only be interpreted in connection with factor B.

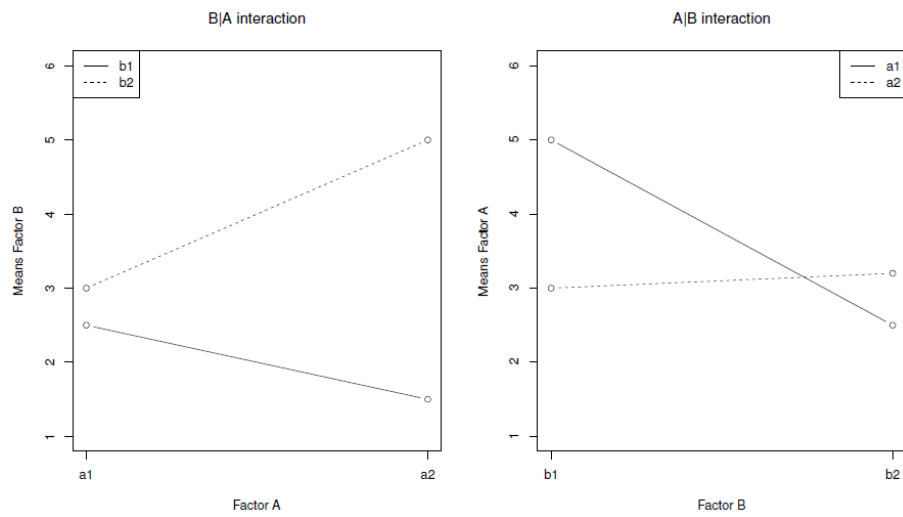


Figure 18. Hybrid interaction between factor A and B (Widaman et al., 2012)

3. Experimental Work

3.1 Microflotation Experiments

A series of microflotation tests were conducted to obtain qualitative information about the depressive effect of colloidal silica (CS), citric acid (CA), and sodium silicate (SS) on pure minerals of calcite, fluorite, and barite using sodium dodecyl sulfate (SDS) and sodium oleate (NaOl) as collectors.

3.1.1 Materials preparation

The pure calcite, barite, and fluorite minerals were obtained from HIF. These minerals were milled with Retsch vibratory disc mill RS 200 in an agate mortar at a speed of 700 rpm for 4 minutes. The milled samples were then dry sieved and the calcite, fluorite, and barite products in the -106+63 μm , -80+63 μm and -80+38 μm , respectively, were collected and each splatted into 1 g samples for microflotation tests. The various particle sizes were chosen so that all the minerals will have the same velocity range according to Stoke's law.

3.1.2 Reagent preparation

10 % stock solution of SDS was prepared and used as collector for barite, fluorite, and calcite microflotation tests. The pH was adjusted with 0.1 M stock solutions of sodium hydroxide (NaOH) or hydrochloric acid (HCl). Potassium chloride (KCl) with a concentration of 1×10^{-2} M was used throughout the experiments, and 1×10^{-4} mol/L solution of BaCl_2 was prepared and used as barite activator. 10 % stock solution each of SS and CA were the depressants used for calcite and fluorite tests, respectively. Both depressants were used in the barite microflotation tests.

Eight (8) CS which differ from each other in modification and structure (specific surface area) were also tested to ascertain their depressive effect on calcite using NaOl as collector. 10 % stock solution of each CS solution was prepared and used. The CS with the strongest depressing effect on calcite was then tested on fluorite. **Table 4** is a summary of the CS solutions with their specifications.

Table 4. Summary of CS solutions and their specifications

Colloidal silica	Solid content (%)	Specific surface area (m ² /g)	Modification
Levasil CS15-150P [®]	15	500	Sodium
Levasil CS15-750P [®]	15	750	Sodium
Levasil CS30-150P [®]	30	250	Sodium
Levasil CC40-401P [®]	40	220	Silane
Levasil CC15-151P [®]	15	500	Silane
Levasil CS15-450P [®]	15	500	Aluminate
Levasil CS30-425P [®]	30	250	Aluminate
Levasil WT110P [®]	7	1100	Aluminate

3.1.3 Flotation Experiment

Microflotation tests were performed in a Hallimond tube. The flotation pulp was prepared by adding 1 g of each mineral sample to 160 mL of KCl while stirring on a magnetic stirrer at a speed of 400 rpm. The pH of the pulp was adjusted using HCl or NaOH and conditioned for 2 minutes. After reaching a stable pH, the activator was added when required, followed by the right concentration of depressant with 3 minutes of conditioning each. The right concentration of collector was added, and the pulp conditioned for 3 minutes. The flotation suspension was then transferred to the Hallimond tube and agitated for further 2 minutes at a speed of 800 rpm. Airflow rate was set to 20 cm³/min and microflotation lasted 2 minutes. The floated (concentrates) and unfloated (tailings) products were collected, filtered, and dried in an oven overnight at 50 °C – 60 °C. The dry weights of the flotation products were measured and used to calculate mass recovery. Each test was performed three times, and the average recovery and standard deviation calculated. The experimental setup is shown in **Figure 19**.

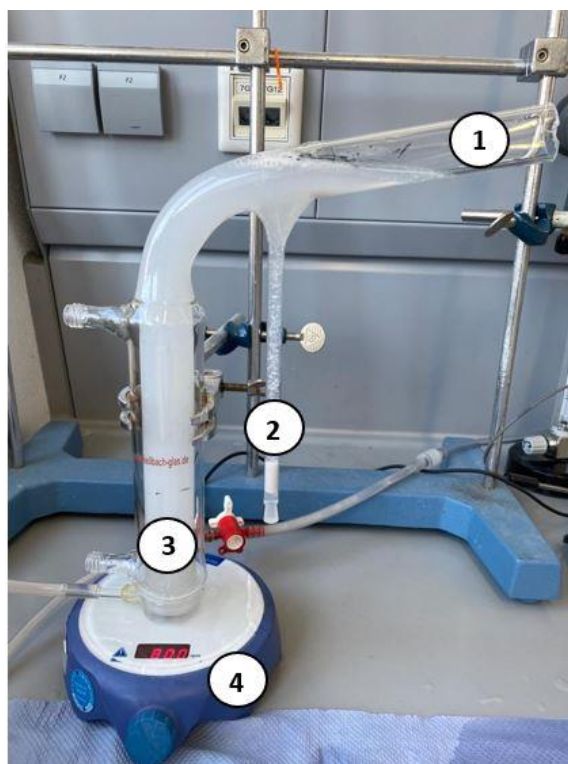


Figure 19. Experimental set-up of the Microflotation showing 1) Hallimond tube, 2) floated products, 3) unfloated products, 4) magnetic stirrer

3.2 Batch Flotation

3.2.1 Materials preparation

The material used for the batch flotation tests was a mix of tailings from Hammam Jedidi barite mine and Hammam Zriba fluorite mine which was provided by Helmholtz Institute Freiberg for Resource Technology, (HIF). These tailings had been investigated in a previous studies involving gravity separation. The gravity separation yielded eight (8) fractions according to their densities. Product of the 7th fraction was used in a previous flotation study.

In this study, the gravity separation products of fractions 3-6 were used as feed. The as-received samples were thoroughly mixed and splatted with a rotary rifle splitter to obtain homogeneous samples, which were further splatted into smaller fractions, each weighing 500 g, bagged and stored. The degree of mineral liberation (**Figure 20**) and XRD analysis (**Figure 21**) of the tailings were retrieved from the database of HIF and are shown below.

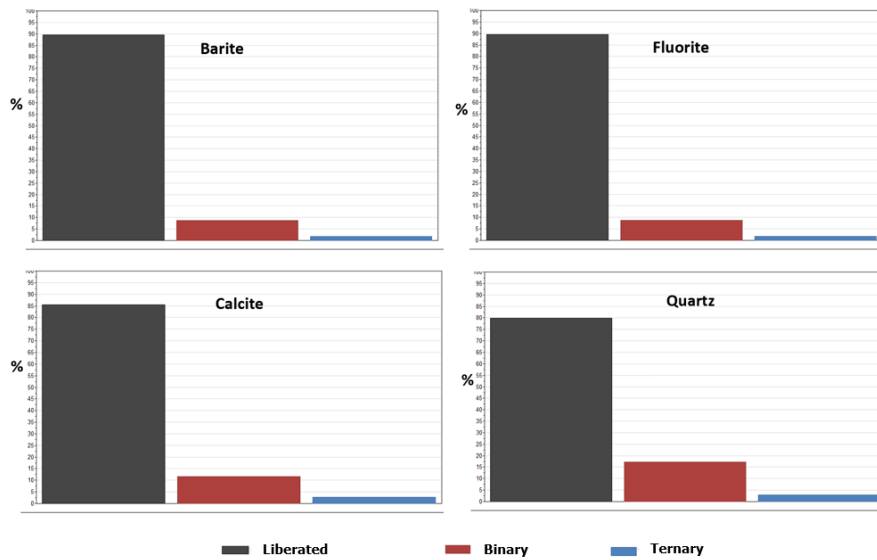


Figure 20. Degree of mineral liberation of abundant minerals in the tailings

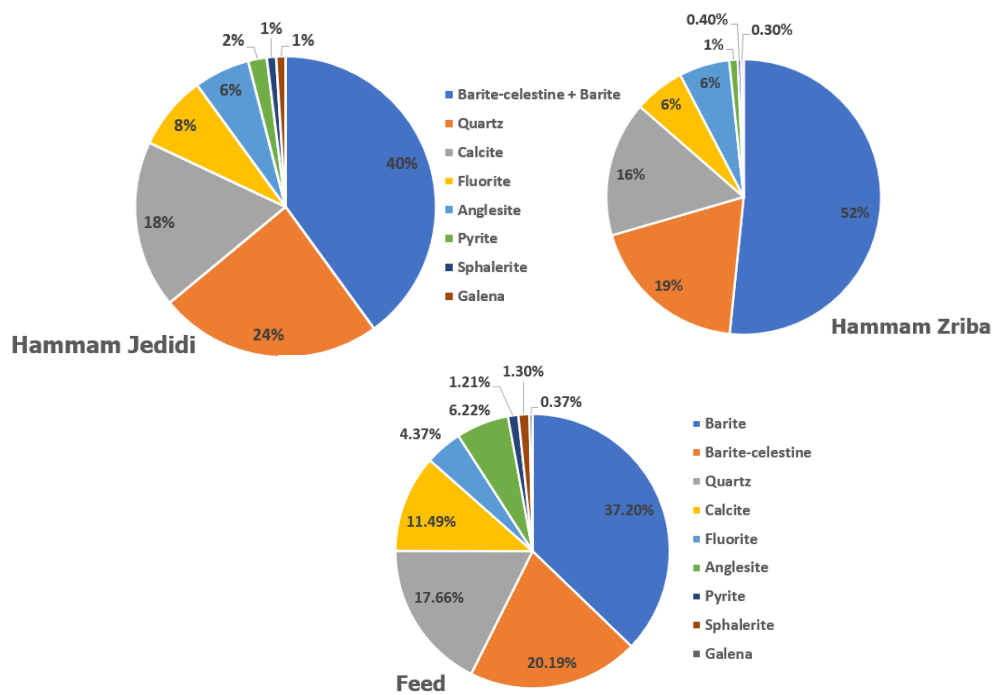


Figure 21. XRD analysis of Hammam Jedidi tailings, Hammam Zriba tailings and feed

3.2.2 Reagent Preparation

For barite flotation, sodium dodecyl sulfate, sodium silicate, citric acid, and barium chloride were prepared and used. For fluorite flotation, sodium oleate, colloidal silica (Levasil WT110P[®]), sodium silicate, corn starch, sodium fluoride (NaF), and MIBC were used. In all cases, sodium carbonate (NaCO₃) and sulphuric acid (H₂SO₄) were used to modify pH of the pulp. **Table 5** is a summary of the reagents used.

Table 5. Summary of flotation reagents

Reagent	Concentration	Purpose
Sodium dodecyl sulfate (SDS)	10 %	Barite collector
Sodium silicate (SS)	10 %	Calcite/silica depressant
Citric acid (CA)	10 %	Fluorite depressant
Barium chloride (BaCl ₂)	10 %	Barite activator
Sodium oleate (NaOl)	5 %	Fluorite collector
Levasil WT110P [®]	10 %	Calcite depressant
Corn starch	10 %	Barite depressant
Sodium fluoride (NaF)	10 %	Fluorite activator
MIBC	10 %	Frother
NaCO ₃ and H ₂ SO ₄	1 M	pH modifier

3.2.3 Experimental procedure

The flotation tests were performed by first floating barite while depressing ca-minerals and quartz, followed by fluorite flotation while depressing barite and associated gangue minerals as illustrated in **Figure 22**.

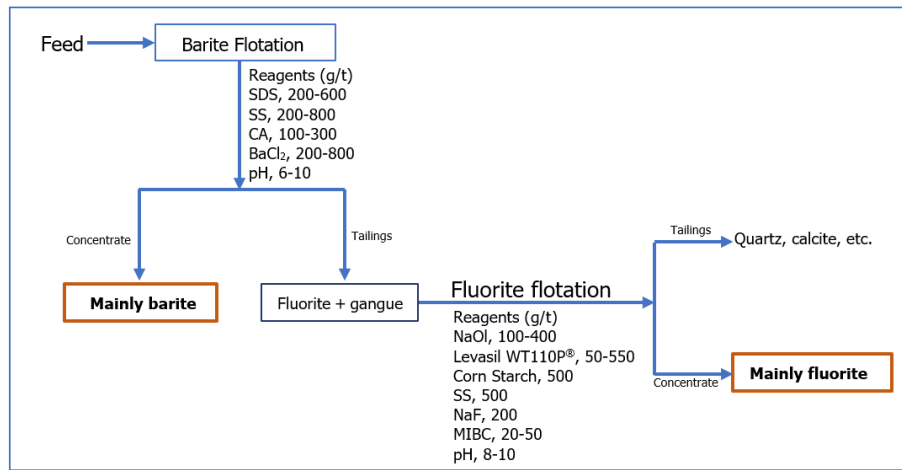


Figure 22. Flowsheet illustrating barite/fluorite flotation scheme

3.2.3.1 Barite flotation

With the help of R-Shiny platform developed at HIF (Ben Said et al., 2022) a fractional factorial experimental design with resolution V and 3 center points was generated by varying the factors; pH, collector, sodium silicate, citric acid, and activator dosages, making a total of 19 experimental points as shown in **Appendix A**. 500 g of each sample was added to 300 ml of water and milled using lab roller ball mill for 3 minutes at a speed of 16 rpm to re-activate the minerals surfaces for enhanced reagent performance.

Froth flotation tests were carried out in a 1.5-liter Magotteaux® bottom-driven flotation cell connected to a Raspberry Pi touch screen system which is equipped with pH probe. The weight of the empty flotation cell, empty trays (for collecting concentrates), wash water, and fill water were measured. The cell was first filled with the pulp and water added until the mark corresponding to 33 % solids is reached. The cell and its content were then measured and placed on the floatation machine and the impeller speed adjusted to 550 rpm. The right amount of activator was added and conditioned for 5 minutes followed by 5 minutes of pH conditioning. Fluorite depressant was then added followed by quartz/calcite depressant and finally the collector, with 3-minute conditioning each. Air flowrate was set to 5 L/min, and the flotation lasted 10 minutes. The simplified flowchart of the flotation scheme is shown in **Figure 23**.

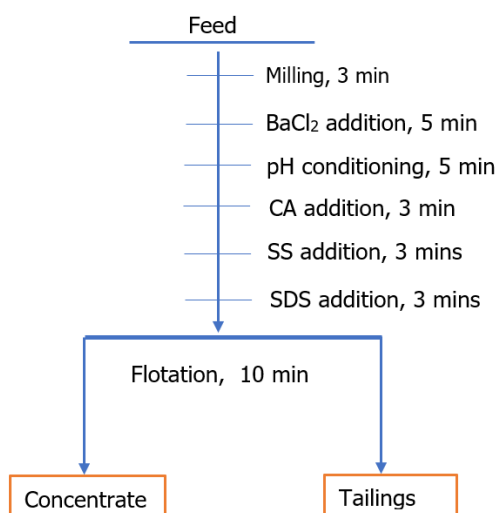


Figure 23. Simplified flowchart of the barite batch flotation

In each case, 4 concentrates with a 5-s scrapping rate were taken at time 1, 2, 3 and 4 minutes. The weights of trays and their contents were measured in each case as well as wash water and fill water after each test. The flotation products (concentrates and tailings) were filtered and dried overnight in an oven at 50 °C – 60 °C. The weights of the dried samples were measured from which the mass pull and water pull were calculated. Each test was performed three times, and the averages calculated. Samples from each dried weight were also prepared for assay.

3.2.3.2 Fluorite Flotation

About 5.4 kg tailings material obtained from the barite flotation experiments were thoroughly mixed and splatted with a rotary rifle splitter to obtain homogeneous samples which were further splatted into 500 g samples. A fractional factorial experimental design with resolution IV and 1 center point repeated 3 times was generated from the R-Shiny platform by varying the factors; pH, collector, colloidal silica, and frother dosages, making a total of 11 experiments (see **Appendix B**). The dosages of NaF, corn starch, and SS were maintained throughout the experiment as 200 g/t, 500 g/t and 500 g/t, respectively.

The flotation tests were conducted in the same cell as the barite tests. After filling the cell with pulp and placing it on the flotation machine, NaF was added and conditioned for 5 minutes followed by 5 minutes of pH conditioning. Corn starch was then added followed by SS and the right amounts of CS, collector and finally frother, with 3-minute conditioning each. Air flowrate was set to 5 L/min, and the flotation lasted 6 minutes. 3 concentrates with a 5-s scrapping rate

were taken at time 1, 2, and 3 minutes. Due to material constraint, each test was performed once. The flotation products were filtered and dried overnight in an oven at 50 °C – 60 °C and samples sent for X-Ray Diffraction (XRD) analysis. **Figure 24** shows the flowchart of the flotation scheme.

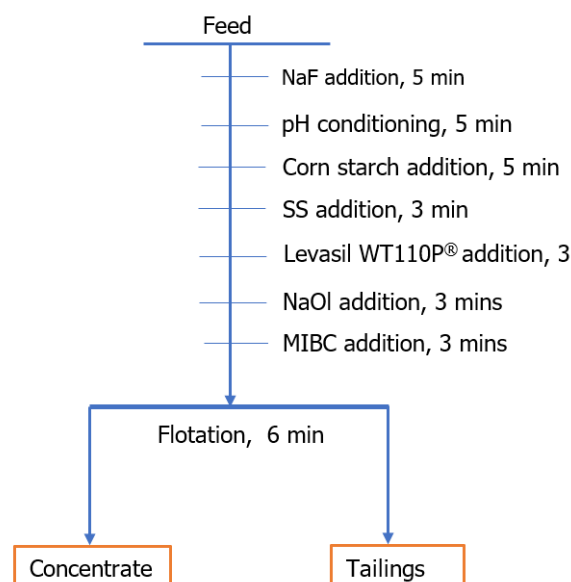


Figure 24. Simplified flowchart of the fluorite batch flotation

3.3 Sample Characterisation

The elemental composition of the barite flotation products was determined using X-ray fluorescence analysis (XRF). This principle works by emitting X-ray radiation which stimulates electrons near the core, creating a void that is filled by more energetic electrons. This electron movement from the outer to inner shell generates energy in the form of fluorescence radiation, which a detector detects. Every element is represented by a distinct fluorescence radiation (Thompson, 2009).

About 5 g samples from each of the dried flotation product were stored in containers and covered with plastic foil roll for analysis. The Bruker S1 Titan analyser was used, and Geochem trace was the method selected for analysis. The samples were placed on the stage, the lid closed, and the trigger pulled to begin analysis which lasted 60 seconds. Each sample was measured three times. After every measurement, the samples were shaken to allow the particles at the different locations of the container to be measured. The results obtained and the XRD data were

used to derive a calibration function from which the respective grades and recoveries were calculated. The setup of the XRF analysis is shown in **Figure 25**.

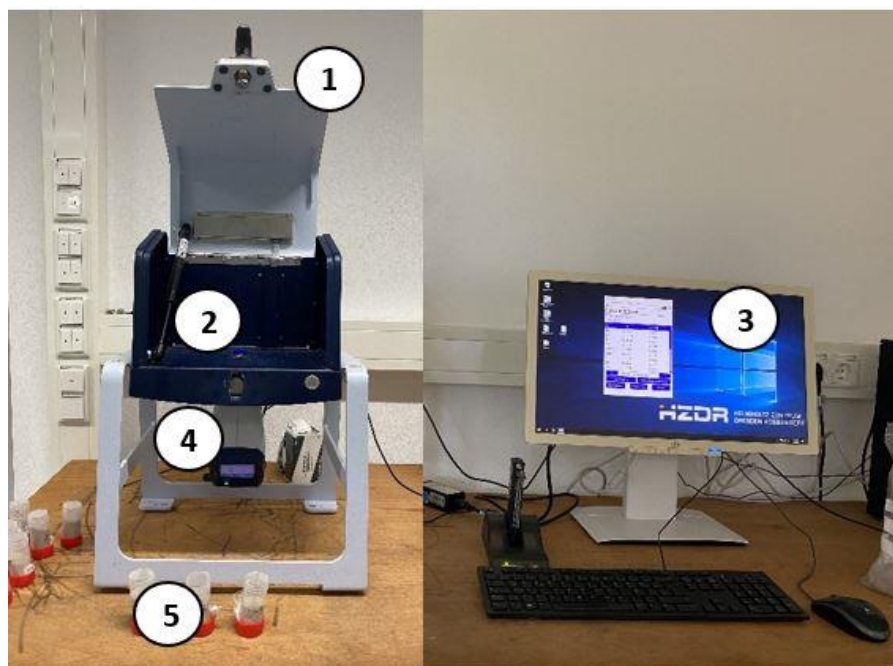


Figure 25. Portable XRF setup showing 1) Lid, 2) stage, 3) display monitor, 4) analyser, 5) samples

4. Results

4.1 Microflotation of Barite, calcite, fluorite

Single mineral microflotation tests of barite, calcite and fluorite were conducted and the effect of pH and collector concentration on the flotation behaviour of barite with and without an activator (BaCl_2) were investigated and the results presented below.

4.1.1 Effect of BaCl_2 on barite flotation

Figure 26 shows the effect of BaCl_2 on the flotation behaviour of barite using SDS as collector at variable pH.

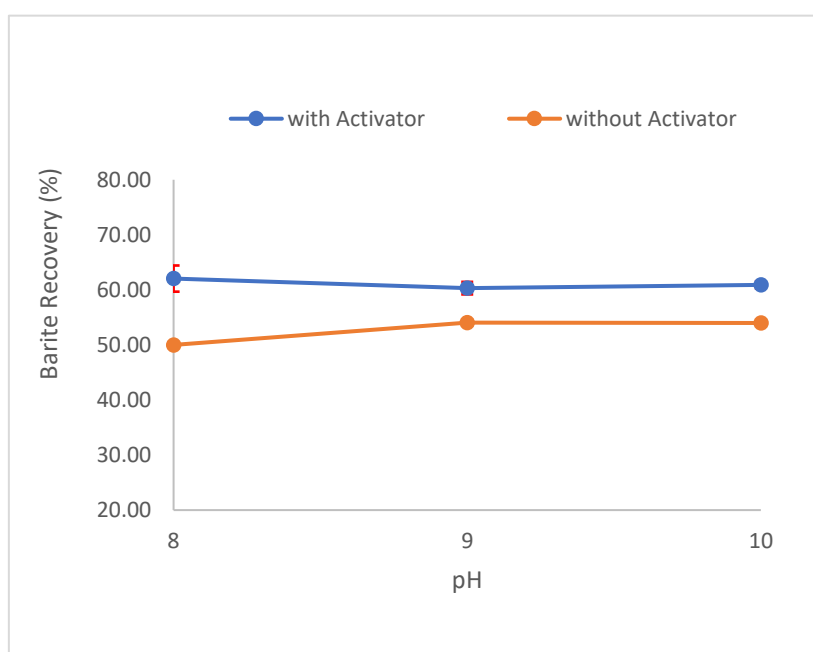


Figure 26. Effect of BaCl_2 on barite recovery at SDS conc. of 1×10^{-4} mol/L at varied pH (Error bars represent the standard deviation of the 3 trials)

In the presence of SDS alone, barite recoveries around 50% were achieved in the entire studied pH range. These recoveries however, increased with the addition of BaCl_2 . At pH 8, the recovery of barite increased considerable from 50 % when SDS alone was used, to 62.05 % in the presence of BaCl_2 . At pH 9 and 10, however, the recovery of barite increased slightly from

around 54 % to about 60 % in the presence of BaCl_2 . The highest barite recovery achieved with and without BaCl_2 were 54 % and 60.9 %, respectively at a pH of 10.

4.1.2 Effect of pH and collector concentration on barite flotation

The effect of pH value and collector concentration on the floatability of barite is illustrated in **Figure 27**.

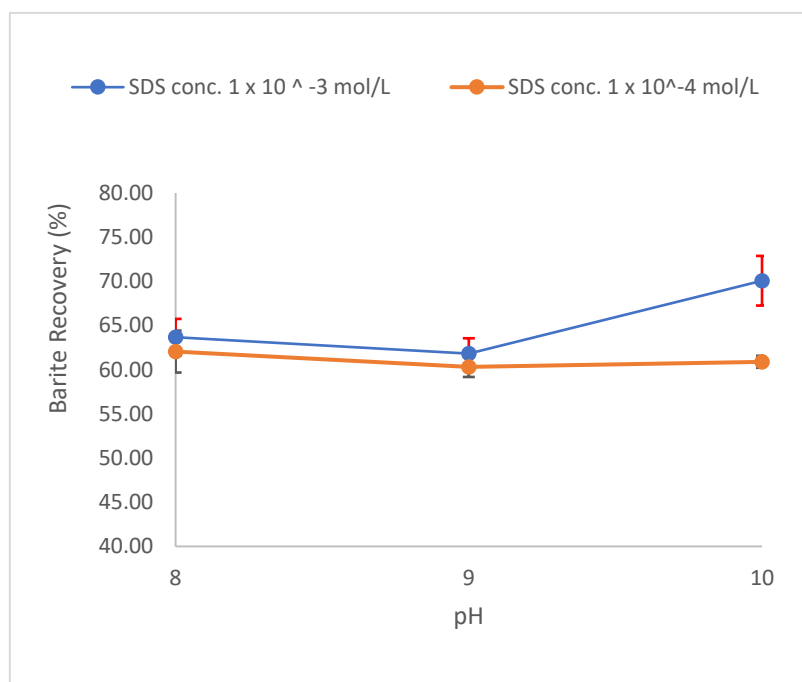


Figure 27. Effect of pH and SDS concentration on barite flotation with BaCl_2 (Error bars represent the standard deviation of the 3 trials)

The result shows that an increase in collector concentration increases the recovery of barite. At a collector concentration of 1×10^{-4} mol/L, the effect of pH on the floatability of barite was not visible as barite recovery slightly increased by about 2 % when the pH was increased from 8-10. Barite recovery however, increased by 10 % at a collector concentration of 1×10^{-3} mol/L when the pH was increased from 8-10. At pH 8 and 9, no appreciable increase in barite recovery was achieved when SDS concentration was increased from 1×10^{-4} mol/L to 1×10^{-3} mol/L, however, there was a 15 % increase in recovery at pH 10 (from 60.9 % to 70.1 %). Therefore, the best operating conditions for the barite flotation were deemed to be pH 10 and collector dosage of 1×10^{-3} mol/L.

4.1.3 Effect of citric acid on barite and fluorite flotation

The depressive effect of CA on the flotation of barite and fluorite was investigated and the result presented in **Figure 28**.

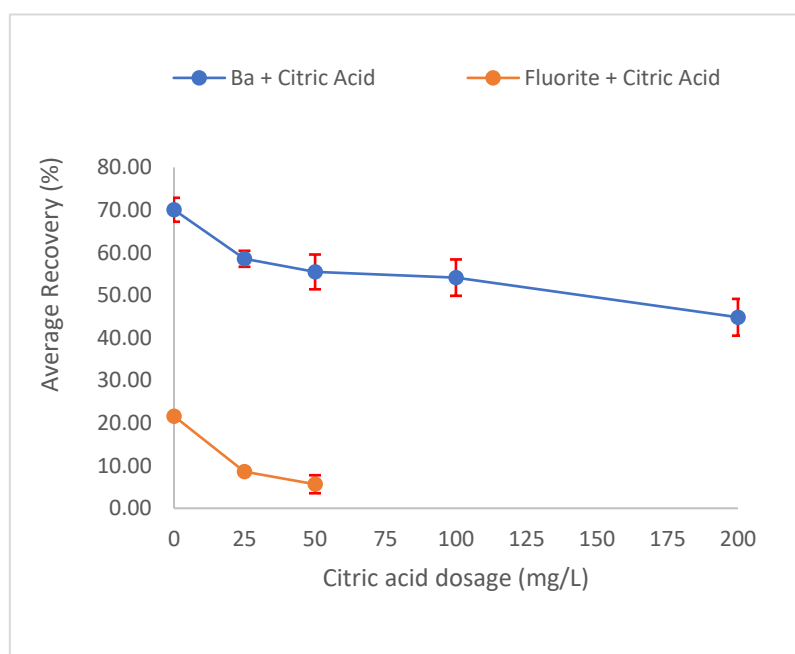


Figure 28. Effect of citric acid on barite & fluorite @ SDS conc. of 1×10^{-3} mol/L, pH 10.0 (Error bars represent the standard deviation of the 3 trials)

As can be seen, an increase in the citric acid dosage affected the recoveries of both barite and fluorite when the pH of the pulp was fixed at 10. However, the recovery of fluorite decreased more rapidly than barite indicating that CA had a stronger depressive effect on fluorite than on barite. Fluorite and barite recoveries decreased by about 74 % and 20 %, respectively at CA dosage of 50 mg/L. With a further increase in CA dosage, the recovery of barite reduced slightly.

4.1.4 Effect of sodium silicate on barite and calcite flotation

The flotation recoveries of barite and calcite with sodium silicate is illustrated in **Figure 29**.

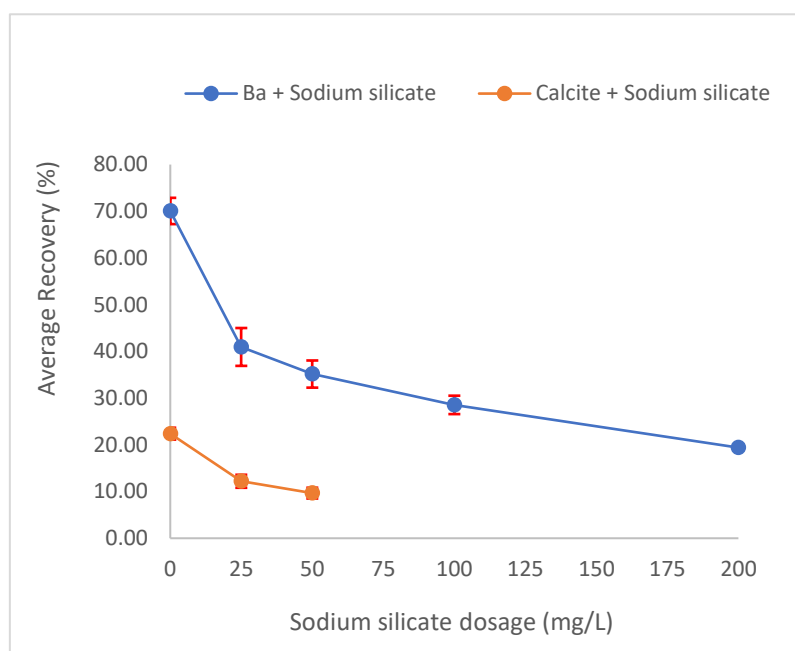


Figure 29. Effect of sodium silicate on barite & calcite @ SDS conc. of 1×10^{-3} mol/L, pH 10.0 (Error bars represent the standard deviation of the 3 trials)

When using SDS as a collector, the floatability of barite and calcite are significantly affected by an increase in SS dosage. The recoveries of barite and fluorite decreased significantly by about 49 % and 57 %, respectively, as the concentration of SS increased to 50 mg/L. A further increase in SS dosage continued to decrease barite recovery considerably.

4.1.5 Effect of colloidal silica on calcite

The depressive effect of the eight colloidal silica solutions on calcite were investigated at different dosages. Based on the information from a previous study obtained from the database of HIF, the best pH for calcite microflotation was found to be 8 using NaOH at a concentration of 1×10^{-3} mol/L. These parameters were, thus, maintained throughout the experiments and the results are summarized below. The different colloidal silica solutions were compared based on their structure as well as modification.

4.1.6 Evaluation based on structure

4.1.6.1 Sodium stabilized depressants

The effect of specific surface area on the depressive effect of sodium stabilized colloidal silica on calcite is presented in **Figure 30**.

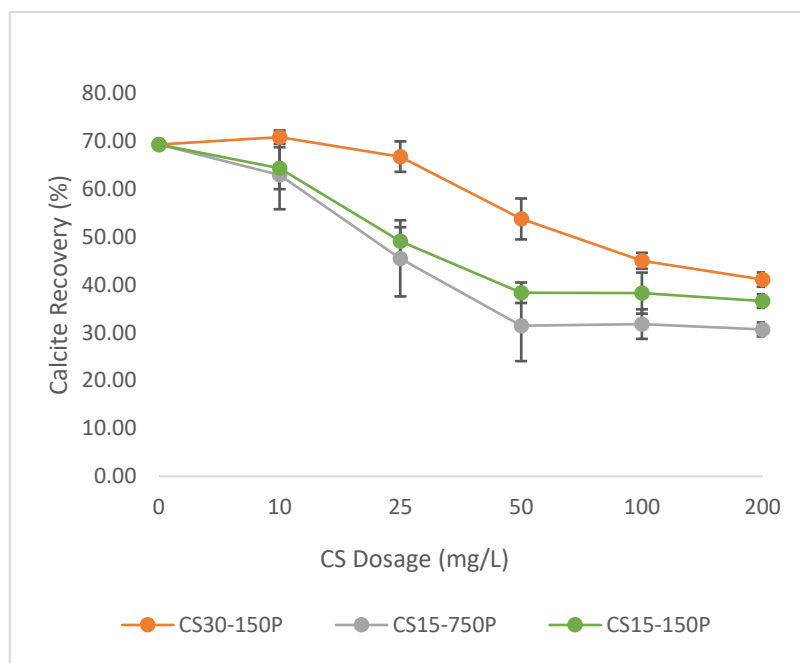


Figure 30. Comparison of effect of specific surface area on sodium stabilized depressants on calcite recovery @ NaOI conc. of 1×10^{-3} mol/L, pH 8.0 (Error bars represent the standard deviation of the 3 trials)

The recovery of calcite decreased with increasing dosage of depressant in all tested conditions. Increasing the specific surface area of the depressant resulted in an increased depressive effect on calcite. Levasil CS15-750P[®] (with specific surface area 750 m²/g) and Levasil CS15-150P[®] (with specific surface area 500 m²/g) had the strongest depressive effect on calcite at a dosage of 50 mg/L beyond which no visible change in calcite recovery was achieved. Overall, Levasil CS15-750P[®] had the strongest depressive effect on calcite, reducing the recovery by more than 50 % (from 69.3 % to 31.5 %) at a dosage of 50 mg/L, followed by Levasil CS15-150P[®] which depressed calcite by 45 % at the same dosage. Levasil CS30-150P[®] (with specific surface area 250 m²/g) had the least depressive effect on calcite, reducing calcite recovery by up to 40 % at a dosage of 200 mg/L.

4.1.6.2 Silane stabilized depressants

The effect of specific surface area on the depressive effect of silane stabilized colloidal silica solution on calcite is presented in **Figure 31**.

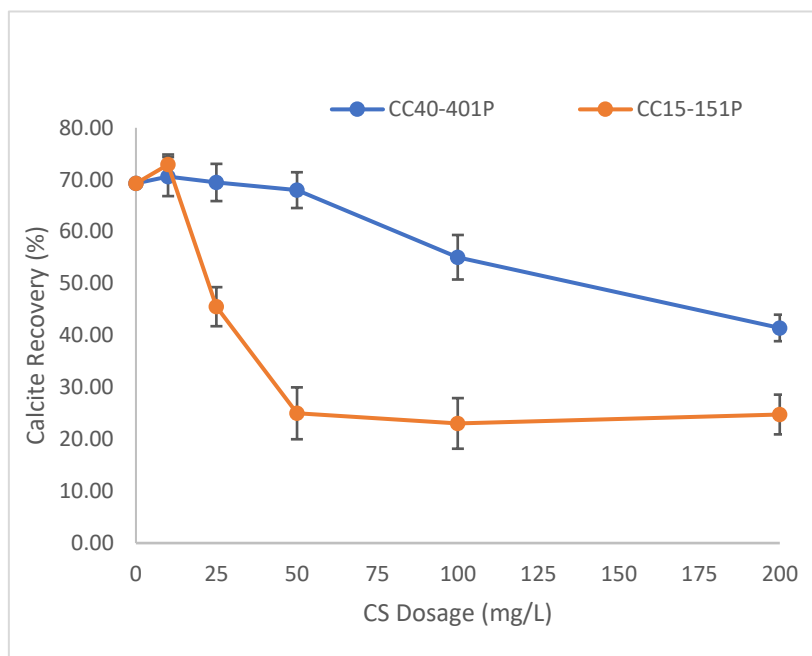


Figure 31. Comparison of effect of specific surface area on silane stabilized depressants on calcite recovery @ NaOH conc. of 1×10^{-3} mol/L, pH 8.0 (Error bars represent the standard deviation of the 3 trials)

The depressive effect of Levasil CC15-151P® (with specific surface area 500 m²/g) on calcite was the strongest. At a depressant dosage of 50 mg/L, about 64 % % of calcite was depressed, and a further increase in dosage had no visible effect on calcite. The recovery of calcite, however, remained almost the same when the dosage of Levasil CC40-401P® (with specific surface area 220 m²/g) was increased up to 50 mg/L. When the dosage was further increased to 200 mg/L, calcite recovery dropped drastically from 68.0 % to 41.5 %.

4.1.6.3 Aluminate stabilized depressants

Figure 32 shows the effect of specific surface area on the depressive effect of aluminate stabilized colloidal silica solution on calcite.

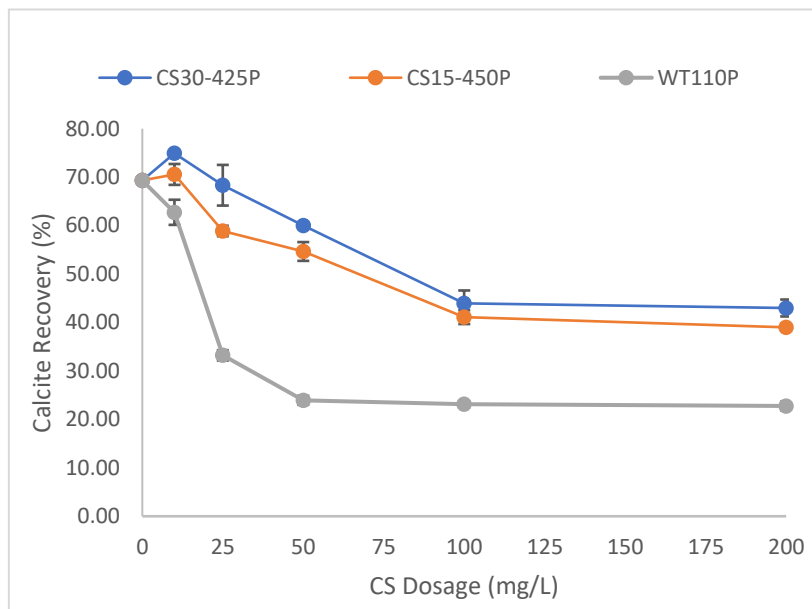


Figure 32. Comparison of effect of specific surface area on aluminate stabilized depressants on calcite recovery @ NaOI conc. of 1×10^{-3} mol/L, pH 8.0 (Error bars represent the standard deviation of the 3 trials)

Both Levasil CS30-425P[®] (with specific surface area 250 m²/g) and Levasil CS15-450P[®] (with specific surface area 500 m²/g) had a low depressive effect on calcite. In both cases, the recovery of calcite increased slightly from 69.3 % to about 70.6 % at a depressant dosage of 10 mg/L. At a dosage of 100 mg/L, there was a rapid decrease in calcite recovery from 70.6 % to 43.9 % and 41.1 % for Levasil CS30-425P[®] and CS15-450P[®], respectively. Increasing the dosages beyond 100 mg/L, however, had no significant effect on calcite recovery for both depressant. Levasil WT110P[®] (with specific surface area 1100 m²/g) on the other hand had a strong depressive effect on calcite. At a dosage of 25 mg/L, the recovery of calcite decreased sharply by more than 50 % (from 69.3 % to 33.2 %). An increase in dosage to 50 mg/L further reduced calcite from 33.2 % - 23.9 % after which no visible change in calcite recovery was observed with increase in depressant dosage.

4.1.7 Evaluation based on modification

To ascertain which of the CS modifications had the strongest depressive effect on calcite, the specific surface area of all 3 modified solutions were kept constant ($500 \text{ m}^2/\text{g}$). The result is presented in **Figure 33**.

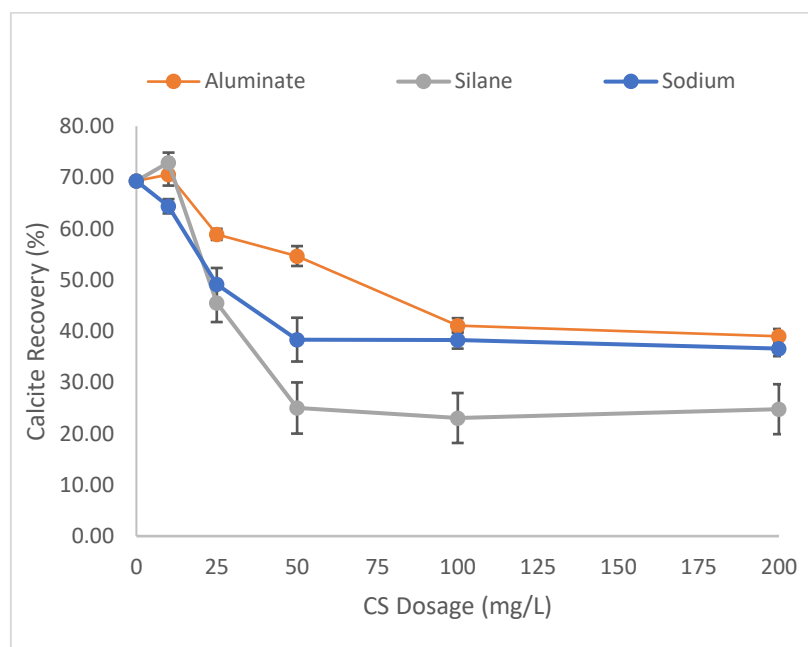


Figure 33. Comparison of different colloidal silica modifications with specific surface area of $500 \text{ m}^2/\text{g}$ on calcite recovery @ NaOH conc. of $1 \times 10^{-3} \text{ mol/L}$, pH 8.0 (Error bars represent the standard deviation of the 3 trials)

At a depressant dosage of 50 mg/L, the silane modified solution showed the strongest depressive effect on calcite by reducing calcite recovery by 64 %. This was followed by the sodium modified solution which reduced calcite recovery by 45 %. The aluminate modified solution had the least effect on calcite, reducing recovery by 21 % at the same dosage. When the depressant dosages were further increased from 50-200 mg/L, the calcite recovery remained the same in the case of silane and sodium modifications. For the aluminate modification, an increase in dosage to 100 mg/L significantly reduced calcite recovery by 25 % after which no visible reduction in recovery was achieved when the dosage was further increased.

4.1.8 Effect of Levasil WT110P® on calcite and fluorite

To use Levasil WT110P® as a calcite depressant in the fluorite batch flotation, its depressive effect on fluorite was investigated and the result is presented in **Figure 34**.

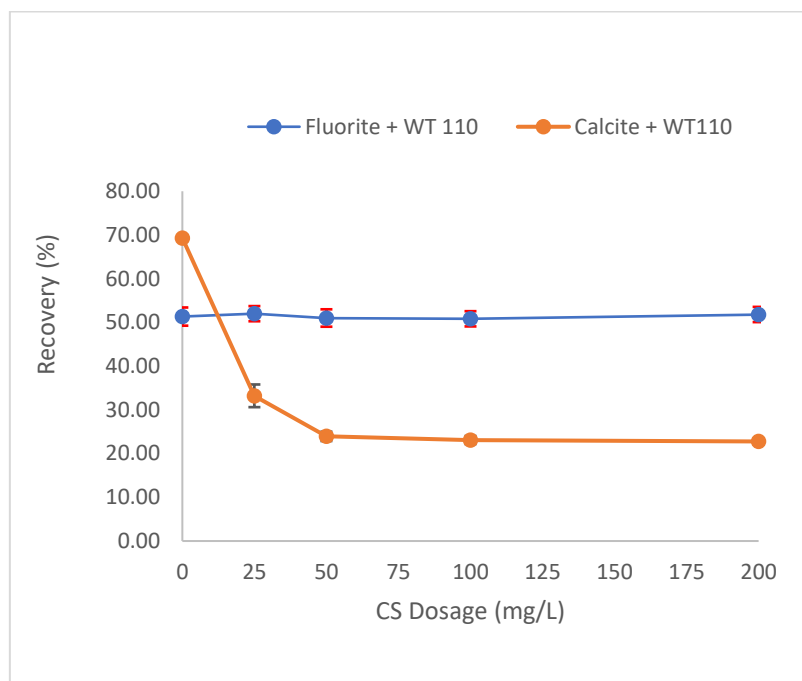


Figure 34. Effect of Levasil WT110P® on calcite and fluorite recovery @ NaOI conc. of 1×10^{-3} mol/L, pH 8.0
(Error bars represent the standard deviation of the 3 trials)

As can be seen from **Figure 34**, in the presence of Levasil WT110P®, the recovery of calcite had a dramatic drop (from 69.3 % to 24 %) at a dosage of 50 mg/L. On the other hand, no visible effect was observed on fluorite at the conditions tested. Fluorite maintained a good floatability with a recovery over 50 % as the depressant dosage was increased from 0-200 mg/L.

4.1.9 Summary of microflotation results

Based on the experiments conducted, the use of BaCl_2 as a barite activator has a positive effect on the recovery of barite, especially at pH 8. The floatability of barite is influenced positively by a change in pH from 8-10, as well as an increase in collector concentration. Citric acid has a depressive effect both on barite and fluorite, however, its effect is stronger on fluorite. Using SS as a calcite depressant also impacts the recovery of barite negatively, as both calcite and barite recoveries decrease significantly when the dosage of SS is increased.

All the colloidal silica tested had a depressive effect on calcite. An increase in the specific surface area of the colloidal silica resulted in an increase in the depressive effect. The aluminate modified depressant (Levasil WT110P[®]), which had the largest surface area (1100 m²/g) of all the depressants tested, showed the strongest depressive effect on calcite. In terms of modification, the silane modified depressant (Levasil CC15-151P[®] with specific surface area 500 m²/g) had the strongest effect on calcite followed by the sodium modified depressant (Levasil CS15-150P[®] with specific surface area 500 m²/g). The aluminate modified depressant (Levasil CS15-450P[®] with specific surface area 500 m²/g) had the weakest depressive effect on calcite. Overall, Levasil WT110P[®] was chosen as the strongest calcite depressant since its performance was slightly better than the silane modified depressant (Levasil CC15-151P[®]). Levasil WT110P[®], however, had no visible depressive effect on the floatability of fluorite.

4.2 Calibration curves

To estimate the amount of barite, ca-minerals, and quartz present in the barite flotation products, a calibration curve was constructed. This was achieved by plotting the values obtained in the XRF measurements against the values of XRD. The amount of barium, Ca and quartz obtained from the XRF measurement were plotted against the calculated amount of barium, ca-minerals, and quartz from the XRD data, respectively. The obtained values were normalized using natural logarithm. The XRD values were plotted on the ordinate and the XRF values on the abscissa as shown in **Figure 35**. Finally, a calibration function (**Table 6**) was obtained after calculating the gradient and slope in each case which were used to calculate the respective grades and recoveries.

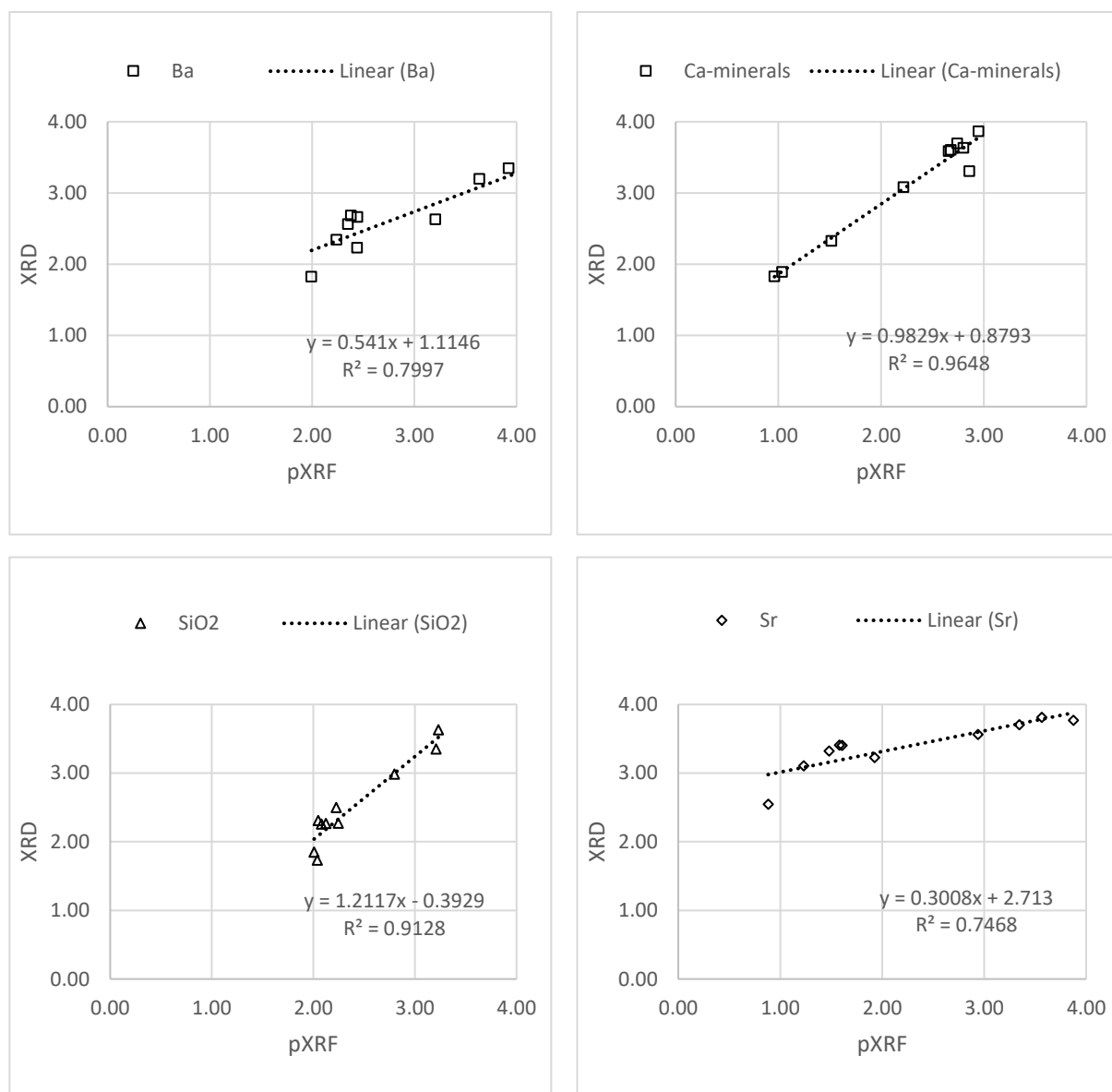


Figure 35. Calibration curves for the important minerals present in the flotation products

Table 6. Calibration function with slope and intercept of various minerals

Calibration function		
Mineral	Slope	Intercept
Ba	0.5410386	1.1145853
Ca-minerals	0.9828513	0.8792743
SiO ₂	1.2116713	-0.3928785
Sr	0.3008422	2.7130349
$\ln(Y\text{-value}) = \text{Slope} \times \ln(X\text{-value}) + \text{Intercept}$		

4.3 Batch flotation results

This section is divided into 2 sections. Sections 1 and 2 contain the evaluation of the experimental designs for barite and fluorite batch flotation, respectively.

4.3.1 Section 1

The fractional factorial experimental design with resolution V and 3 center points was used to evaluate the effect and level of significance of the factors defined in section 3.2.3.1 on the target variables; barite recovery, barite grade, and ca-minerals recovery, which were the main investigations of this experiment. For each target variable, the results are presented in the order of the main diagrams, the Pareto diagrams and finally the interaction diagrams. Due to the extensive data of the statistical experimental design, a summary of the results of the main investigation are presented in this section. The evaluation is carried out with a confidence interval of 99 %.

4.3.2 Main effect diagrams

The following main effect plots of the individual target variables are used to evaluate the level of effects of the factors, i.e., from low to high levels. The values of the target variable are plotted on the ordinate and the value of the factors are on the abscissa in each case. The main effect plots for barite recovery (**Figure 36**), barite grade (**Figure 37**) and ca-minerals recovery (**Figure 38**) are presented below.

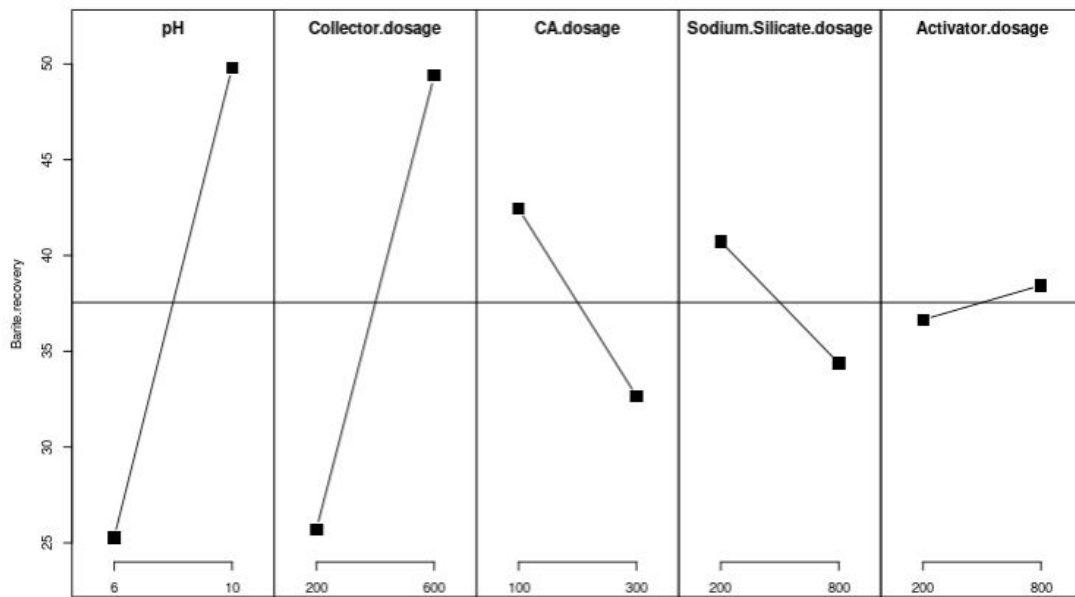


Figure 36. Main effect plots for barite recovery

The barite recovery is mainly influenced by the pH of the pulp and the collector dosage. An increase in pH from 6-10 significantly increases barite recovery from around 25% to > 50%. Also increasing collector dosage from 200-600 g/t results in a considerable increase in barite recovery. Conversely, an increase in CA dosage as well as SS dosage led to a negative effect on barite recovery. An increase in activator dosage has a weak but positive influence on barite recovery.

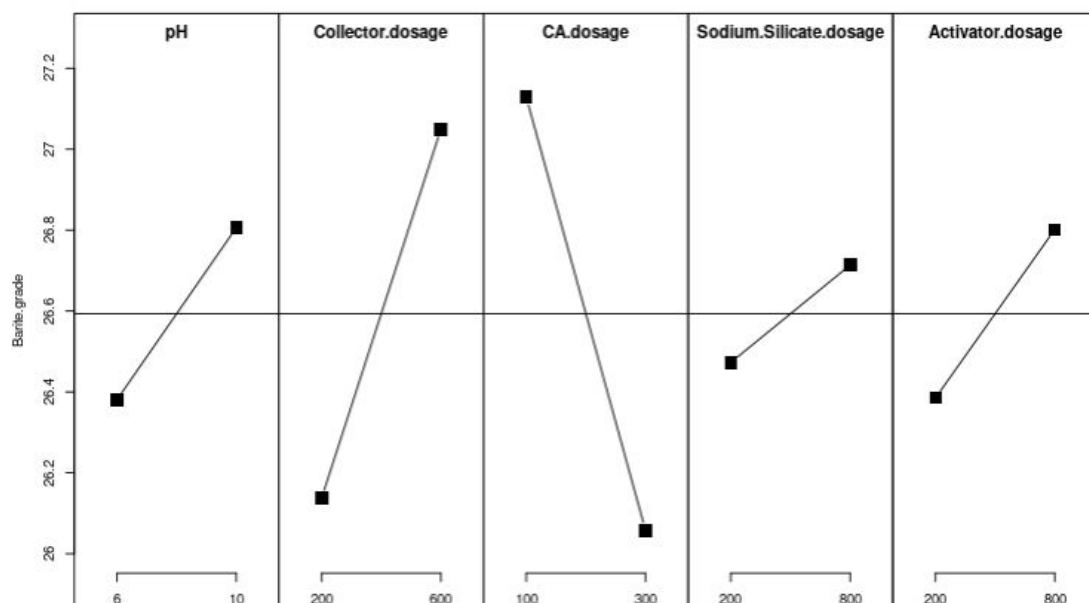


Figure 37. Main effect plots for barite grade

The CA dosage had the most significant influence on the barite grade. An increase in CA dosage from 100-300 g/t reduced barite grade from about 27 % to about 25 %. The collector dosage showed a significantly positive influence on barite grade, with pH of the pulp, SS dosage as well activator dosage having a positive but insignificant influence on barite grade.

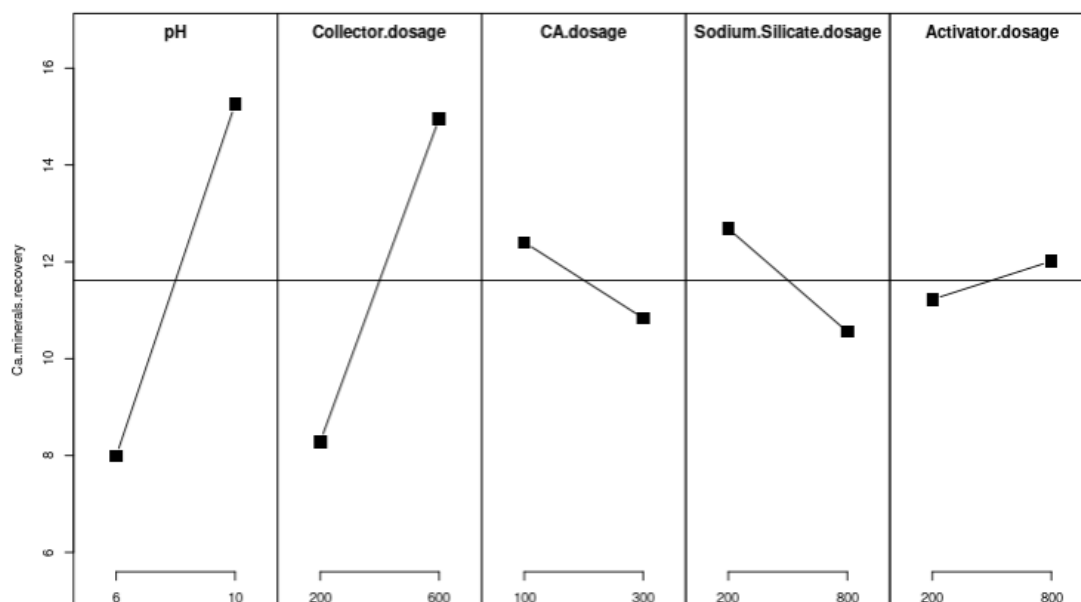


Figure 38. Main effect plot for ca-minerals recovery

The influence of the factors on ca-minerals (calcite and fluorite) recovery was like that of the barite recovery. Both pH and collector concentration had the strongest positive influence on ca-minerals recovery. An increase in both pH and collector concentration lead to > 40% increase in the recovery of ca-minerals. An increase in SS dosage had a significantly negative influence on ca-minerals recovery. Increasing both activator and CA dosages had an insignificant positive and negative influence on ca-minerals recovery, respectively.

4.3.3 Pareto charts

The Pareto chart arranges effects in descending order of magnitude in bars and can be used to make sense of effects and two-way interactions between the factors. The bars are represented by two shades of colours. A grey bar represents a negative effect on the target variable, whereas a black bar represents a positive effect. The outcomes were calculated by the DoE platform using tests of significance with a confidence level of 99 %. The significance confirms how relevant the effect and the interaction are.

The Pareto plots for barite recovery (**Figure 39**), barite grade (**Figure 40**), and ca-minerals recovery (**Figure 41**) are shown below. The factors and interactions are plotted on the ordinate, and the effect of the factors are on the abscissa. Here, the two-way interactions between the factors were considered because for resolution V designs, there is no confusion of one main effect or two-factor interaction with another, though two-factor interactions are confused with three-factor interactions.

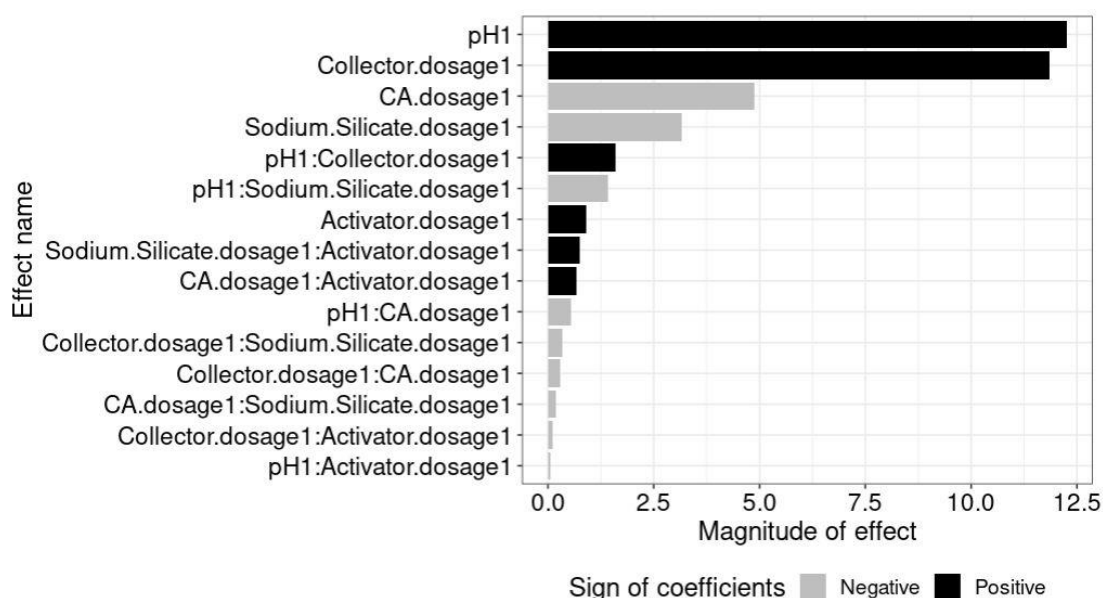


Figure 39. Pareto chart for barite recovery

The factors with the most significant influence on barite recovery are pH, collector dosage, CA dosage and SS dosage. The interaction between pH and collector dosage shows a significantly positive influence on barite recovery. On the other hand, the interaction between pH and SS dosage significantly affects barite recovery negatively.

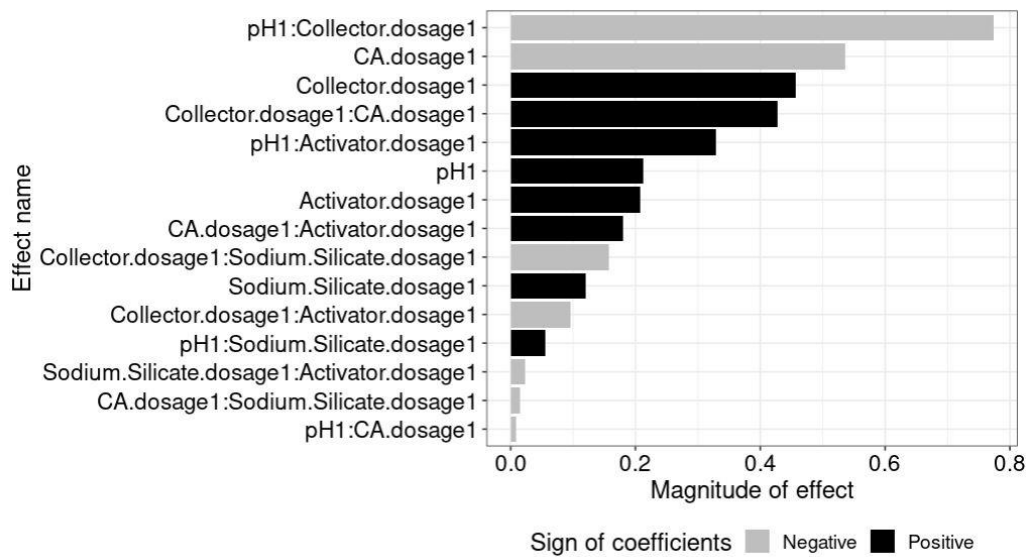


Figure 40. Pareto chart for barite grade

Barite grade is significantly influenced by collector and CA dosages. The interaction between pH and collector dosage showed the strongest impact, affecting barite grade negatively. In contrast, the interaction between collector and CA dosages had a significant and positive effect on barite grade.

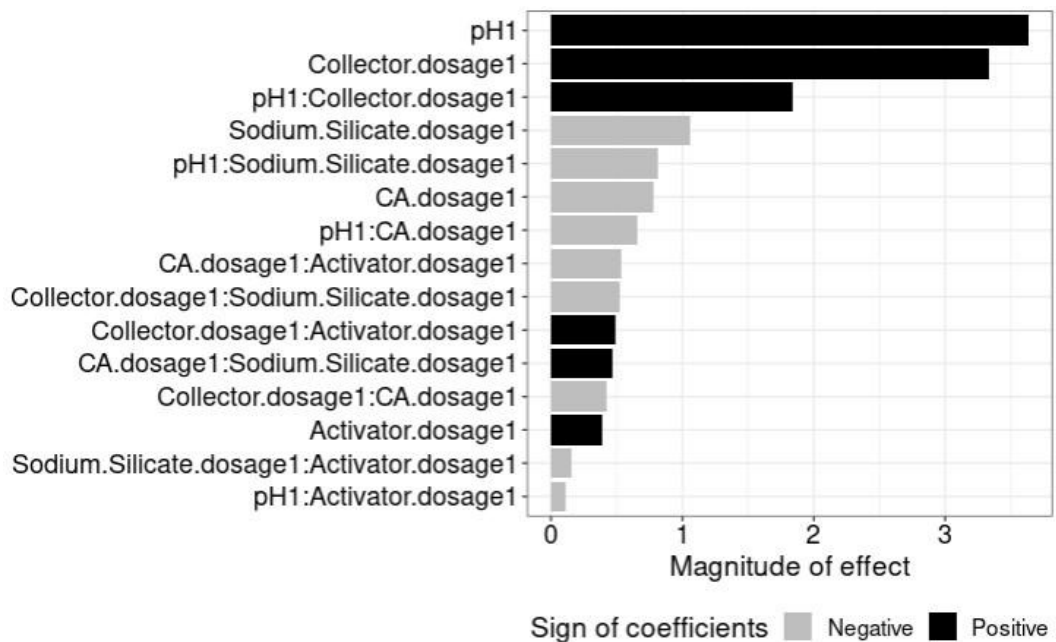


Figure 41. Pareto chart for ca-minerals recovery

The recovery of ca-minerals is significantly influenced by pH, collector, and SS dosages. The interaction between pH and collector dosage showed the strongest impact, with a positive influence on ca-minerals recovery. However, the interaction between pH and SS dosage had a significantly negative effect on ca-minerals recovery.

4.3.4 Interaction diagrams

The interaction diagrams are equivalent to main effect diagrams and are used to investigate the interactions between the factors. The values of the target variable are represented on the ordinate, and the levels of the factors are plotted on the abscissa. Only the interactions with significant influence on the target variables are considered. The interaction diagram for barite recovery (Figure 42), barite grade (Figure 43), and ca-minerals recovery (Figure 44) are presented below.

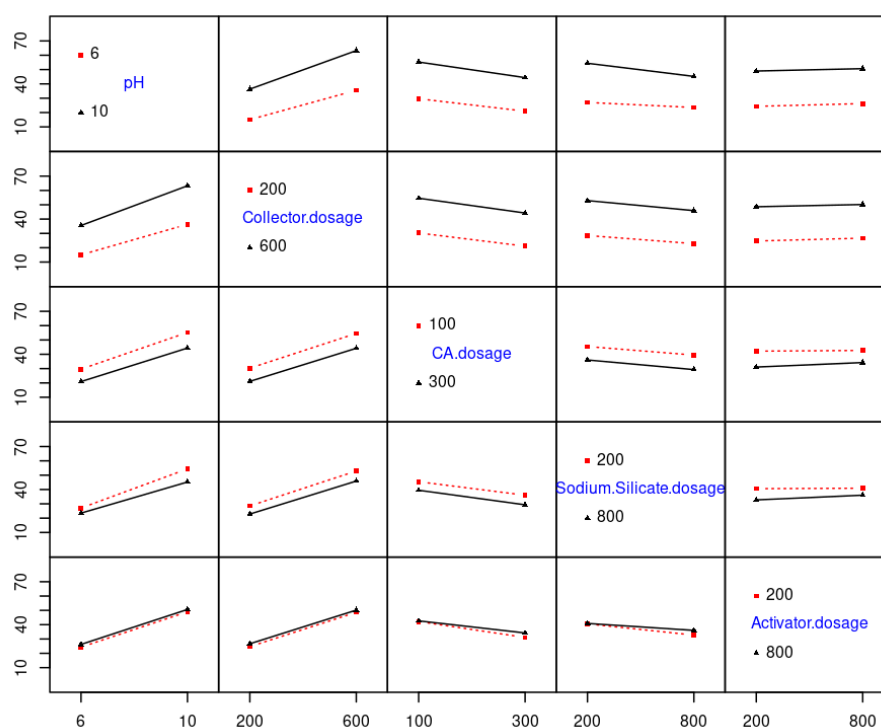


Figure 42. Interaction plot for barite recovery

The interactions between pH and collector dosage as well as between pH and SS dosage have the most significant influence on barite recovery. Both interactions are ordinal, hence, their effects can be interpreted globally. At both high and low pH values, an increase in collector

dosage has a significantly positive effect on the recovery of barite. Also, regardless the SS dosage, an increase in pH value has a significantly positive effect on barite recovery.

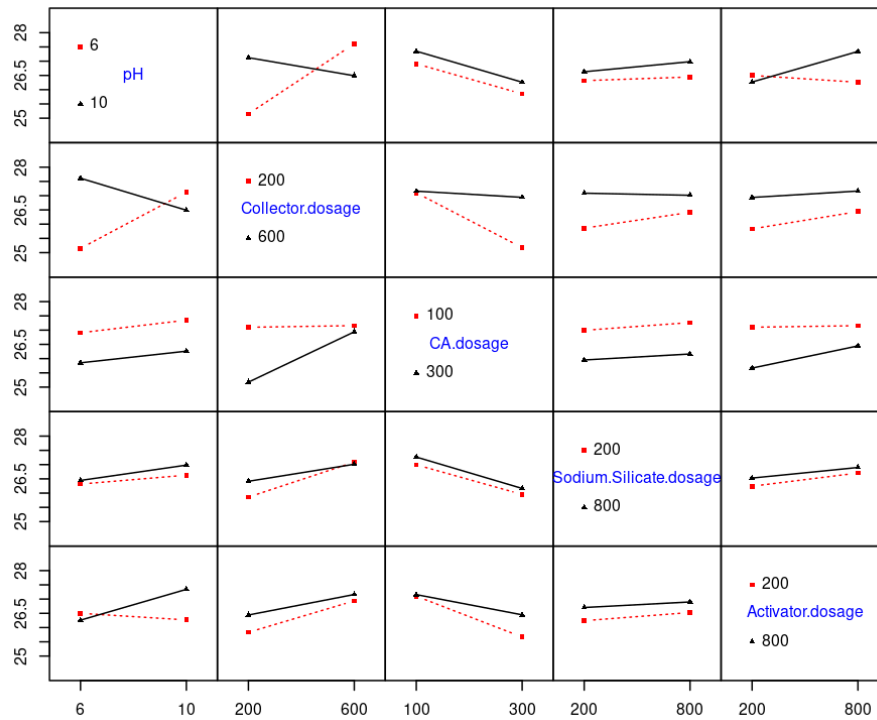


Figure 43. Interaction plot for barite grade

The main interactions with significant influence on barite grade are that of pH and collector dosage, and collector and CA dosages. The interaction between pH and collector dosage is disordinal, while that of collector and CA dosage is ordinal. At high pH values, an increase in collector dosage negatively affects barite grade. However, at low pH values, an increase in collector dosage influences barite grade positively. At a high collector dosage, increasing the CA dosage has no appreciable influence on the barite grade. However, at low collector dosage, an increase in CA dosage negatively affects barite grade.

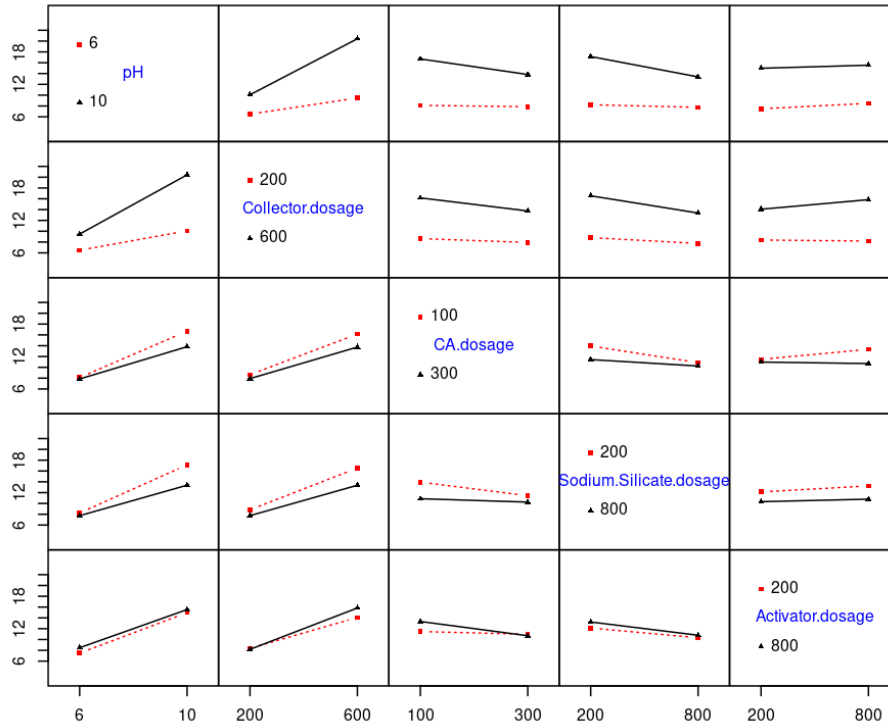


Figure 44. Interaction plot for ca-minerals recovery

The main interactions with significant influence on ca-minerals recovery are that of pH and collector dosage, and pH and SS dosage, both of which are ordinal, hence, can be interpreted globally. At high pH values, increasing the collector dosage significantly increase the recovery of ca-minerals. At low pH, however, an increase in collector dosage results in a slight increase in ca-minerals recovery. At a high pH value, an increase in SS dosage has a negative influence on ca-minerals recovery, however, an increase in SS dosage has no effect on ca-minerals recovery at low pH values.

4.3.5 Model Assumption

In order to conduct the fluorite flotation experiments, it was necessary to investigate the best operating conditions which yield high barite recovery and low ca-minerals recovery since the tailings would serve as the feed for the fluorite flotation. To achieve this, barite recovery and ca-mineral recovery were chosen as response variables and a model assumption was made for both. Here, only the steps involved in creating the model assumption for barite recovery has been outlined because the same steps were followed for the model of ca-mineral recovery.

First, a plot of the different residuals versus the chronological sequence of the experiments performed was made for the different model assumptions to see whether temporal or spatial

variables influence the results. Secondly, by plotting the residuals against the fitted values, the variance of the residuals was checked to ensure that they were equal. Thirdly, a Q-Q plot was utilized to determine whether the residuals were normally distributed. Finally, a plot of the surface of the supposed model and the measured points was created to test the linearity, allowing to determine how well the measured points fit the assumed model. **Figure 45** shows the various plots for the model assumption for barite recovery obtained from the R-Shiny platform. From the plot of the residuals, for all three models, the residuals seem to be randomly dispersed in the “residual vs order of observation” and “residuals vs fitted, hence, all models were applicable. The full second order model, however, was the most appropriate model assumption, according to a linearity check that displays the surface plot with the measured center points.

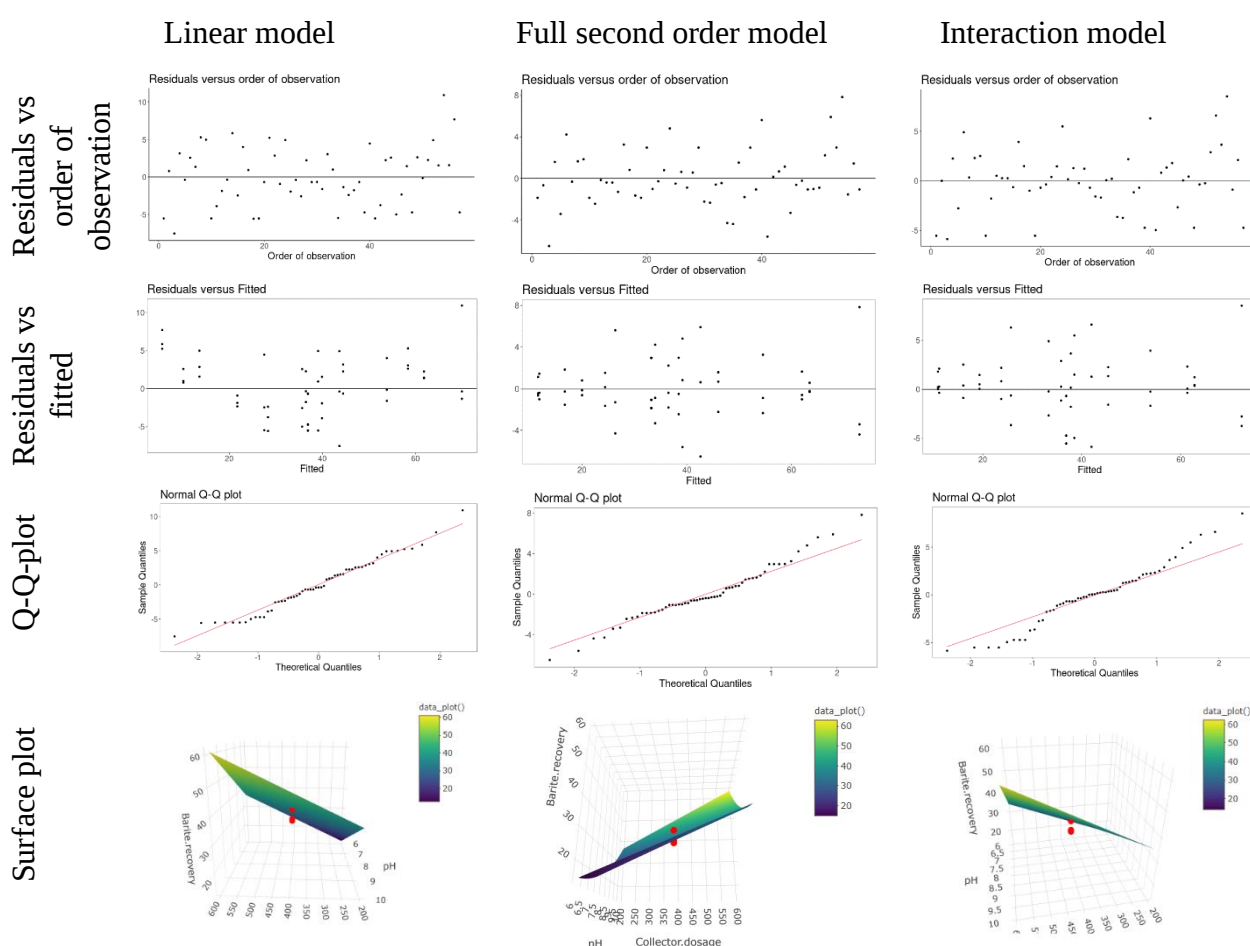


Figure 45. Residuals and surface plots for the model assumption for barite recovery

4.3.6 Optimizing

To optimize the two response variables; barite recovery and ca-minerals recovery, the “multi response optimization” option was used. This option allows to simultaneously optimize two response variables. The platform calculated the optimum barite recovery with low ca-minerals recovery by varying the factors, and the results are shown in **Table 7**.

Table 7. Parameter settings for achieving optimum barite recovery and low ca-minerals recovery

Calculated parameter settings	Optimum recovery
pH: 10 Collector dosage: 600 g/t CA dosage: 100 g/t SS dosage: 200 g/t BaCl ₂ dosage: 800 g/t	BaSO ₄ recovery: 72.85 % Ca-minerals recovery: 26.52 %

The above parameter settings corresponded to one of the experimental points earlier generated for the barite flotation tests. These settings were thus, used to perform 14 additional barite flotation tests to obtain adequate tailings for the fluorite flotation experiments.

4.3.7 Section 2

This section evaluates the fractional factorial experimental design with resolution IV and 1 center point repeated 3 times that was used to investigate the effect and level of significance of the factors defined in section 3.2.3.2 in the fluorite batch flotation. The chemical composition of the feed used for the fluorite flotation is shown in **Table 8**. The target variables considered in this section are fluorite recovery, fluorite grade, and Gaudin's selectivity index (SI) for calcite and fluorite separation. For each target variable, only the Pareto diagrams are presented in this section. The two-way interactions between the factors were also not considered. This is because in resolution IV designs, although main effects are not confused with two-factor interactions, there is, however, an aliasing of two-factor interactions with each other. The evaluation was also carried out with a confidence interval of 99 %.

Table 8. Chemical composition of feed used for fluorite batch flotation

Mineral	Wt. %
Quartz	31.1
Fluorite	5.6
Calcite	22.7
Sphalerite	1.2
Pyrite	2.9
Barite-celestine	21.3
Anglesite	4.8
Galena	0.6
Barite	7.8
Smithsonite	2.0
Sum	100.0

4.3.8 Pareto charts

The Pareto plots for fluorite recovery (left) and fluorite grade (right) are shown in **Figure 46**. The factors are plotted on the ordinate, and the effect of the factors are on the abscissa.

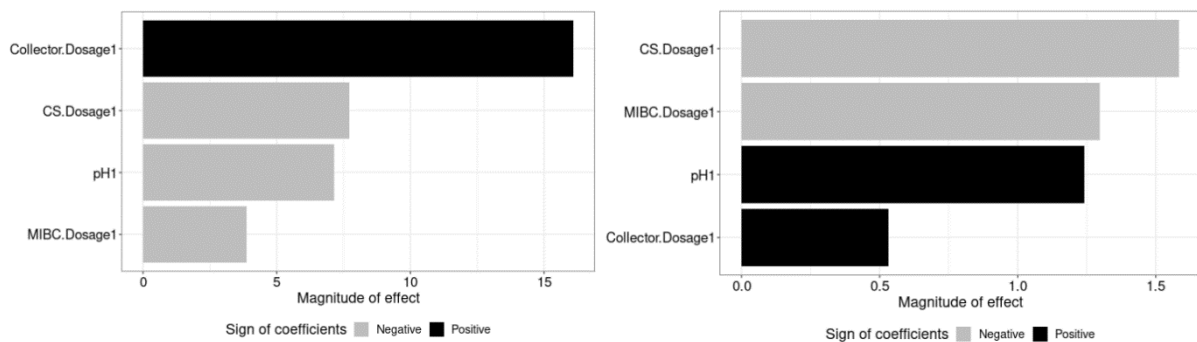


Figure 46. Pareto charts for fluorite recovery (left) and fluorite grade (right)

The recovery of fluorite is mainly influenced by the collector dosage. An increase in the dosage of collector significantly increases fluorite recovery. The other factors such as CS dosage, pH and MIBC had a negative but insignificant influence on the recovery of fluorite.

The pH of the pulp, MIBC dosage and CS dosage had the most significant effect on the grade of fluorite. Increase in CS and MIBC dosages influenced fluorite grade negatively, while an increase in pH resulted in a positive effect.

Figure 47 shows the pareto chart for Gaudin's selectivity index (SI) for calcite and fluorite separation.

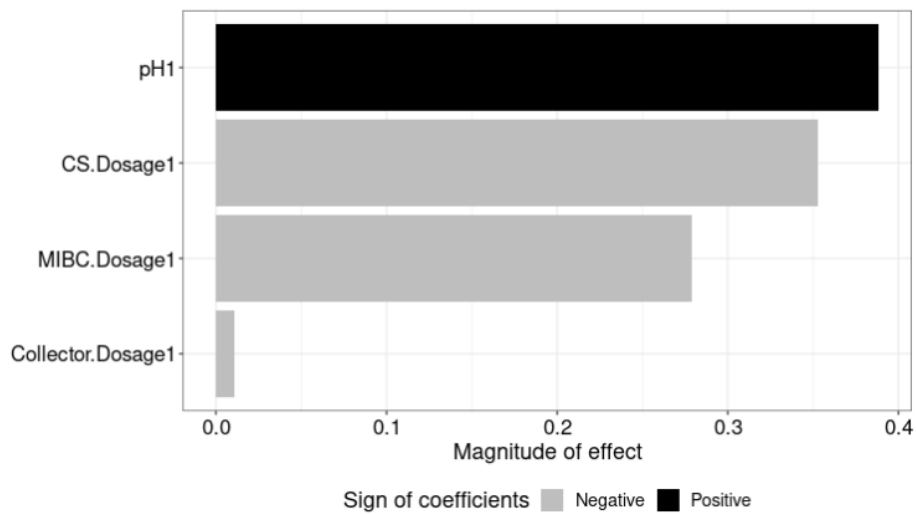


Figure 47. Pareto chart for Gaudin's selectivity index (SI) for calcite and fluorite separation

The selectivity between calcite and fluorite was mainly influenced by pH, MIBC dosage and CS dosage. The pulp pH had a significantly positive influence on the selective separation of fluorite from calcite. On the other hand, MIBC and CS dosages had a significantly negative influence on the Ca-CaF₂ selectivity index.

4.3.9 Summary of main findings

There is a direct relationship between pH and collector concentration on barite and ca-minerals recovery. As such , an increase in pH from 6-10, and collector dosage from 200-600 g/t results in an increase in both barite and ca-minerals recovery. Increasing the CA dosage negatively affects barite grade, with activator dosage having a less significance on all the target variables. The recovery of barite is significantly influenced by the interaction between pH and collector dosage and that of pH and SS dosage. Increasing the collector dosage from 200-600 g/t results in an increase in barite recovery regardless of the working pH range. Also, regardless the SS dosage, an increase in pH value influences barite recovery positively.

Barite grade is influenced by the interaction between pH and collector dosage, as well as between collector and CA dosages. At a pH of 10, an increase in collector dosage from 200-600 g/t has a negative influence on barite, however, at a pH of 6, an increase in collector dosage has a positive influence on barite grade. Again, at a collector dosage of 600 g/t, an increase in

CA dosage from 100-300 g/t shows almost no effect on barite grade, however, at collector concentration of 200 g/t, increasing CA dosage from 100-300 g/t significantly decreases barite grade.

An increase in collector dosage significantly increases the recovery of fluorite, with pH having an insignificant effect. Increasing the dosages of MIBC and CS negatively affects the grade of fluorite as well as the Gaudin's selectivity index (SI) for calcite and fluorite separation. An increase in pH, however, improves fluorite grade as well Ca-CaF₂ selectivity index.

The highest achievable results obtained from the barite and fluorite flotation experiments are summarized in **Table 9** including the operating parameters.

Table 9. Summary of the highest achievable recovery and grade of barite, fluorite, quartz

Barite flotation	
<u>Operating parameters</u>	<u>Results</u>
pH: 10	Mass pull: 52.95 %
Collector dosage: 600 g/t	BaSO ₄ recovery: 73 %
CA dosage: 100 g/t	BaSO ₄ grade: 26.85 %
SS dosage: 200 g/t	Ca-minerals recovery: 26.64 %
BaCl ₂ dosage: 800 g/t	Ca-minerals grade: 12.09 %
Fluorite flotation	
<u>Operating parameters</u>	<u>Results</u>
pH: 8	Mass pull: 46.61 %
Collector dosage: 400 g/t	CaF ₂ recovery: 86.83 %
CS dosage: 550 g/t	CaF ₂ grade: 11.92 %
MIBC dosage: 20 g/t	CaCO ₃ recovery: 63.64 %
	CaCO ₃ grade: 33.73 %
	Gaudin's selectivity index (SI): 1.94
	SiO ₂ recovery: 9.24 %
	SiO ₂ grade: 6.00 %

5. Discussion

5.1 Evaluation of flotation results

5.1.1 Influence of structure of colloidal silica on calcite recovery

The effect of specific surface area of the different colloidal silica solution on their depressive effect on calcite are shown in (**Figure 30-Figure 32**). Increasing the specific surface area of the colloidal silica increased their depressive effect on calcite especially for the sodium and silane modified solutions as low dosages decreased calcite recovery significantly.

This effect is assumed to be partly due to the surface texture (roughness) of the mineral and the size of the silica particles. The smaller the silica particles, the larger the specific surface area for better absorption onto the rough mineral surface, preventing further adsorption of collector molecules. Again, an increase in the surface roughness of the mineral increases the available sites for silica particles adsorption. Therefore, larger specific surface area of colloidal silica coupled with a large available mineral surface leads to a high adsorption capability of the colloidal silica, hence, increasing its depressive effect (Gore & Banker, 1979).

5.1.2 Influence of modification of colloidal silica on calcite recovery

From (**Figure 33**), all the 3 modifications of colloidal silica had a depressive effect on the floatability of calcite, and thus, colloidal silica can be said to have a depressive effect on calcite as proposed by Fuerstenau et al., (1968). Overall, the silane modification had the strongest depressive effect on calcite. Silane modification of colloidal silica enhances the negative surface charge and improves dispersibility, according to Sivanandini et al., (2015). Increased negative surface charge increases colloidal silica's affinity to form a bond with the Ca^{2+} cation of calcite, thereby, increasing its depressive effect. The sodium modified colloidal silica had an intermediate effect on calcite with the aluminate modification having the least effect. Tsai and Wu, (2004) measured and compared the zeta potentials of sodium and aluminium modified colloidal silica (**Figure 48**). According to their findings, at a pH around 8.5, the negative surface charge of the aluminate modification is lowered significantly compared to the standard sodium modification. A lower negative surface charge reduces colloidal silica's ability to bind with the Ca^{2+} cation of calcite, decreasing the depressive effect.

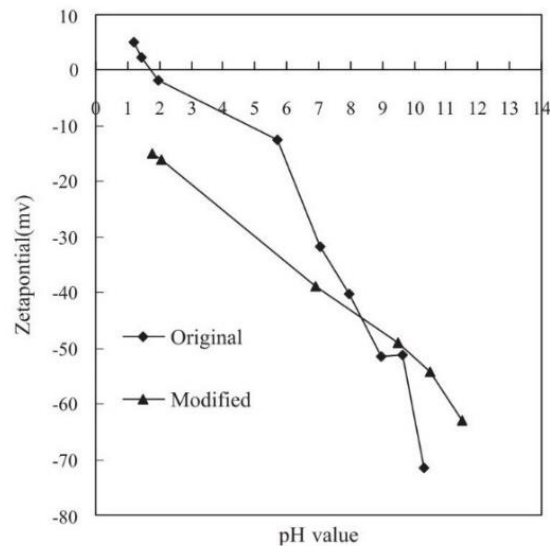


Figure 48. The zeta potential of colloidal silica (a) sodium modified, (b) aluminate modified (Tsai & Wu, 2004)

5.1.3 Influence of BaCl_2 on barite flotation

As can be seen in **Figure 26**, the addition of BaCl_2 increased the recovery of barite, hence, can be said to have an activating effect on barite. This is consistent with the results obtained in the barite batch flotation. An increase in BaCl_2 dosage had a positive influence on barite recovery although the effect was minimal. The addition of BaCl_2 adsorbed onto the surface of barite to reduce the surface hydration and provided sites to promote the adsorption of SDS anions on the surface of barite. This intensified the action of SDS on the mineral surface, thereby, enhancing the floatability of barite (Wills, 1985).

5.1.4 Influence of pH on barite and fluorite flotation

The pH of the pulp is a critical factor in barite flotation with fatty acids and their effects were investigated as shown in the microflotation tests. The pH regulates the dissociation of fatty acids, the distribution of acid/soap species in solution, and the interfacial properties of the flotation system Labidi, (2018). From (**Figure 27**), no appreciable change in barite recovery was observed at pH values 8 and 9. However, at pH 10, a significant increase in barite recovery was achieved. This is consistent with the results obtained in the barite batch flotation tests (**Figure 36**).

The recovery of barite is seen to be largely influenced by pH, with an increase in pH from 8-10 resulting in an increase in barite recovery. Again, the recovery of barite is seen to be influenced by the interaction between collector dosage and pH, and between pH and SS dosage. An increase in pH value results in an increased barite recovery independent of the collector and SS dosages. A possible explanation is that an increase in the pH of the pulp favours the dissociation and distribution of SDS anions in solution. This causes an increase in the adsorption of collector molecules onto the barite particles, rendering them hydrophobic and increasing their ability to float. It can, therefore, be concluded that SDS is an effective barite collector at high pH values than at low pH.

In the fluorite batch flotation experiments, pH had an insignificant influence on the recovery of fluorite (**Figure 46**). According to literatures, fluorite has a positive surface charge in water at pH range 7-11, making it easy to be electrostatically bonded to a negatively charged bubble surface (Gao et al., 2016; Kowalczyk & Zawala, 2016; Song et al., 2006). Since the experiments were conducted in the same pH range (8-10), it can be concluded that the surface of fluorite maintained a positive charge in all cases, making it susceptible to be chemically bound to NaOH anions. A change in the pulp pH, thus, had no significant influence on the hydrophobicity of the fluorite particles. The pulp pH however, had a negative influence on the recovery of calcite and quartz, and a positive influence on fluorite grade. This is because the concentrate grade increases with a decrease in amount of gangue minerals present in the concentrate.

5.1.5 Influence of collector on barite and fluorite flotation

According to Labidi, (2018) the amount of target mineral to be recovered in a flotation system strongly depends on the concentration of the surfactant. Therefore, the effect of collector on barite flotation was studied in both microflotation and batch flotation tests. From (**Figure 27**), a direct relationship between collector dosage and barite recovery was observed. This result agrees with the findings of the barite batch flotation tests (**Figure 36**), where the collector dosage showed a significantly positive influence on barite recovery. The recovery of barite increased significantly with an increase in collector dosage independent of the working pH. At both high and low pH levels, an increase in collector dosage resulted in a significant increase in barite recovery.

Similar to the fluorite flotation, an increase in the NaOl dosage significantly increased the recovery of fluorite. This can be explained that an increase in the concentration of SDS/NaOl increases the collector molecules/ions present in the pulp which are adsorbed onto the $\text{Ba}^{2+}/\text{Ca}^{2+}$ active sites of the minerals' surface to form a firmly adherent, hydrophobic adsorption layer, causing more barite/fluorite to float (Xing et al., 2017). Again, the presence of collector molecules regulates the hydrophobicity of minerals by decreasing the interfacial energies of the solid-gas, solid-water, and water-gas interfaces, with the most notable being the decrease in interfacial energy of the solid-gas interface. According to the Young equation, this enhances the mineral's hydrophobicity and promotes flotation. Generally, as collector concentration increases, the contact angle of the mineral increases as well, which increases the mineral's ability to float (Drzymała & Swatek, 2007). Also, since SDS can actively interact with the Ca^{2+} sites on the surface of ca-minerals such as calcite and fluorite, an increase in SDS dosage resulted in an increased ca-minerals recovery (**Figure 38**).

5.1.6 Influence of citric acid on barite flotation

Liu et al., (2020) measured the zeta potential of fluorite and barite. According to the findings, the surface charge of fluorite and barite reduced by 35 mV and 5 mV, respectively, after the addition of CA to both minerals, showing that the interaction of CA with fluorite was stronger than that of CA and barite. Gao et al., (2016) and Wang et al., (2019) stipulated that in the presence of CA, the selective dissolution of Ca^{2+} from the surface of fluorite results in the effective separation of barite from fluorite.

The results obtained from the microflotation tests (**Figure 28**), agreed with the findings in literatures. The flotation recovery of barite and fluorite were affected by an increase in CA recovery, although the effect was higher on fluorite than on barite. This result was similar to the findings in the barite batch flotation. An increase in CA dosage had a negative effect on the recovery of barite and ca-minerals (**Figure 36, Figure 38**). The adsorption of CA on the surface of calcium mineral occurs through chemical chelation with Ca^{2+} ions present on the active sites of the mineral surface, which blocks the subsequent adsorption of collectors (Wang et al., 2019). This depressive mechanism has been attributed to two aspects. First, CA^{3-} ions could strongly dissolve Ca^{2+} present on the ca-minerals surface, thereby decreasing the number of adsorption sites of calcium ions on the surface of the ca-minerals for collector adsorption. Second, CA can have a strong chemical adsorption on ca-mineral surfaces, blocking the subsequent adsorption

of collector on the minerals surface (Dong et al., 2021; Wang et al., 2019). These mechanisms could be the possible reason for the negative influence of CA on ca-minerals.

5.1.7 Influence of Sodium silicate on barite flotation

The effect of SS dosage on the flotation of barite and calcite in the presence of SDS was studied by Chen et al., (2019). Based on their findings, SS had a depressing effect on both calcite and barite, with the effect on calcite being the strongest. Marinakis et al., (1985) also conducted a study on the adsorption of SS by calcite, fluorite, and barite in the presence of oleic acid, and concluded that SS depresses these minerals by preventing oleate species from reacting with the surface sites of these minerals.

The effect of adding SS as a calcite depressant in an attempt to reduce calcite content in the barite flotation was investigated in the microflotation test as shown in (**Figure 29**). The result obtained agrees with the findings in literatures, i.e., SS has a depressing effect on both barite and calcite. A similar observation was made in the barite batch flotation tests. An increase in SS dosage from 100-300 g/t negatively affected barite and ca-minerals recoveries (**Figure 36**, **Figure 38**). This could be attributed to the adsorption of metasilicate ions at the cationic surface sites of ca-minerals and barite, limiting the sites from reacting with SDS species. An increase in SS dosage, however, increased barite grade since the associated ca-minerals were strongly depressed by the metasilicate ions, inhibiting their floatability.

5.1.8 Gaudin's selectivity index (SI) for calcite and fluorite separation

The results obtained in **Figure 34** shows that Levasil WT110P[®] has a strong depressive effect on calcite, but no visible depressive effect on fluorite. This could be explained that the silicate ions present in the depressant quickly adsorbed onto the surface sites of calcite minerals rather than the fluorite minerals, limiting the available active surface sites on calcite for the adsorption of collector molecules. This implied that Levasil WT110P[®] could be used to separate fluorite from calcite.

The results from the fluorite batch flotation tests shows that increasing the dosage of Levasil WT110P[®] has a depressive effect on fluorite recovery and grade (**Figure 46**). However, the effect of CS dosage is not significant for the response variables calcite grade and recovery. These results contradict the microflotation results obtained. One reason could be that already at a CS dosage of 50 g/t, the depressing effect on calcite was nicely exceeded and already in the

investigated area the CS hinders the flotation of particles which also explains the negative effect of CS dosage on the target variables mass pull and quartz recovery as shown in **Figure 49**.

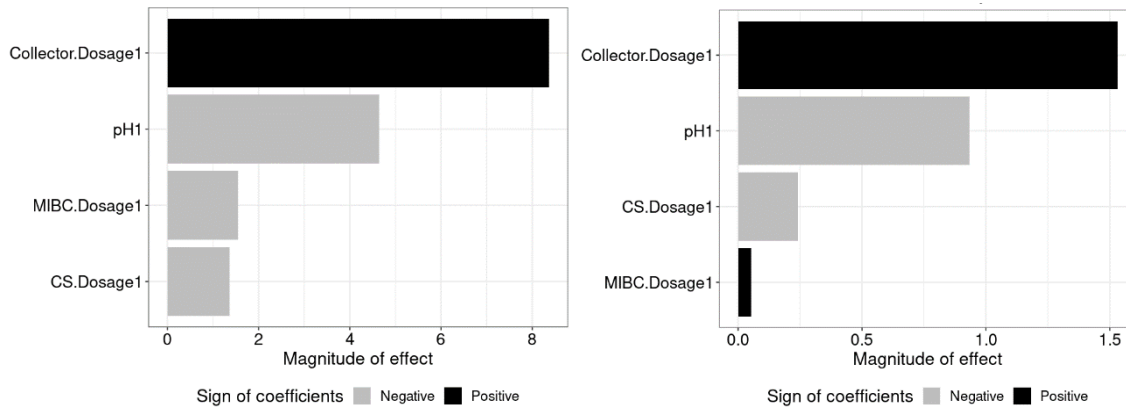


Figure 49. Pareto chart of Mass pull (left) and quartz recovery (right)

A blank test was conducted without Levasil WT110P[®] at a pulp pH of 10, NaOl dosage of 100 g/t and MIBC dosage of 20 g/t and compared to the results obtained when the dosage of Levasil WT110P[®] was 50 g/t. The Gaudin's selectivity index (SI) obtained was 2.9 in the presence of the depressant, and 1.7 in the absence of the depressant. This shows that Levasil WT110P[®] has a positive influence on the selective separation of fluorite and calcite. However, an increase in the depressant dosage showed a significantly negative effect on the selectivity of fluorite and calcite (**Figure 47**). A hypothesis could be made that Levasil WT110P[®] has a depressive effect on calcite at low dosages. To verify this hypothesis, a full experimental design must be made with investigating the CS dosage under 50 g/t.

5.2 Alternative applications of the Ultimate tailings

The future sustainable built environment is primarily concerned with environmental conservation as well as innovations in technology and development. However, the demand for raw materials such as cement, sand, gypsum, and stones has increased rapidly due to the development in infrastructure. As a result, the use of industrial waste as a raw material in building has been advocated as a sustainable and environmentally friendly option (Mporas et al., 2020). Furthermore, growing demand for mineral commodities has resulted in greater mining and thus, increased the generation of mine waste, with approximately 5-7 billion tonnes of mine tailings being produced each year. Much study has focused on metal recovery by

reprocessing tailings, however, there remain the ultimate tailings after the metal has been recovered.

Generally, tailings contain compounds of SiO_2 , Al_2O_3 , CaO , Fe_2O_3 , including significant levels of heavy metals and metalloids such as Pb, Co, Cu, Zn, and Cr which is similar to the ultimate tailings obtained in this research (Wan et al., 2018). The physical, mineralogical, and chemical makeup of the tailings obtained in this study, thus, make it a viable material to be used in civil engineering applications, which can minimize the pressure on existing natural (Mporas et al., 2020). The following are possible areas in which the ultimate tailings can be utilized.

5.2.1 Brick production

The tailings can be utilized as an alternative to natural fine aggregates in brick manufacture, thus, reducing the demand on sand mining in riverbeds. Chen et al., (2011) used hematite mine tailings containing low amounts of SiO_2 (24.40 wt.%), Al_2O_3 (10.95 wt.%), and CaO (6.20 wt.%) to produce fired bricks by mixing with clay and fly ash containing high silicon and aluminium to make up for the deficit of the tailing material. The presence of similar compounds; SiO_2 (51.4 wt.%), and CaO (9.40 wt.%) in the tailings make it a suitable alternative for this purpose.

5.2.2 Fine aggregate

Concrete contains coarse and fine aggregates, which account for 60-75% of total volume, with fine aggregate accounting for 35 % (Chow et al. 2013; Mundra et al. 2016). Because of the rising demand for and scarcity of high-quality fine aggregate, alternative sources for fine aggregates are being investigated globally (Kirthika et al., 2020). Mine tailing has been extensively researched as a fine aggregate replacement in mortar and concrete, owing to its particle size ($< 1\text{mm}$) and specific gravity (Mporas et al., 2020). The physical properties of tailings influence the workability, strength, and durability of concrete (Gou et al., 2019). Ince, (2019) used gold mine tailings containing CaO (14.89 wt.%), SiO_2 (44.62 %), Al_2O_3 (8.64 %) as partial replacement of sand (up to 30 %) in cement mortars and achieved a significant increase in compressive strength (47 Mpa) and frost resistance. It is worth mentioning that in construction, the maximum allowed fines (particles passing through $75\text{ }\mu\text{m}$) are limited to 15 % because high fines cause shrinkage in concrete (Kirthika et al., 2020).

5.2.3 Supplementary cementitious material (SCM)

The cement manufacturing process consumes a lot of energy and emits a lot of CO₂. To reduce these amounts, SCMs with high silica content such as fly ash, blast furnace slag, and steel slag are used to replace cement in cement mixes (Puthipad et al., 2018; Rehman et al., 2018). The ultimate tailing can thus, be investigated to determine its suitability as SCM. Furthermore, due to the tailings' weak cementitious properties, physical and chemical pre-treatment steps such as drying, grinding (to < 45 m), and/or calcination should be considered to achieve the desirable properties (Gou et al., 2019; Xiong et al., 2017).

5.2.4 Cement clinker production

Over the last few decades, the cement industry has made significant efforts to decrease the environmental burden, i.e., to reduce greenhouse gas emissions and to produce more energy-efficient clinker. One solution is to make cement clinkers with altered chemical and physical properties with the aid of mineralizers. Mineralizers are primarily inorganic chemicals that alter the processes in the solid, liquid, and solid-liquid interfaces during cement clinker combustion (Oien, 2005). They are reported to reduce sintering temperatures by 100-150 °C, promote the formation of C₃S while also improving the mechanical properties (hydraulic activity, strength) of the cement produced (Gou et al., 2019). Mineralizers are added as minor components and include BaO, CaO, CaF₂, SiO₂, and Al₂O₃, all of which are present in the ultimate tailings.

Hayouni et al., (2022) used celesto-barite mine waste from Tunisia (the tailings for this project) as mineralizing agents in the production of eco-friendly white cement. The particle size of the tailings before firing was < 100µm as coarse grains prevent exchange of heat and matter during sintering, resulting in low burnability of the input feed. The results indicated that the use of mine waste reduces clinkering temperatures by around 100 °C, speeds up reactions, and stabilizes formation of β-C₂S. The strength attained was 5 % higher than that of standard grey clinker of all ages examined. The synthesized clinker was, therefore, appropriate for long-term sustainable materials for infrastructure development.

High contents of CaF₂, however, pose production problems. Fluorine escape during the burning process deteriorates the kiln linings. Nevertheless, following a well-controlled burning procedure, some researchers have observed the successful incorporation of up to 85 % of the fluorine in the clinker. It is consequently critical to keep the CaF₂ level in tailings below 2 % (Blanco et al., 1994).

5.2.5 Glass production

Alfonso et al. (2020) investigated the feasibility of using fluorite tailings from the Osor mine in Spain as a raw material for commercial glass production. Two favourable properties of the tailings were of particular interest: the presence of fluorine and calcium, both of which favour glass production. The addition of CaF_2 lowers the melting and sintering temperatures. Fluorine disturbs and weakens the glass network by replacing bridging oxygens with nonbridging fluorine (Hill et al., 1999; Jordanov et al., 2021). Calcium can operate as a network modifier and charge compensator for the positive charge shortfall caused by the Al-Si substitution in the tetrahedral sites of silicate glasses, which depolymerizes the glass network after the creation of nonbridging oxygen (Angeli et al., 2007). The particle-size of the tailing material was less than 200 μm , with D_{80} smaller than 70 μm . The test for leachability of potentially harmful elements (such as Pb, Co, Cd, Sb) from the glasses revealed that metal concentrations in the leachates were below the standard threshold levels, indicating that the metals were fixed in the structure of the glasses (Alfonso et al., 2020). The ultimate tailing containing similar compounds can thus, be investigated for this application.

5.2.6 Other applications

Mine tailings are used in other civil engineering applications such as cemented back fill, soil stabilization, landfills, and embankments (Vegas et al., 2015; Zheng et al., 2016). These applications have the potential not only to minimize demand on existing natural resources, but also to provide an effective and environmentally friendly method of mine tailings disposal. However, these areas of applications must be approached with caution due to the danger of heavy metal leaching and acid mine drainage. Such dangers can be reduced by using alkali activation, chemical bonding, and hydration (Mporas et al., 2020).

6. Conclusion

This master thesis sought to investigate the technological feasibility of recovering barite and fluorite from mine tailings with the aid of statistical design of experiment including economic consideration. To achieve this, microflotation experiments were conducted according to the procedures described in section 3.1.3 to investigate the depressive effect of citric acid and sodium silicate on pure minerals of calcite, fluorite, and barite using SDS and NaOl as collectors. Also, 8 colloidal silica which differ in modification and specific surface area were tested to ascertain their depressive effect on calcite.

The results obtained from this study showed that, the floatability of barite is highly dependent on the pH of the pulp as well the collector dosage. The best working pH was found to be 10, and a collector dosage of 1×10^{-3} mol/L. Citric acid had a depressive effect on fluorite, however, at an increased dosage, the floatability of barite was negatively affected. Sodium silicate had a significant depressive effect on both calcite and barite.

The different colloidal silica tested all had a depressive effect on calcite, and their depressive effect increased with increasing specific surface area. In terms of modification, the silane modified depressant had the strongest depressive effect on calcite followed by the sodium modified depressant. The aluminate modified depressant had the weakest depressive effect on calcite. Overall, the aluminate modified depressant (Levasil WT110P®) showed the strongest depressive effect on calcite, however, it had no depressive effect on fluorite. These results agree with the proposals of Fuerstenau et al., (1968) and Rudolph & Kupa (2018) that the mechanism of sodium silicate as a depressant is the adsorption of colloidal silica onto the active sites of Ca^{2+} present on the surface of Ca-bearing minerals, preventing the adsorption of collector molecules.

Based on the information obtained from the microflotation experiments, barite batch flotation tests were conducted while depressing fluorite, followed by reverse fluorite flotation while depressing barite as described in section 3.2.3. The recovery of barite and fluorite increased with increasing collector dosage. In the barite flotation, an increase in citric acid dosage had a negative influence on barite recovery and grade. The highest achieved barite concentrate grade was 26.85 % with a recovery of 73 %. For the fluorite flotation, low dosage of Levasil WT110P® positively influenced the selective separation of fluorite and calcite, however, high

dosage of Levasil WT110P[®] negatively influenced fluorite recovery and grade. The highest achieved fluorite concentrate grade was 11.92 % with a recovery of 86.83.

To fully understand the interaction between colloidal silica and the surface of Ca-bearing minerals, further research should be conducted. This includes the use of atomic force microscopy to study the surface texture of the calcium-bearing minerals to verify the assumption that the roughness of the mineral surface affects the adsorption of colloidal silica, and to obtain data on how the different mineral surfaces interact with colloidal silica. Another area of study is to measure and analyse the zeta potential of the adsorption of collector molecules onto minerals treated with colloidal silica. The depressive effect of Levasil WT110P[®] must be fully investigated through full experimental design to understand its depressive mechanism on both calcite and fluorite.

To improve the recoveries and grades of barite and fluorite for commercial applications, it is recommended that the processes be performed in pilot scale by combining roughers, cleaners, and scavengers. The proposed flowsheet for improving the overall process as shown in **Figure 50** was modified after Bulatovic (2015b). This is because typical flotation plants which process barite-fluorite ores by first floating barite followed by reverse flotation of fluorite use similar flowsheets. However, in this case, the exact number of cells required in each of the flotation stages can only be determined by establishing a specific required barite and fluorite recovery and grade followed by further pilot scale tests.



Figure 50. Proposed flowsheet for recovering barite and fluorite from the tailings (Modified after Bulatovic, 2015b)

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Appendices

Appendix A Fractional factorial experimental design for barite batch flotation experiments

Run	pH	Collector dosage (g/t)	CA dosage (g/t)	Sodium silicate dosage (g/t)	Activator dosage (g/t)
1	8	400	200	500	500
2	10	200	100	800	800
3	6	600	100	200	200
4	6	200	100	800	200
5	6	600	100	800	800
6	10	600	100	200	800
7	6	200	300	800	800
8	6	600	300	200	800
9	10	200	300	200	800
10	8	400	200	500	500
11	10	200	100	200	200
12	10	600	300	200	200
13	10	600	100	800	200
14	10	600	300	800	800
15	6	200	300	200	200
16	6	600	300	800	200
17	6	200	100	200	800
18	10	200	300	800	200
19	8	400	200	500	500

Appendix B Fractional factorial experimental design for fluorite batch flotation experiments

Run	pH	Collector dosage (g/t)	MIBC dosage (g/t)	CS dosage (g/t)
	9	250	35	300
2	10	400	20	50
3	8	100	50	550
4	8	400	50	50
5	10	100	50	50
6	9	250	35	300
7	8	100	20	50
8	8	400	20	550
9	10	100	20	550
10	10	400	50	550
11	9	250	35	300