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Mechanical, chemical, and Thermal processing of acid-grade fluorspar concentrates

Bachelor Thesis

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Place, Date


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Acknowledgement

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Abstract

This study investigates the chemical purification of fluorite (CaF_2) concentrate toward acid-grade quality ($\geq 97\%$ CaF_2) using sequential hydrochloric acid (HCl) and sodium hydroxide (NaOH) leaching. The feed material, obtained as a flotation concentrate from a Mongolian deposit, contained approximately **93.02% CaF_2** , with silica (2–4%), iron (0.11–0.13%), and carbonate minerals as the primary impurities.

The purification process was evaluated through a series of controlled experiments, varying NaOH concentration (1–4 M) and temperature (70–90°C) while maintaining consistent HCl leaching conditions (1 M, 50°C). Chemical and mineralogical characterization was conducted using X-ray fluorescence (XRF), supported by titration and gravimetric analysis for accurate determination of CaF_2 , CaCO_3 , and SiO_2 contents.

HCl leaching was found to be highly effective in removing carbonate and iron impurities, resulting in a consistent decrease in iron content and an apparent increase in calcium concentration due to gangue dissolution. However, silica remained largely unaffected during acid treatment, confirming the chemical stability of quartz. In contrast, NaOH leaching demonstrated that temperature is the dominant factor controlling silica removal. At 70°C, silica reduction was negligible, whereas at 90°C, a maximum reduction of approximately **16.5%** was achieved, indicating enhanced dissolution of silica under elevated temperature conditions.

The combined treatment resulted in an increase in CaF_2 grade to a maximum of **95.18%**, representing a significant improvement over the feed material. However, the acid-grade specification was not achieved, primarily due to incomplete silica removal, with residual silica remaining in the range of **3–4%**.

The results confirm that sequential HCl and NaOH leaching is an effective approach for fluorite purification, particularly for the removal of iron and carbonate impurities. Nevertheless, further optimization of alkaline treatment conditions, including increased temperature, extended reaction time, or improved mineral liberation, is required to achieve complete silica removal and meet industrial acid-grade specifications.

Table of Contents

Statutory Declaration.....	1
Acknowledgement.....	2
Abstract.....	3
Table of Contents.....	4
List of Figure.....	6
List of Table.....	7
1. Introduction.....	8
1.1. Background and Industrial Importance of Fluorspar.....	8
1.2. Fluorspar Beneficiation in Mongolia.....	8
1.3. Problem statement.....	9
1.4. Aim and objectives of the study.....	9
1.5. Scope and limitations of the study.....	9
1.6. Structure of the thesis.....	10
2. Literature Review.....	11
2.1. Fluorite mineralogy and properties.....	11
2.2. Industrial Grades, Applications, and Global Supply.....	12
2.2.1. Industrial Grades and Quality Requirements of Fluorspar.....	12
2.2.2. Industrial applications.....	12
2.2.3. Global Production and Supply Context.....	13
2.3. Common Impurities in Fluorspar Concentrates.....	14
2.4. Mechanical Beneficiation of Fluorite Ores.....	16
2.4.1. Overview and objectives.....	16
2.4.2. Comminution.....	17
2.4.3. Froth flotation.....	17
2.4.4. Flotation reagents.....	17
2.4.5. Flotation circuit design.....	20
2.5. Acid Leaching for Removal of Carbonate and Iron Impurities.....	20
2.6. Alkaline Leaching for Silica Removal.....	21
2.7. Challenges in Producing Acid-Grade Fluorspar.....	22
2.8. Research Gap and Relevance of This Study.....	23
3. Materials and Methods.....	25
3.1. Feed Material and Sample Origin.....	25
3.2. Chemicals and Reagents.....	26
3.3. Experimental Design.....	26
3.4. HCl Leaching Procedure.....	27

3.5. NaOH Leaching Procedure.....	28
3.6. Solid–Liquid Separation, Washing, and Drying.....	28
3.7. Drying and Sample Preparation.....	29
3.8. Analytical Methods.....	30
3.8.1. X-ray Fluorescence (XRF) Analysis.....	30
3.8.2. X-ray Diffraction (XRD) Analysis.....	31
3.8.3. Titration and Gravimetric Analysis.....	32
3.9. Calculation Methods.....	32
3.10. Reliability and Limitations of the Experimental Methods.....	34
4. Results and Discussion.....	35
4.1. Feed Concentrate Characterization.....	35
4.1.1. Chemical Composition (XRF).....	35
4.1.2. Mineralogical Composition (XRD).....	36
4.1.3. Initial CaF_2 , CaCO_3 , and SiO_2 Contents.....	36
4.2. Flotation Beneficiation: Result and Discussion.....	37
4.2.1. Feed Characterisation.....	37
4.2.2. Sample Preparation and Sieve Analysis.....	37
4.2.3. Grinding Optimization.....	38
4.2.4. pH Optimization.....	38
4.2.5. Collector and Depressant Optimization.....	38
4.2.6. Open-Circuit Flotation.....	38
4.2.7. Closed-Circuit Flotation.....	39
4.2.8. Additional Fine Grinding and Final Flotation.....	40
4.2.9. Conclusions from Flotation Study.....	40
4.3. Effect of HCl Leaching.....	41
4.3.1. Removal of Iron and Carbonate Impurities.....	41
4.4. Effect of NaOH Leaching.....	42
4.5. Combined Effect of Sequential Treatment (HCl + NaOH).....	43
4.6. Final Product Quality and Acid-Grade Evaluation.....	44
4.6.1. Achieved CaF_2 Grade.....	44
5. Conclusions and Recommendations.....	44
5.1. Main Conclusions.....	44
5.2. Recommended Operating Conditions.....	46
5.3. Recommendations for Further Study.....	47
References.....	48
Appendix.....	49

List of Figure

Figure 1: Diagram of the cubic fluorite crystal structure

Figure 2: World fluorspar mine production (2022–2023e) and reserves (thousand metric tons CaF_2). Source: USGS Mineral Commodity Summaries [6].

Figure 3: Schematic mineral association in a typical fluorite concentrate, showing fluorite (CaF_2) grains alongside quartz (SiO_2), calcite (CaCO_3), and iron oxide (Fe_2O_3) phases.

Figure 4: Indicative impurity composition of a raw fluorite flotation concentrate (values illustrative; actual composition varies by deposit).

Figure 5: Overview of experimental approach and methodology

Figure 6: Classification of ionizing collectors used in froth flotation, showing anionic (sulfhydryl and oxyhydryl) and cationic (amine) types. Source: adapted from [14].

Figure 7: Schematic cross-section of a mechanical froth flotation cell, showing the impeller, air inlet, pulp zone, froth layer, and concentrate overflow.

Figure 8: Effect of NaOH concentration and temperature on silica (SiO_2) removal efficiency (XRF data, present study).

Figure 9: Schematic representation of the reaction mechanism for silica dissolution in sodium hydroxide solution.

Figure 10: Chemical composition of fluorite concentrate before and after sequential HCl and NaOH leaching, based on XRF analysis (mass-balance-corrected values, present study).

Figure 11: Experimental procedure flowsheet for the purification of the fluorite concentrate

Figure 12: Leaching experiment setup in lab

Figure 13: Vacuum filtration system

Figure 14: Oven for sample drying

Figure 15: Portable XRF analyzer

Figure 16: XRD Analysis of Chemically Purified Fluorite Concentrate

Figure 17: Result of NaOH treatment

Figure 18: Titration analysis of chemically purified fluorite concentrates and the feed

Figure 19: Raw titration vs. mass-balance-corrected CaF_2 . Correction factor = $100 \div \text{mass balance total per sample}$.

Figure 20: Titration Analysis Results of Acid and Base Leaching

Figure 21: XRD diffractogram of fluorite feed

Figure 22: XRD diffractogram of Final Flotation Concentration

List of Table

Table 1: Quality specifications and impurity limits for commercial fluorspar grades

Table 2: XRF elemental composition of all feed concentrate samples

Table 3: Titration analysis of chemically purified fluorite concentrates and the feed

Table 4: Chemical analysis results of the primary ore sample

Table 5: Mineralogical composition of feed ore by XRD analysis

Table 6: Flotation results for grinding optimization (pH 11, JKTM 400 g/t, Na_2SiO_3 900 g/t)

Table 7: Effect of pulp pH on rougher flotation performance (P_{80} —74 μm)

Table 8: Open-circuit flotation results—progressive cleaner stages

Table 9: Closed-circuit flotation mass balance results

Table 10: Result of HCl of leaching

1. Introduction

1.1. Background and Industrial Importance of Fluorspar

Fluorite (CaF_2), commonly referred to as fluorspar, is a strategically important industrial mineral and the primary commercial source of fluorine. It is an essential raw material for the production of hydrofluoric acid (HF), which serves as a key precursor in a wide range of chemical industries [1]. Hydrofluoric acid is used in the manufacture of fluoropolymers, refrigerants, aluminum fluoride, lithium-ion battery electrolytes, and various specialty chemicals applied in pharmaceuticals, electronics, and advanced materials. [2]

In recent years, global demand for fluorite has increased significantly due to the rapid growth of energy-related technologies, particularly lithium-ion batteries and renewable energy systems. As a result, fluorite has been classified as a critical raw material in several regions, including the European Union and the United States [4]. This classification reflects both its economic importance and the vulnerability of its supply chain.

Industrial applications require fluorite of varying purity levels, depending on the end use. Among these, acid-grade fluorspar is the most valuable, requiring a minimum purity of approximately 97% CaF_2 along with strict limits on impurities such as silica, carbonates, and iron [2, 5]. Achieving this level of purity is essential for efficient hydrofluoric acid production and downstream chemical processing.

1.2. Fluorspar Beneficiation in Mongolia

Mongolia is one of the important producers of fluorite, with several deposits supplying raw material to both domestic and international markets. Fluorite ores in Mongolia are typically processed through crushing, grinding, and flotation to produce a concentrate with increased CaF_2 content.

Although flotation is effective in upgrading fluorite ores, it does not always achieve the purity required for acid-grade applications. Residual impurities, particularly silica (SiO_2), carbonate minerals (CaCO_3), and iron-bearing phases, often remain in the concentrate. These impurities can negatively affect product quality and limit the commercial value of the material.

Silica is particularly problematic because it is commonly present as quartz, which is highly stable and resistant to chemical treatment. Carbonate minerals and iron oxides can also interfere with downstream processing, especially in hydrofluoric acid production. Therefore,

additional purification steps beyond conventional mineral processing are often required to meet industrial specifications.

1.3. Problem statement

Despite the application of flotation for fluorite beneficiation, many concentrates produced in Mongolian processing plants do not consistently meet acid-grade specifications [5]. The presence of residual impurities, especially silica and iron, limits the usability of these concentrates in high-value chemical applications. Chemical purification methods, such as acid and alkaline leaching, are known to improve fluorite quality by selectively removing different types of impurities [2]. However, the effectiveness of these methods depends strongly on operating conditions, including reagent concentration, temperature, and treatment sequence.

For fluorite concentrates of Mongolian origin, there is limited systematic information on the optimization of sequential acid and alkaline treatment processes. In particular, the conditions required to effectively remove silica without significant loss of CaF_2 are not well defined.

1.4. Aim and objectives of the study

The main aim of this study is to evaluate the effectiveness of sequential chemical treatment for upgrading fluorite concentrate to acid-grade quality.

To achieve this aim, the following objectives are defined:

- To characterize the chemical and mineralogical composition of the fluorite concentrate
- To evaluate the effectiveness of hydrochloric acid (HCl) leaching in removing carbonate and iron impurities
- To investigate the effect of sodium hydroxide (NaOH) treatment on silica removal under different conditions
- To assess the influence of temperature and reagent concentration on impurity removal efficiency
- To determine the final CaF_2 grade and evaluate whether acid-grade specifications can be achieved

1.5. Scope and limitations of the study

This study focuses on laboratory-scale chemical purification of a fluorite flotation concentrate obtained from a beneficiation plant in Mongolia. The investigation is limited to sequential treatment using hydrochloric acid and sodium hydroxide under controlled experimental conditions.

The analysis of the samples is primarily based on X-ray fluorescence (XRF), X-ray diffraction (XRD), and titration methods. It should be noted that XRF analysis does not directly detect fluorine, and therefore the CaF_2 content is estimated indirectly.

The study does not include pilot-scale or industrial-scale validation, and the economic feasibility of the process is not evaluated. In addition, variability in feed composition may influence the reproducibility of the results.

Despite these limitations, the study provides valuable insight into the behavior of impurities during chemical treatment and identifies key parameters affecting fluorite purification.

1.6. Structure of the thesis

This thesis is organized into six chapters. Chapter 1 introduces the background, problem statement, objectives, and scope of the study. Chapter 2 presents a review of relevant literature on fluorite processing and chemical purification methods. Chapter 3 describes the materials, experimental procedures, and analytical methods used in the study. Chapter 4 presents and discusses the experimental results. Chapter 5 provides a detailed interpretation of the findings, and Chapter 6 summarizes the main conclusions and recommendations for future work.

2. Literature Review

2.1. Fluorite mineralogy and properties

Fluorite (CaF_2) is a halide mineral that crystallizes in the cubic system, exhibiting relatively low hardness (Mohs hardness of 4) and high chemical stability under moderate conditions. Its low solubility in water and resistance to chemical attack make it well suited for selective purification processes [5].

This structural stability is reflected in fluorite's physical and chemical properties. It has a Mohs hardness of 4, a specific gravity of approximately 3.18 g/cm^3 , and exhibits perfect octahedral cleavage in four directions. Its solubility in water is extremely low ($K_{sp} \approx 3.45 \times 10^{-11}$), and it remains largely unreactive in dilute acids and alkalis at moderate temperatures. These properties are central to chemical purification: because CaF_2 is chemically inert under conditions that dissolve carbonate and iron-bearing gangue minerals, selective impurity removal is possible without significant loss of the valuable phase [2,5].

Fluorite (CaF_2) crystallizes in the cubic system and commonly forms well-developed cubic or octahedral crystals. The mineral occurs in a wide range of colors, including purple, green, yellow, blue, and colorless, depending on the presence of trace impurities and crystal defects. Fluorite is also characterized by its strong fluorescence under ultraviolet light, a property from which the term "fluorescence" is derived [1].

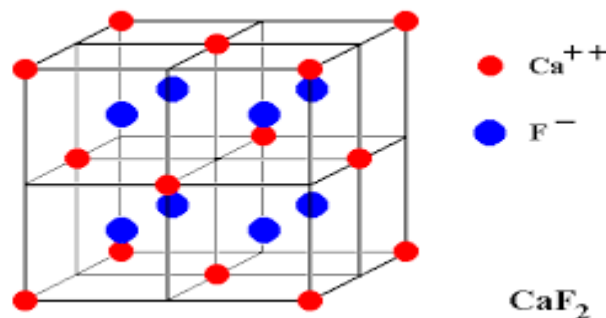


Figure 1: Diagram of the cubic fluorite crystal structure

2.2. Industrial Grades, Applications, and Global Supply

2.2.1. Industrial Grades and Quality Requirements of Fluorspar

Fluorspar is commercially classified into grades according to its CaF_2 content and impurity profile. Acid-grade fluorspar is the most commercially valuable, typically requiring a minimum purity of 97% CaF_2 alongside strict limits on impurities such as silica (SiO_2), calcium carbonate (CaCO_3), and iron [6].

Grade	CaF_2 Content (Min)	SiO_2 Content (Max)	CaCO_3 Content (Max)	Other Critical Impurities
Acidspar	97%	1.00%	1.00%	Sulfides, Arsenic (≤ 3 ppm), Phosphorus
Ceramicspar	85% – 95%	3.00%	1.0% – 1.5%	Ferric oxide, Lead, Zinc
Metspar	60% – 85%	5.00%	Variable	Sulfur, Lead

Table 1: Quality specifications and impurity limits for commercial fluorspar grades

High purity is essential for hydrofluoric acid production, as impurities can disrupt chemical reactions and reduce process efficiency. Silica, in particular, can give rise to undesirable by-products, while iron can adversely affect reaction kinetics and downstream processing. Achieving acid-grade purity therefore represents a primary objective in fluorite beneficiation.

2.2.2. Industrial applications

The primary use of acid-grade fluorite is in the manufacture of hydrofluoric acid (HF), which is produced by reacting fluorspar with concentrated sulfuric acid at elevated temperatures. HF is a foundational chemical in the fluorine industry and serves as the precursor for a wide range of downstream products [2,3]:

- Fluoropolymers, including polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF), used in industrial coatings, seals, and membranes.
- Hydrofluorocarbon (HFC) and hydrofluoroolefin (HFO) refrigerants used in air conditioning and refrigeration systems.

- Aluminum fluoride (AlF_3), used in aluminum smelting to lower the melting point of the electrolyte bath.
- Lithium hexafluorophosphate (LiPF_6), the electrolyte salt in lithium-ion batteries, demand for which has grown substantially with global electrification of transport [3,4].
- Specialty fluorochemicals used in pharmaceuticals, agrochemicals, and semiconductor manufacturing [3].

2.2.3. Global Production and Supply Context

Global fluorite production is concentrated in a small number of countries. China is the dominant producer, accounting for approximately 60% of world mine output, followed by Mexico, Mongolia, South Africa, and Spain [6]. Mongolia is an increasingly important supplier, with several large fluorite deposits under active exploitation in Tov, Dornod, and Khovd provinces. Mongolian fluorite ore tends to be associated with significant silica and carbonate gangue, making chemical purification a critical processing step.

Global demand for fluorite has increased in recent years, driven primarily by growth in fluorochemicals and battery materials. The European Union and the United States have each classified fluorite as a critical raw material, citing the strategic vulnerability of supply chains concentrated in a small number of producing countries [4]. Long-term demand is expected to continue growing as electric vehicle adoption accelerates and fluorine-containing battery components become more widely used.

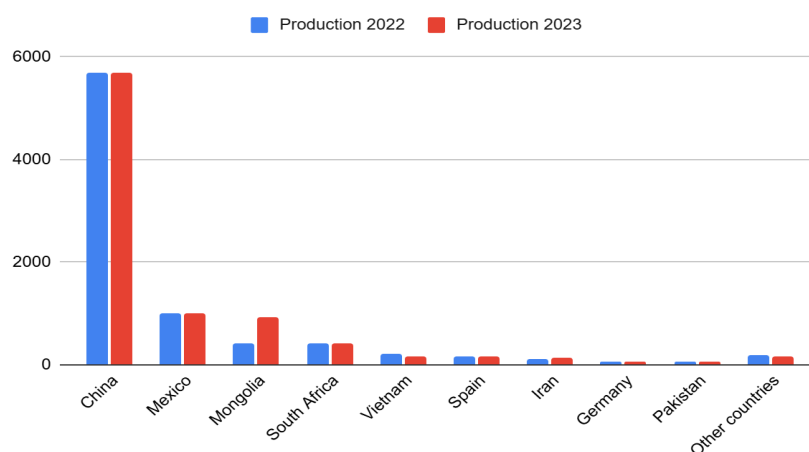


Figure 2: World fluorite mine production (2022–2023e) and reserves (thousand metric tons CaF_2). Source: USGS Mineral Commodity Summaries [6].

2.3. Common Impurities in Fluorspar Concentrates

Natural fluorite deposits are invariably associated with gangue minerals, the identity and abundance of which depend on deposit type and geological setting. The most commonly encountered impurities in fluorite ores and flotation concentrates are quartz, calcite, barite, and iron oxides [5, 7].

Quartz (SiO_2) is the most problematic impurity in fluorite processing. It is chemically stable under most conditions, insoluble in acids, and only slowly dissolved in alkalis at moderate temperatures, making it difficult to remove selectively. Quartz may occur as discrete grains, as fine particles entrained within the fluorite matrix, or as intergrowths with fluorite crystals, all of which impede complete separation. In the feed material used in the present study, silicon (measured by XRF) ranged from 2.12% to 3.79% across feed batches, corresponding to an estimated SiO_2 content of approximately 4.5–8.1% [5,11].

Calcite (CaCO_3) is a common gangue mineral in vein-type fluorite deposits and presents a particular analytical challenge because it contains calcium. Without correction for the calcium contributed by calcite, XRF-based estimation of CaF_2 will be systematically overestimated. Calcite is, however, readily dissolved by hydrochloric acid, making it amenable to removal by acid leaching [2,9].

Iron oxides (principally hematite, Fe_2O_3 , and goethite, FeOOH) are typically present in minor amounts but are undesirable in acid-grade fluorspar because they contaminate HF product streams and affect downstream reaction kinetics. Iron oxide minerals dissolve readily in hydrochloric acid, and their removal is one of the primary targets of the acid leaching stage [2,5].

Aluminosilicate minerals such as kaolinite, illite, and K-feldspar contribute both aluminum and potassium to the concentrate. These phases may dissolve partially under alkaline conditions, releasing aluminum species that can re-precipitate as aluminum hydroxide ($\text{Al}(\text{OH})_3$) during cooling or washing, a process-related challenge identified in the present study [10,13].

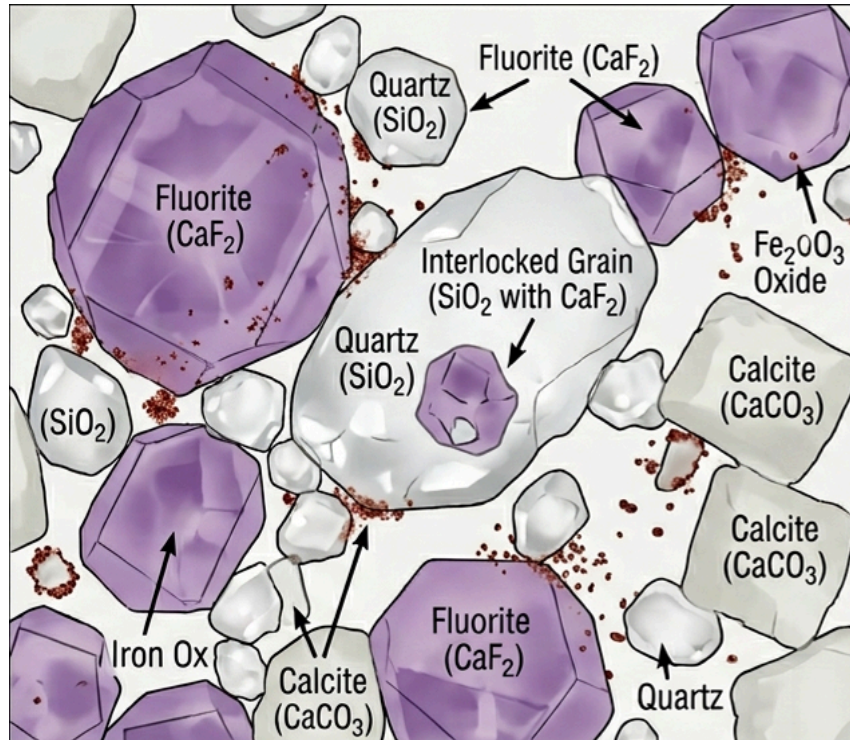


Figure 3: Schematic mineral association in a typical fluorite concentrate, showing fluorite (CaF_2) grains alongside quartz (SiO_2), calcite (CaCO_3), and iron oxide (Fe_2O_3) phases.

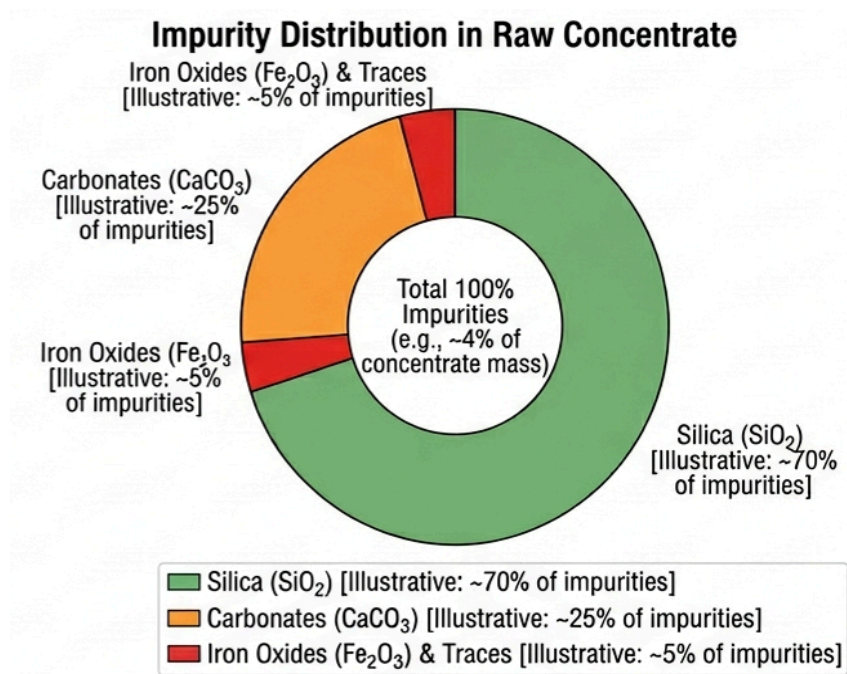


Figure 4: Indicative impurity composition of a raw fluorite flotation concentrate (values illustrative; actual composition varies by deposit).

2.4. Mechanical Beneficiation of Fluorite Ores

2.4.1. Overview and objectives

Mechanical beneficiation constitutes the first stage of fluorite processing and typically encompasses crushing, grinding, and froth flotation. The primary objective is to liberate fluorite from associated gangue minerals and thereby increase the CaF_2 content of the concentrate [5].

Flotation is the predominant beneficiation technique, exploiting differences in the surface properties of fluorite and gangue minerals. Collectors are employed to render fluorite particles hydrophobic, while depressants selectively inhibit minerals such as calcite and quartz [7,12]. Despite its effectiveness in upgrading fluorite ores, flotation frequently falls short of achieving acid-grade purity, particularly in the presence of fine particles and chemically stable impurities such as quartz. Additional chemical purification steps are therefore required.

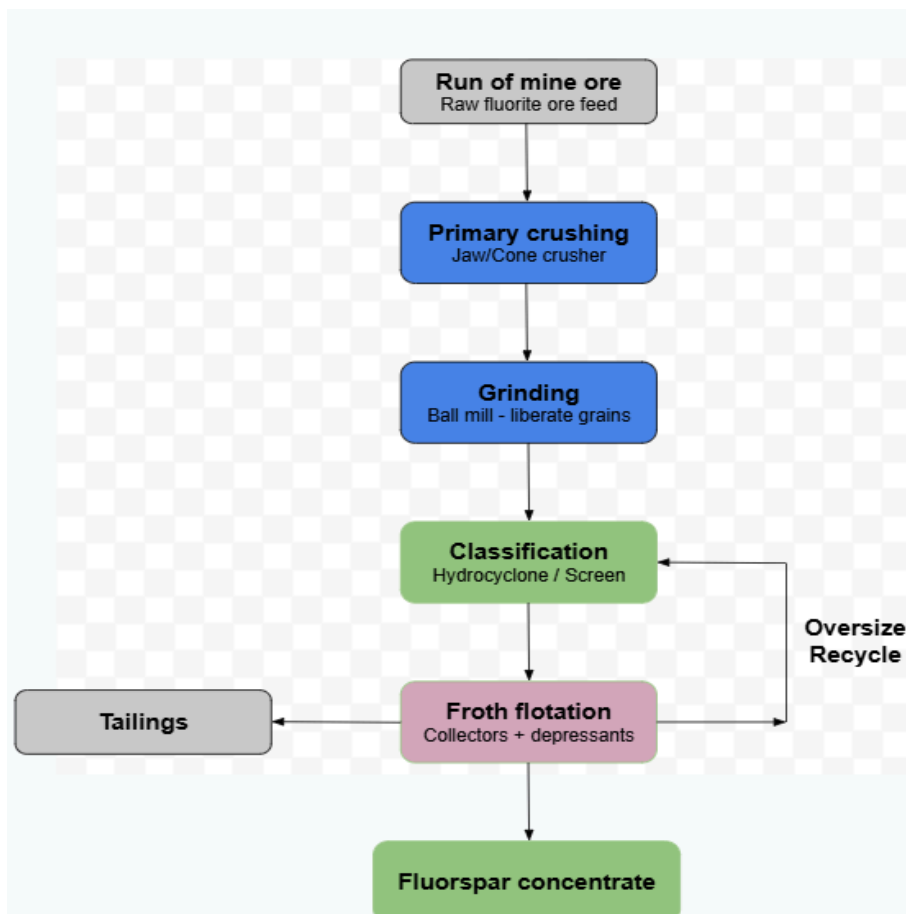


Figure 5: Overview of experimental approach and methodology

2.4.2. Comminution

Liberation of fluorite from gangue minerals requires reduction of particle size to expose mineral grain boundaries. This is achieved through comminution, which encompasses crushing and grinding operations. Crushing reduces run-of-mine ore to centimeter-scale fragments using jaw or gyratory crushers, while grinding further reduces the material to micrometer-scale particles in rotating ball mills [5].

The degree of grinding must be carefully controlled. Insufficient comminution results in composite particles in which fluorite and gangue remain interlocked, reducing separation efficiency. Excessive grinding generates fine particles that are difficult to recover by flotation and may contribute to impurity entrainment in the concentrate [5,12].

2.4.3. Froth flotation

Froth flotation is the dominant concentration method for fluorite ores, exploiting differences in surface chemistry between fluorite and gangue minerals. In flotation, the ground ore is suspended in water and conditioned with chemical reagents that selectively modify mineral surface properties [7,12].

Collectors, typically oleic acid or its sodium salt, adsorb onto the surface of fluorite, rendering it hydrophobic. Air is then introduced into the pulp, and hydrophobic fluorite particles attach to rising air bubbles and are recovered in the froth overflow as concentrate. Depressants such as sodium silicate and starch are used to maintain hydrophilicity on silica and calcite surfaces, preventing their recovery in the concentrate [7,12]. The selectivity of flotation is influenced by several parameters, including particle size, pulp pH, reagent type and dosage, and temperature.

Despite its effectiveness for upgrading fluorite ores to 85–95% CaF_2 , flotation frequently fails to achieve acid-grade purity due to the entrainment of fine silica particles and the close surface chemical similarity between fluorite and calcite [5,12]. Additional chemical purification steps are therefore required.

2.4.4. Flotation reagents

The effectiveness of flotation depends on the careful selection and dosage of chemical reagents, which are used to modify the surface properties of minerals and control froth stability. These reagents can be grouped into four main categories [14]:

Collectors are organic compounds that adsorb onto mineral surfaces, rendering target particles hydrophobic and enabling their attachment to air bubbles. Collectors are classified as either non-ionizing (e.g., kerosene, used for naturally hydrophobic minerals) or ionizing. Ionizing collectors include anionic types such as oxyhydryl collectors (fatty acids and carboxylates), widely used for fluorite flotation, and cationic types such as fatty amines and ether amines. Thiophosphate-based collectors such as Aerophine® 3422 are used for more selective flotation of metallic and aluminosilicate phases [15, 16]. Collector concentration must be carefully controlled: overdosing reduces selectivity and promotes gangue entrainment [14].

Frothers promote the formation and stability of small bubbles, reducing bubble rise velocity and supporting a persistent froth layer from which concentrate can be collected. Modern frothers are predominantly alcohols such as methyl isobutyl carbinol (MIBC) and polyglycols, which account for over 80% of frother usage in metallic ore flotation [14].

Depressants selectively suppress unwanted minerals by modifying their surface to maintain hydrophilicity, preventing attachment to air bubbles. In fluorite flotation, sodium silicate is commonly used to depress silica and clay minerals, while starch depresses calcite. Sodium silicate acts by dispersing fine particles and stabilizing the slurry, preventing gangue from floating [17]. However, overdosing or misapplication of depressants can suppress valuable minerals alongside gangue, reducing overall recovery [14].

Activators enhance the interaction between collectors and target mineral surfaces. Copper(II) sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) is a commonly used activator that modifies the surface chemistry of target minerals by replacing surface iron ions with copper, improving collector adsorption and attachment to air bubbles [14].

pH modifiers control the pulp acidity or alkalinity, influencing the surface charge of minerals and the effectiveness of collector adsorption. For alumino-silicate mineral flotation, near-neutral pH is generally optimal, as strongly acidic or alkaline conditions can suppress collector adsorption or cause surface dissolution [14].

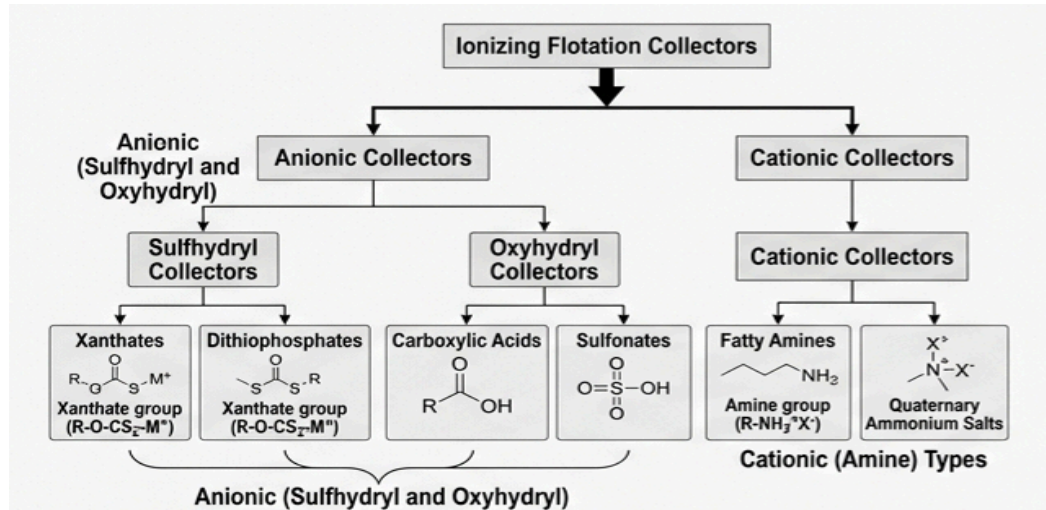


Figure 6: Classification of ionizing collectors used in froth flotation, showing anionic (sulfhydryl and oxyhydryl) and cationic (amine) types. Source: adapted from [14].

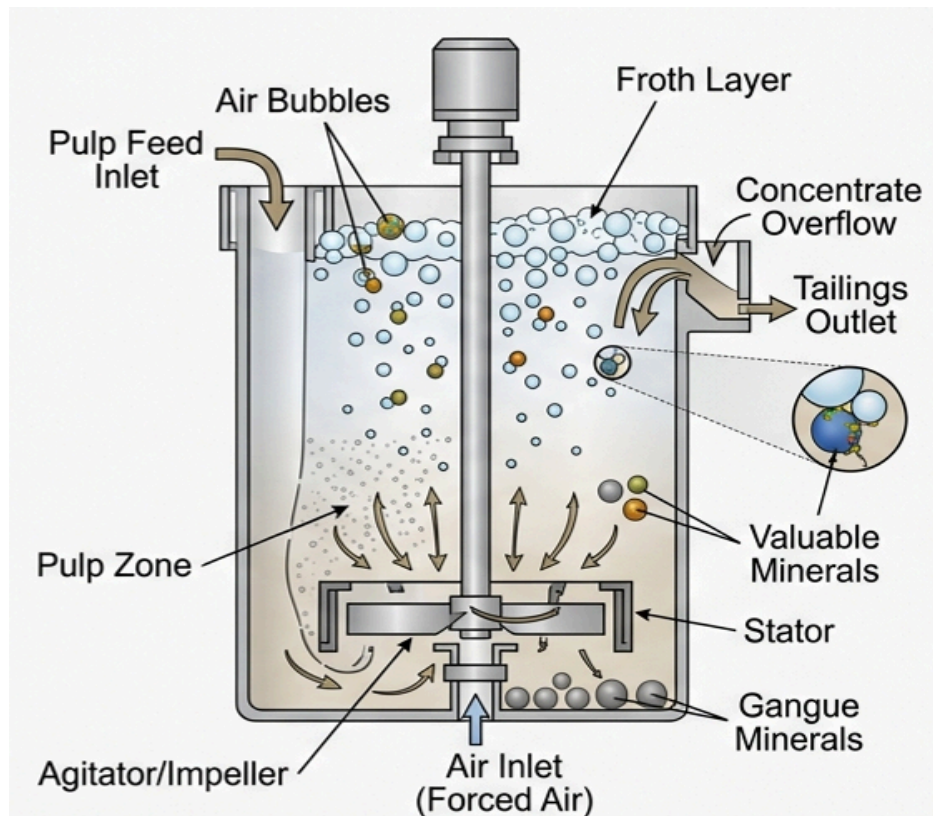


Figure 7: Schematic cross-section of a mechanical froth flotation cell, showing the impeller, air inlet, pulp zone, froth layer, and concentrate overflow.

2.4.5. Flotation circuit design

In practice, fluorite beneficiation requires multiple flotation stages to achieve high-grade concentrates. Open-circuit flotation is typically employed during the optimization phase to test individual processing parameters such as pH, collector type, and activator performance. Once optimal conditions are established, closed-circuit flotation comprising rougher, cleaner, and scavenger stages is applied to simulate continuous processing and evaluate overall recovery and grade [5].

The metallurgical performance of a flotation circuit is evaluated using mass balance equations relating the mass flows and compositions of the feed, concentrate, and tailings streams. Key performance indicators include mass recovery (yield), mineral grade in the concentrate, and overall recovery of the target mineral.

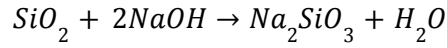
2.5. Acid Leaching for Removal of Carbonate and Iron Impurities

Acid leaching is an established chemical purification technique for removing carbonate and iron-bearing impurities from fluorite concentrates. Hydrochloric acid (HCl) is particularly effective, readily dissolving calcite and iron oxides under moderate conditions [2].

The reaction of calcite with HCl yields soluble calcium chloride and carbon dioxide gas, facilitating the removal of carbonate impurities. Iron oxides are similarly dissolved to form soluble iron species. Leaching efficiency is governed by factors including temperature, acid concentration, and reaction time; elevated temperatures enhance reaction kinetics and improve impurity removal. However, excessive acid consumption increases operational costs and may result in material loss if not carefully controlled. Notably, silica remains largely unaffected by acid leaching due to the chemical stability of quartz [5,11].

2.6. Alkaline Leaching for Silica Removal

Alkaline treatment with sodium hydroxide (NaOH) is widely employed to remove silica from fluorite concentrates. The strong Si–O–Si bond network of quartz renders it resistant to acid attack, yet susceptible to alkaline dissolution at elevated temperatures [11]. Under alkaline conditions, silica reacts with NaOH to form soluble sodium silicate:



The resulting sodium silicate is then removed during subsequent washing stages. Temperature is the dominant factor governing reaction efficiency; at lower temperatures, the dissolution rate is slow, while higher temperatures markedly accelerate silica removal [10,11]. NaOH concentration also plays a role, though its influence is secondary to that of temperature. Despite these advantages, complete silica removal remains difficult due to the inherent stability of quartz and its possible intergrowth with fluorite particles.

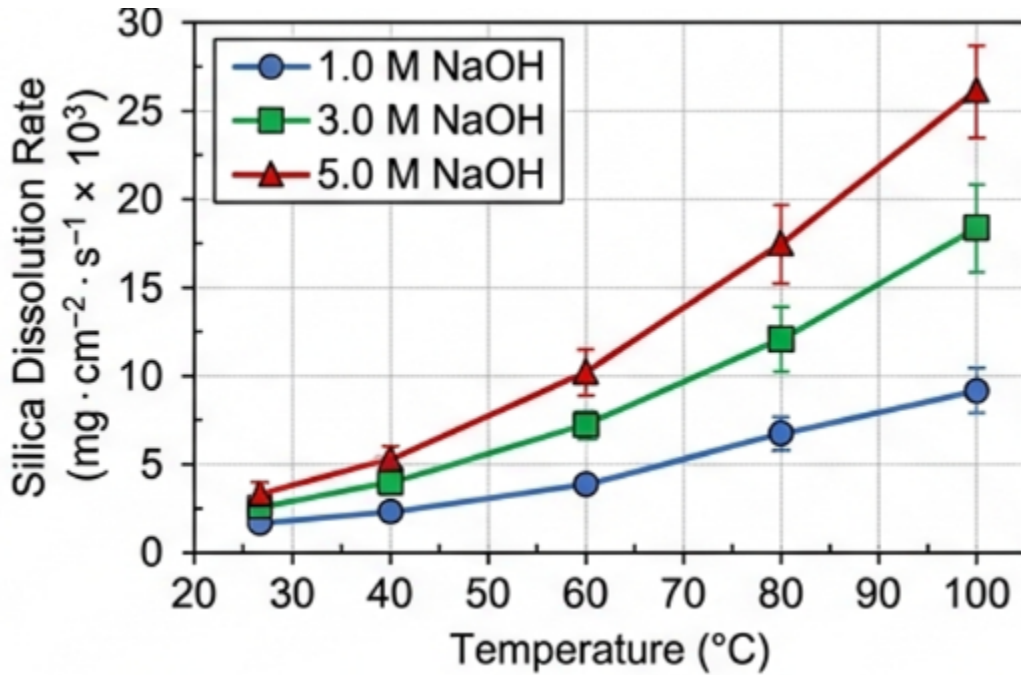


Figure 8: Effect of NaOH concentration and temperature on silica (SiO_2) removal efficiency (XRF data, present study).

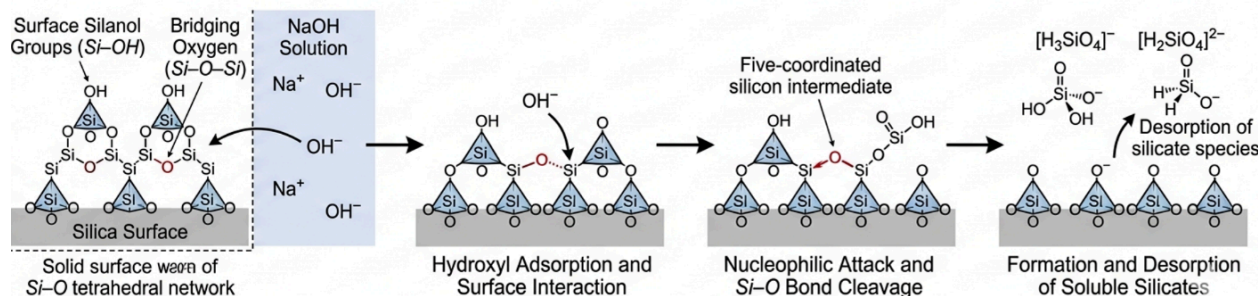


Figure 9: Schematic representation of the reaction mechanism for silica dissolution in sodium hydroxide solution.

2.7. Challenges in Producing Acid-Grade Fluorspar

Despite the availability of both mechanical beneficiation and chemical purification methods, several persistent challenges complicate the production of acid-grade fluorite.

Incomplete silica removal. Quartz is the most resistant common impurity in fluorite concentrates. Even under optimized alkaline leaching conditions, complete dissolution of crystalline quartz is rarely achieved in a single treatment stage. Fine quartz particles intergrown with fluorite are particularly difficult to remove, as they are physically inaccessible to the leaching solution [5,11].

Fine particle entrainment. During flotation, fine gangue particles may be physically entrained in the froth alongside hydrophobic fluorite particles. These entrained particles are not removed by chemical treatment and contribute to residual impurity levels in the final product [12].

Aluminium re-precipitation. When aluminosilicate minerals dissolve during NaOH leaching, aluminium is released into solution as aluminate. If washing is insufficiently thorough, aluminium hydroxide re-precipitates onto the surface of fluorite particles, introducing a new impurity. This was identified as a process issue in the present study, where Batch 4 (elevated Al content) showed elevated Al in the product after NaOH treatment [13].

Residual chloride contamination. HCl leaching introduces chloride ions into the system. Incomplete washing results in residual chloride remaining on the solid surface, observed across multiple experiments in this study. Chloride contamination affects both product quality and the accuracy of XRF analysis [5].

Feed heterogeneity. Natural variability in flotation concentrate composition, particularly in silica and aluminosilicate content, means that leaching conditions optimized for one feed

batch may not perform equivalently on another. This was evident in the present study, where Batch 4 had notably higher Si and Al content than Batches 1–3 [12].

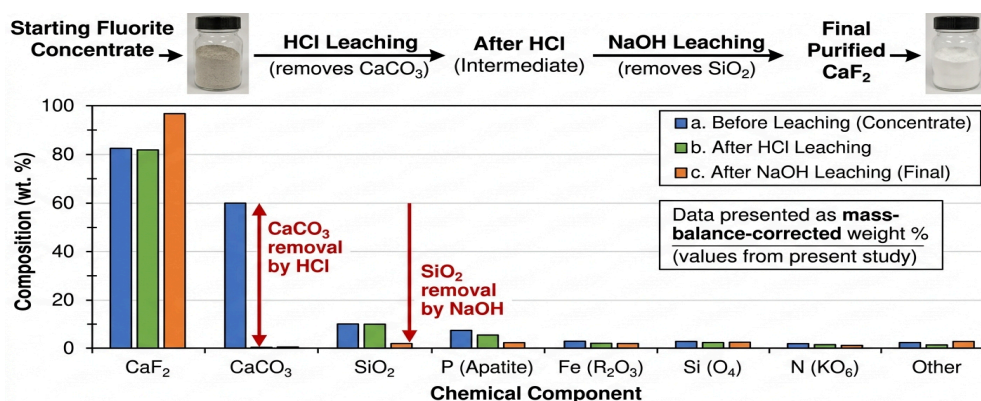


Figure 10: Chemical composition of fluorite concentrate before and after sequential HCl and NaOH leaching, based on XRF analysis (mass-balance-corrected values, present study).

2.8. Research Gap and Relevance of This Study

The review of the literature reveals that sequential HCl and NaOH leaching is well established as a viable route to chemical purification of fluorite concentrates. The fundamental chemistry of carbonate dissolution by HCl and silica dissolution by NaOH is well understood, and the general importance of temperature as a controlling variable for silica removal has been demonstrated in multiple studies [10,11].

However, several areas remain insufficiently characterized in the published literature. First, most published studies on fluorite chemical purification focus on carbonate and iron removal by acid leaching, with comparatively less systematic attention given to the conditions required for effective silica removal [5,12]. Second, the interaction between leaching stages, in particular the risk of aluminium re-precipitation when NaOH leaching follows acid treatment of aluminosilicate-bearing feeds, has received limited systematic investigation [13]. Third, published studies rarely report mass-balance-based product yield data alongside compositional analysis, making it difficult to assess whether improvements in purity come at the expense of CaF₂ recovery [9].

For Mongolian fluorite concentrates specifically, which tend to carry significant silica gangue, there is a practical need for data on the leaching conditions required to bridge the gap

between typical flotation concentrate quality (93% CaF_2) and the acid-grade specification ($\geq 97\%$ CaF_2). No published study was identified that systematically evaluates the combined effect of NaOH concentration (across the 1–4 M range) and temperature (70–90°C) on silica removal from Mongolian fluorite concentrates using quantitative XRF analysis at each process stage.

This study addresses these gaps through a controlled laboratory investigation in which seven experimental conditions are evaluated, NaOH concentration and temperature are systematically varied, and product composition is tracked at each stage using handheld XRF supported by mass balance calculations.

3. Materials and Methods

3.1. Feed Material and Sample Origin

The feed material used in this study was obtained as a fluorite flotation concentrate from an industrial operation in Mongolia. For confidentiality reasons, the exact location of the deposit is not disclosed. The concentrate was used as the primary feed material for the subsequent chemical purification experiments.

Prior to chemical treatment, the flotation concentrate was characterized to determine its chemical composition and mineralogical features. Chemical analysis was carried out using handheld X-ray fluorescence (XRF), which provides rapid, semi-quantitative elemental composition of mineral samples [9]. The results indicated that calcium was the dominant element, corresponding to CaF_2 , while silicon (2–4%), iron (~0.11–0.13%), and other minor elements were present as impurities requiring removal.

Additional mineralogical characterization using Mineral Liberation Analysis (MLA) confirmed that fluorite was the predominant mineral phase, with minor amounts of quartz, calcite, and iron oxide minerals [5]. The presence of quartz as the primary silica-bearing phase is particularly significant, as it is resistant to acid leaching and requires alkaline treatment for effective removal [5,11].

Variability in feed composition was observed, particularly in silica content (approximately 2–4%), reflecting the inherent heterogeneity of flotation concentrates [12]. This variability has a direct influence on the efficiency of subsequent chemical purification processes and necessitates careful control of operating parameters such as temperature and reagent concentration.

A separate flotation beneficiation study conducted at the German-Mongolian Institute for Resources and Technology (GMIT) was also considered for contextual comparison. However, it should be noted that the GMIT flotation study used a different fluorite ore sample from the concentrate investigated in the present chemical purification experiments. Therefore, the GMIT results are not treated as part of the experimental feed material in this study, but only as supporting background information to demonstrate the limitations of flotation and the need for additional chemical purification.

Overall, the characterization of the fluorite flotation concentrate provided the necessary baseline information for designing the purification procedure. Based on the identified impurity minerals, a sequential treatment approach was selected: HCl leaching was used to remove acid-soluble carbonate and iron-bearing impurities, while NaOH leaching was applied to target silica-bearing minerals such as quartz [2, 5, 11].

3.2. Chemicals and Reagents

The chemical reagents used in this study were hydrochloric acid (HCl) and sodium hydroxide (NaOH), both of analytical grade and used without further purification. Hydrochloric acid was prepared at a concentration of 1 M by dilution with distilled water and used for the removal of acid-soluble impurities, including carbonate minerals and iron oxides. Sodium hydroxide solutions were prepared at concentrations of 1 M, 2 M, and 4 M to investigate their effect on silica removal. Distilled water was used for all reagent preparation, washing, and dilution steps in order to minimize contamination and ensure consistency of experimental conditions.

3.3. Experimental Design

The purification process was carried out using a sequential chemical treatment approach consisting of acid leaching followed by alkaline treatment. This approach was selected to target different types of impurities based on their chemical reactivity. The overall process flow is illustrated in Figure 11.

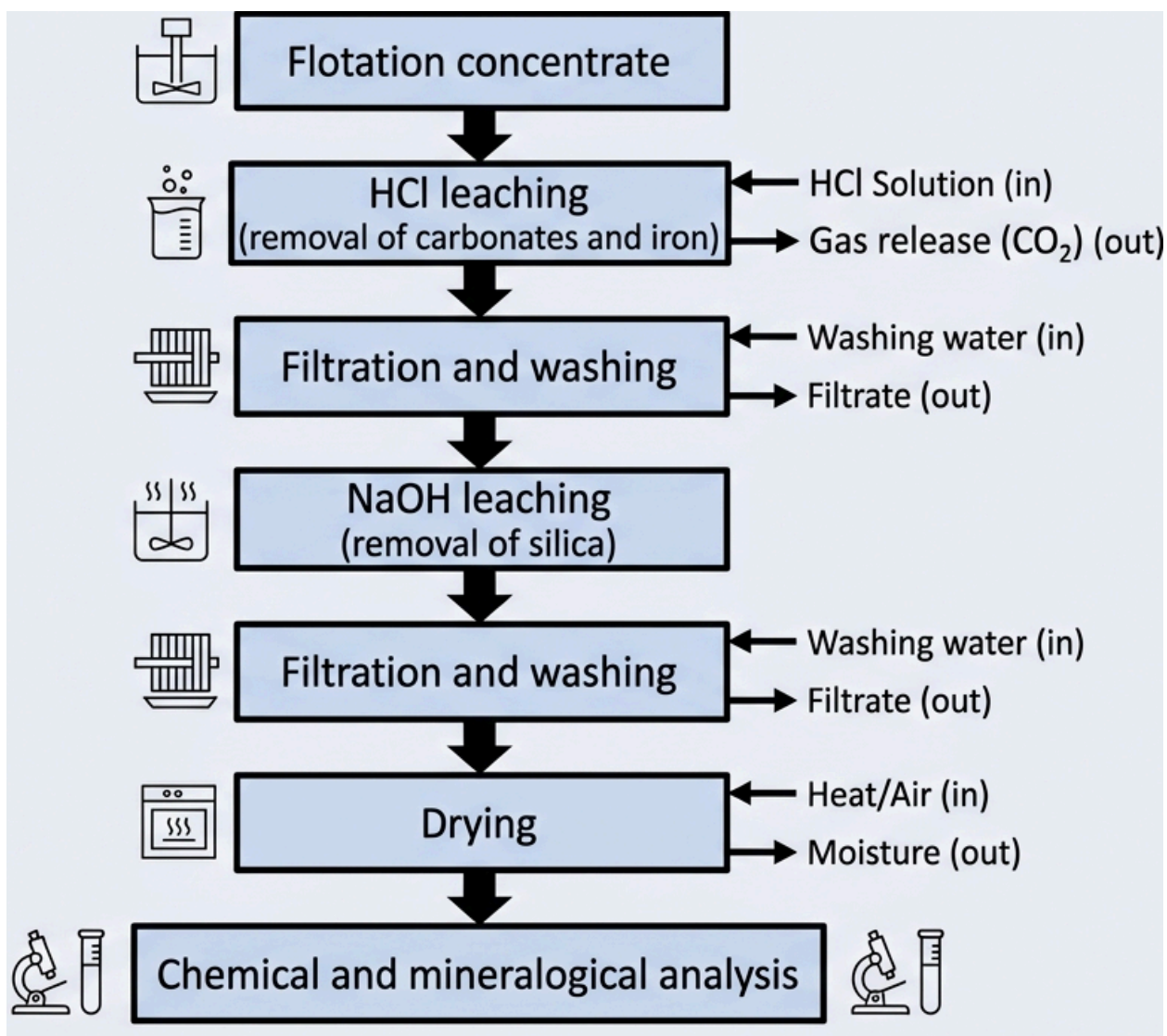


Figure 11: Experimental procedure flowsheet for the purification of the fluorite concentrate

A series of experiments were conducted under different conditions, varying the temperature and concentration of NaOH, in order to evaluate their influence on impurity removal efficiency.

3.4. HCl Leaching Procedure

Acid leaching experiments were carried out using hydrochloric acid at a concentration of 1 M. A fixed mass of fluorite concentrates (100 g) was added to the leaching solution in a glass reactor. The slurry was maintained at a temperature of approximately 50°C using a temperature-controlled water bath shown in Figure 12. Continuous stirring was applied throughout the experiment to ensure uniform mixing and effective contact between the solid and

liquid phases. The leaching process was conducted for a specified duration, after which the slurry was removed from the reactor and transferred for solid–liquid separation.



Figure 12: Leaching experiment setup in lab

3.5. NaOH Leaching Procedure

Following acid leaching and washing, the solid residue was subjected to alkaline treatment using sodium hydroxide solutions. NaOH solutions of varying concentrations (1 M, 2 M, and 4 M) were used to evaluate the effect of reagent strength on silica dissolution. The experiments were conducted at temperatures of 70°C and 90°C in order to investigate the influence of temperature on reaction kinetics. The treated slurry was continuously stirred during the leaching process to ensure proper mixing. After completion of the reaction, the slurry was transferred for filtration and washing.

3.6. Solid–Liquid Separation, Washing, and Drying

After each leaching stage, solid–liquid separation was carried out using vacuum filtration (Figure 13). The slurry was filtered through fine filter paper to retain solid particles while allowing

the liquid phase containing dissolved impurities to pass through. The solid residue was washed multiple times with distilled water to remove residual reagents and dissolved species. Washing was continued until the filtrate approached neutral conditions, indicating the removal of acid or alkaline residues. This step is critical for preventing contamination of the final product and avoiding re-precipitation of dissolved species during drying.



Figure 13: Vacuum filtration system

3.7. Drying and Sample Preparation

After washing, the solid residue was transferred to a drying oven (Figure 14) and dried at 105°C for at least 12 hours to remove residual moisture. The dried samples were cooled to room temperature and weighed using an analytical balance. The dried material was then prepared for subsequent chemical and mineralogical analysis.



Figure 14: Oven for sample drying

3.8. Analytical Methods

3.8.1. X-ray Fluorescence (XRF) Analysis

The chemical composition of the feed and treated samples was determined using handheld X-ray fluorescence (XRF) analysis with a Niton XL2 (Figure 15). This method provides rapid and semi-quantitative elemental composition of the samples. It should be noted that XRF does not detect light elements such as fluorine, and therefore CaF_2 content cannot be directly measured using this technique.



Figure 15: Portable XRF analyzer

However, it should be noted that XRF has limitations in detecting light elements, particularly fluorine. As a result, the CaF_2 content cannot be directly measured using this method and must be estimated indirectly from calcium content or determined using complementary analytical techniques such as titration.

Additionally, the accuracy of handheld XRF may be influenced by factors such as sample heterogeneity, surface conditions, and calibration, which can introduce a degree of uncertainty in the results.

Therefore, XRF analysis was primarily used for trend evaluation and elemental comparison, while more accurate quantitative results were obtained from titration and gravimetric methods.

3.8.2. X-ray Diffraction (XRD) Analysis

Mineralogical composition of selected samples was analyzed using X-ray diffraction (XRD). This technique was used to identify crystalline phases present in the material, including fluorite, quartz, and calcite.

XRD provides qualitative and semi-quantitative information on phase composition and serves as a complementary method to chemical analysis. It is particularly useful for

distinguishing mineral phases with similar elemental composition that cannot be differentiated by XRF alone. The relative intensity of diffraction peaks was used to assess changes in phase abundance before and after treatment, providing insight into impurity removal and fluorite enrichment.

3.8.3. Titration and Gravimetric Analysis

Quantitative determination of CaF_2 , CaCO_3 , and SiO_2 content was carried out using titration and gravimetric methods (MNS4928:2000). These methods provide more accurate determination of fluorite grade compared to XRF analysis alone.

XRD provides qualitative and semi-quantitative information on phase composition, allowing validation of the results obtained from chemical analyses. It is particularly useful for distinguishing between mineral phases with similar elemental compositions, which cannot be differentiated by XRF alone. Therefore, XRD analysis served as an essential complementary method for verifying phase transformations and assessing the effectiveness of the purification process.

The relative intensity of diffraction peaks was also used to assess changes in phase abundance before and after treatment, providing further insight into impurity removal and fluorite enrichment.

3.9. Calculation Methods

Product yield was calculated based on the mass of the dried residue relative to the initial feed mass:

$$Yield (\%) = \frac{m_{residue}}{m_{feed}} \times 100 \quad (3.9.1)$$

Mass loss during the process was determined by comparing the initial feed mass with the final residue mass:

$$Mass Loss (\%) = \frac{m_{feed} - m_{residue}}{m_{feed}} \times 100 \quad (3.9.2)$$

Since XRF measures elemental silicon, it was converted to silica content using the molecular weight ratio:

$$\text{SiO}_2(\%) = \text{Si}(\%) \times 2.139 \quad (3.9.3)$$

The recovery of CaF_2 during flotation was calculated using the mass and grade of the concentrate relative to the feed. Recovery represents the percentage of valuable mineral recovered into the concentrate and was calculated using Equation 3.9.4:

$$\text{Recovery}(\%) = \frac{m_{\text{conc}} \times C_{\text{conc}}}{m_{\text{feed}} \times C_{\text{feed}}} \times 100$$

where:

m_{conc} = mass of concentrate (g)

m_{feed} = mass of feed (g)

C_{conc} = CaF_2 grade in concentrate (%)

C_{feed} = CaF_2 grade in feed (%)

The removal efficiency of impurities such as Fe, Si, and CaCO_3 was calculated by comparing the initial and final concentrations before and after leaching. (3.9.5)

$$\text{Removal}(\%) = \frac{C_i - C_f}{C_i} \times 100$$

where:

C_i = initial concentration of impurity before treatment (%)

C_f = final concentration of impurity after treatment (%)

The mass balance total of the titration and gravimetric analysis was calculated as:

$$\text{MB}(\%) = \text{CaF}_2(\%) + \text{CaCO}_3(\%) + \text{SiO}_2(\%)$$

Corrected CaF_2 values were calculated by normalizing the raw CaF_2 value to a 100% mass balance:

$$\text{Corrected CaF}_2(\%) = \text{CaF}_2(\text{raw}) \times \frac{100}{\text{MB}}$$

where MBMBMB is the mass balance total (%). This correction was used only to support interpretation of the analytical results and does not replace the measured titration values.

3.10. Reliability and Limitations of the Experimental Methods

The experimental results may be influenced by variability in feed composition, particularly in silica content. In addition, the use of handheld XRF introduces some uncertainty due to its semi-quantitative nature. Despite these limitations, the combination of XRF, XRD, and titration methods provides a reliable basis for evaluating the effectiveness of the purification process.

4. Results and Discussion

4.1. Feed Concentrate Characterization

4.1.1. Chemical Composition (XRF)

The fluorite concentrate used in this study was characterized by handheld XRF analysis prior to chemical treatment. The results showed that calcium was the dominant element, confirming CaF_2 as the primary component of the material. Silicon, iron, and potassium were identified as the main impurities.

Batch	Sample	Bal (%)	Si (%)	S (%)	Cl (%)	K (%)	Ca (%)	Fe (%)	Al (%)	Sr (%)	P (%)	Nb (%)
Feed batch 1 was used for Experiments 1, 2, and 3												
1	#191	53.44	2.14	0.060	0.028	0.210	43.51	0.136	—	0.023	—	0.010
1	#192	53.42	2.31	0.086	—	0.198	43.47	0.121	—	0.021	—	—
1	#193	53.55	1.91	0.097	0.023	0.185	43.61	0.121	—	0.022	—	—
Average Batch 1		53.47	2.12	0.081	0.026	0.198	43.53	0.126	—	0.022	—	—
Feed batch 2 was used for Experiment 5 (HCl 50°C + NaOH 2M 90°C)												
2	#410	56.34	2.25	0.058	0.044	0.423	40.13	0.116	—	0.020	0.058	—
2	#411	55.52	2.06	0.025	0.040	0.383	41.46	0.111	—	0.021	0.097	—
2	#412	54.57	2.23	0.034	0.031	0.427	41.84	0.122	—	0.021	—	—
Average Batch 2		55.48	2.18	0.039	0.038	0.411	41.14	0.116	—	0.021	—	—
Feed batch 3 was used for Experiments 6 and 7 (NaOH 2M 70°C and 4M 70°C)												
3	#482	53.07	2.18	0.025	0.042	0.216	43.62	0.112	—	0.021	0.070	—
3	#483	52.86	2.09	—	0.039	0.188	44.25	0.122	—	0.021	—	—
3	#485	53.07	2.24	0.025	0.045	0.212	43.49	0.117	—	0.021	0.081	—
Average Batch 3		53.00	2.17	0.025	0.042	0.205	43.79	0.117	—	0.021	—	—
Feed batch 4 was used for Experiment 8 (HCl 50°C + NaOH 4M 90°C)												
4	#537	46.68	4.80	0.064	0.031	0.268	45.98	0.149	1.880	0.021	—	—
4	#538	48.06	3.30	0.068	0.036	0.213	46.63	0.129	1.370	0.021	—	0.046
4	#539	49.02	3.28	0.066	0.028	0.230	45.89	0.120	1.250	0.020	0.070	—
Average Batch 4		47.92	3.79	0.066	0.032	0.237	46.17	0.133	1.500	0.021	—	—

Table 2: XRF elemental composition of all feed concentrate samples

Note: (—) indicates element not detected or below instrument detection limit. Yellow rows show batch averages used for comparative analysis.

Silicon content ranged approximately from 2.1% to 3.8% across different feed batches, while iron content remained relatively consistent at around 0.11–0.13%. In one batch, aluminum was detected at significantly higher levels (1.5%), indicating the presence of aluminosilicate minerals. The observed variation in silica and aluminum content reflects the natural heterogeneity of the flotation concentrate. This variability is expected to influence the efficiency of chemical purification, particularly for silica removal.

4.1.2. Mineralogical Composition (XRD)

XRD analysis shown in Figure 16 confirmed that fluorite (CaF_2) is the dominant mineral phase in the concentrate. However, minor peaks corresponding to quartz (SiO_2) and calcite (CaCO_3) were also identified.

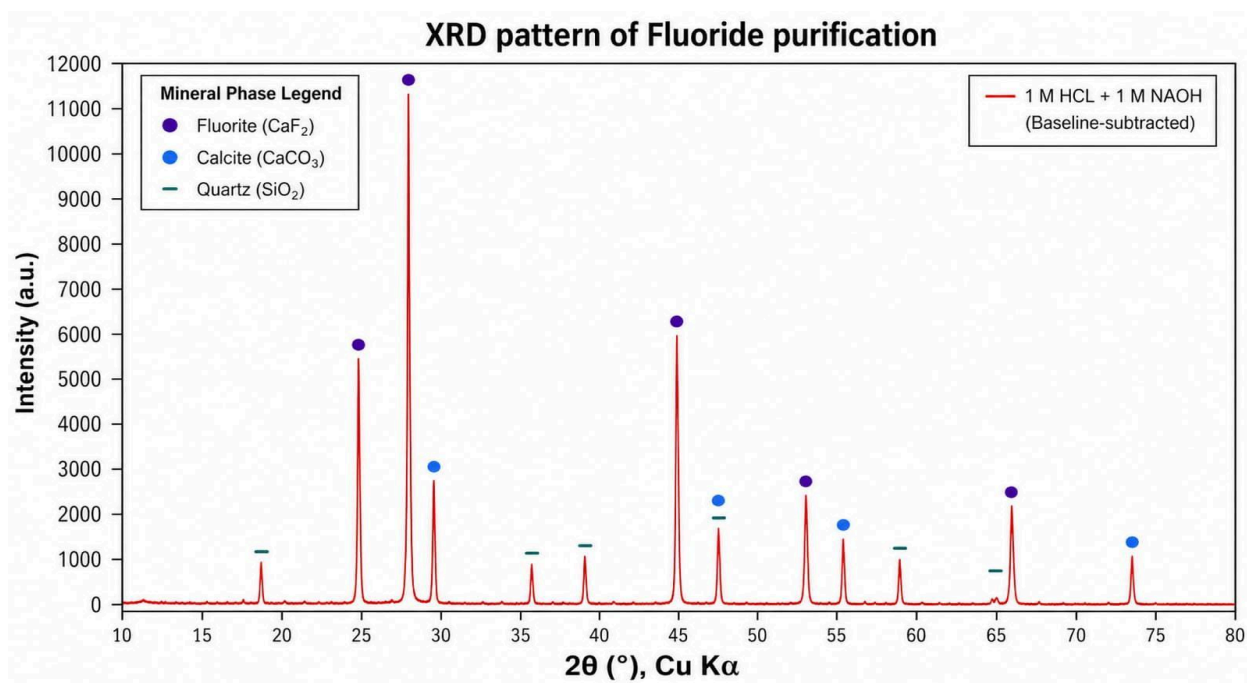


Figure 16: XRD Analysis of Chemically Purified Fluorite Concentrate

The presence of quartz is particularly significant, as it is known to be highly stable and resistant to chemical attack. This explains the difficulty of silica removal during chemical treatment. Similarly, calcite contributes to calcium content and may interfere with accurate estimation of CaF_2 grade if not removed.

4.1.3. Initial CaF_2 , CaCO_3 , and SiO_2 Contents

Titration and gravimetric analysis (Table 3) showed that the feed material contained approximately 93% CaF_2 , with minor amounts of CaCO_3 (~1%) and a relatively high silica

content (~6–7%). These results indicate that although the concentrate is already of relatively high grade, it does not meet the acid-grade requirement of $\geq 97\%$ CaF_2 . The removal of silica and carbonate impurities is therefore necessary to improve product quality.

Numbers	Mineral	CaF_2	CaCO_3	SiO_2
8	(Feed sample)	93.02	1.06	6.98

Table 3: Titration analysis of chemically purified fluorite concentrates and the feed

The characterization results indicate that the main purification challenges are the removal of silica and carbonate impurities. While carbonate minerals are expected to be removed effectively by acid leaching, silica, primarily present as quartz, requires more aggressive conditions for dissolution. This confirms the need for a sequential treatment approach combining acid and alkaline leaching.

4.2. Flotation Beneficiation: Result and Discussion

4.2.1. Feed Characterisation

The flotation results presented in this section are from a separate GMIT study and are used only for comparison. The ore sample was characterized by chemical analysis (MNS 4928:2000, MNS 4929:2000) and XRD mineralogical analysis using a Rigaku Miniflex 300/600 D/TeX Ultra2 with Cu-K α radiation. Chemical analysis showed the feed contained 34.65% CaF_2 , 56.2% SiO_2 , 4.21% CaCO_3 , and less than 0.05% each of total sulfur and phosphorus. XRD analysis identified three principal phases: fluorite (CaF_2) at 39.0%, quartz (SiO_2) at 52.3%, and calcite (CaCO_3) at 8.7%. The high quartz content confirmed that significant gangue rejection would be required to achieve acid-grade purity. The ore was described as comprising fluorite-cemented rock with quartz veining, exhibiting dark grey, blue-grey, and green-colored fluorite.

No.	Sample	CaF_2 (%)	SiO_2 (%)	CaCO_3 (%)	S / P (%)
1	Primary ore (feed)	34.65	56.2	4.21	<0.05

Table 4: Chemical analysis results of the primary ore sample

4.2.2. Sample Preparation and Sieve Analysis

The 50 kg sample was crushed to -2.0 mm using a laboratory jaw crusher, then homogenized and split using the cone-and-quartering method and a Jones riffle splitter into representative 1 kg subsamples for test work. Sieve analysis was carried out across size fractions from +2 mm to -0.074 mm. Results showed that CaF₂ content was relatively uniform across all size fractions, ranging from 28.4% in the +2 mm fraction to 51.35% in the -0.5+0.25 mm fraction, indicating that fluorite is distributed throughout the particle size range without significant size-dependent concentration.

Mineral Phase	Formula	Reference Code	Content (%)
Fluorite	CaF ₂	96-100-0044	39
Quartz	SiO ₂	96-900-0776	52.3
Calcite	CaCO ₃	96-101-0929	8.7

Table 5: Mineralogical composition of feed ore by XRD analysis

4.2.3. Grinding Optimization

Grinding experiments were carried out using a laboratory rod mill on 1 kg sub-samples crushed to -2.0 mm, at a solid-to-liquid-to-rod ratio of 1.0:0.65:9.0. Grinding times of 15, 20, and 25 minutes were tested, producing P₈₀ products at approximately 74 µm, P₇₀ at 74 µm, and P₆₀ at 74 µm, respectively. Single-stage rougher flotation tests were run at each grind size under fixed reagent conditions (JKTM 400 g/t, aluminium sulfate 0.6 g/t, sodium silicate 900 g/t, pH 11). Results showed that P₆₀-74 µm gave the best balance of concentrate grade and fluorite recovery, and this grind size was selected for all subsequent experiments.

Grind Size	Product	Yield (%)	CaF ₂ Grade (%)	Fluorite Recovery (%)
P ₈₀ -74 µm	Concentrate	28.55	89.5	62.3
P ₈₀ -74 µm	Tailings	71.45	21.78	37.7
P ₇₀ -74 µm	Concentrate	34.58	71.2	60
P ₇₀ -74 µm	Tailings	65.42	22.95	40
P ₆₀ -74 µm	Concentrate	39.81	78.6	76.3
P ₆₀ -74 µm	Tailings	60.19	14.39	23.7

Table 6: Flotation results for grinding optimization (pH 11, JKTM 400 g/t, Na₂SiO₃ 900 g/t)

4.2.4. pH Optimization

The effect of pulp pH on flotation performance was investigated at pH values of 6, 8, 10, and 11 at a P_{80} –74 μm grind size. Results showed that pH 10 gave the best combination of concentrate grade (82.9% CaF_2) and fluorite recovery (75.18%) at a yield of 37.2%. At pH 11, grade improved to 89.5%, but recovery dropped to 62.3%. At pH 8 and 6, both grade and recovery declined significantly. Consequently, pH 10 was selected as the standard operating condition for subsequent flotation tests.

pH	Product	Yield (%)	CaF_2 Grade (%)	Fluorite Recovery (%)
pH 11	Concentrate	28.55	89.5	62.3
pH 11	Tailings	71.45	21.78	37.7
pH 10	Concentrate	37.2	82.9	75.18
pH 10	Tailings	62.8	14	24.82
pH 8	Concentrate	31.23	73.1	55.7
pH 8	Tailings	68.77	19.06	44.3
pH 6	Concentrate	11.83	64.6	18.63
pH 6	Tailings	88.17	38.12	81.37

Table 7: Effect of pulp pH on rougher flotation performance (P_{80} –74 μm)

4.2.5. Collector and Depressant Optimization

A comparative collector trial evaluated JKTm at 400, 800, and 1000 g/t and a combined JKTm + Berol mixture at 400 + 400 g/t. The combination of JKTm and Berol at 400 + 400 g/t gave the best result, achieving a 73.5% CaF_2 grade at 76.35% fluorite recovery with a yield of 42.58% and was selected as the optimal collector system. For calcite depression, three depressants were compared: F100 (1000 g/t), lignosulfonate (1000 g/t), and Benefloat (1000 g/t). Benefloat produced the lowest CaCO_3 content in the concentrate (1.99%) and was selected as the calcite depressant. Dosage optimization showed that Benefloat at 100–250 g/t per flotation stage gave acceptable fluorite recovery without over-suppression, and this range was adopted for circuit testing.

4.2.6. Open-Circuit Flotation

Open-circuit flotation was conducted using 1 kg sub-samples ground to P_{80} –74 μm , with one rougher, one scavenger, and four cleaner stages. The reagent suite comprised JKTm +

Berol (400+400 g/t), aluminium sulfate (0.6 g/t), sodium silicate (900 g/t), Benefloat (250 g/t), and MIBC frother, at pH 10. After four cleaning stages, the concentrate contained 96.10% CaF_2 at a yield of 22.3% and a fluorite recovery of 58%. The tailings assayed 2.15% CaF_2 , confirming effective rejection of gangue. Although the concentrate grade approached the acid-grade threshold, it did not consistently reach 97% CaF_2 by chemical analysis.

Stage	Yield (%)	CaF_2 Grade (%)	Recovery (%)	pH
Rougher concentrate	43.2	76.2	90	10
Cleaner 1	36.3	88.1	87	10
Cleaner 2	31.2	93.1	79	10
Cleaner 3	27.2	95.27	71	10
Cleaner 4 (final)	22.3	96.1	58	10
Combined tailings	54.8	2.15	3.4	10

Table 8: Open-circuit flotation results—progressive cleaner stages

4.2.7. Closed-Circuit Flotation

Closed-circuit flotation tests were conducted on two 1 kg sub-samples following the open-circuit optimized conditions, with one rougher, four cleaner stages, and one scavenger stage. The combined result of both closed-circuit tests yielded a concentrate with 94.53% CaF_2 at 25.4% yield and 68.8% fluorite recovery. Concentrate 1 assayed 92.66% CaF_2 (yield 11.3%, recovery 30.0%), and Concentrate 2 assayed 96.03% CaF_2 (yield 14.1%, recovery 38.8%). XRD analysis of the final concentrate confirmed 97.0% fluorite and 3.0% calcite. The tailings were predominantly quartz (96.9% SiO_2) with only 2.0% residual CaF_2 and 1.1% CaCO_3 , confirming effective gangue rejection.

Product	Mass (g)	Yield (%)	CaF_2 (%)	Recovery (%)
Concentrate 1	226.3	11.3	92.66	30
Concentrate 2	282	14.1	96.03	38.8
Combined concentrate	508.3	25.4	94.53	68.8
Scavenger product	50.5	2.5	35.14	2.5

Combined tailings	1095.8	54.8	2.15	3.4
Feed	2000	100	34.93	100

Table 9: Closed-circuit flotation mass balance results

4.2.8. Additional Fine Grinding and Final Flotation

Since chemical analysis of the combined concentrate did not consistently reach 97% CaF_2 , concentrates 1 and 2 were subjected to additional fine grinding using a laboratory attrition mill, followed by a further single-stage cleaning flotation under reduced reagent conditions (JKTM + Berol 200+200 g/t, sodium silicate 200 g/t, Benefloat 100 g/t, pH 10, and agitation 800 rpm). The final product after this additional treatment achieved 97.42% CaF_2 and 0.78% CaCO_3 by chemical analysis, meeting the acid-grade specification. This confirms that the ore can be upgraded to acid-grade quality, but only with an additional fine-grinding and cleaning stage beyond the standard four-cleaner circuit.

4.2.9. Conclusions from Flotation Study

The flotation study on the Mongolrostsvetmet fluorite ore established the following key findings. The ore contained 34.65% CaF_2 and 56.2% SiO_2 as feed, requiring substantial upgrading. A grind size of P_{80} –74 μm was optimal for mineral liberation. The collector combination of JKTM + Berol (400 + 400 g/t) at pH 10 with Benefloat (100–250 g/t) as a calcite depressant gave the best selectivity. Four-stage closed-circuit flotation produced a combined concentrate of 94.53% CaF_2 at 68.8% recovery, confirmed at 97.0% CaF_2 by XRD. Chemical analysis reached the acid-grade threshold of $\geq 97\%$ CaF_2 only after an additional fine-grinding and cleaning stage, yielding 97.42% CaF_2 . These results demonstrate that while flotation alone can approach acid-grade quality, the combination of optimized flotation and additional fine grinding is required to consistently meet the specification, underscoring the importance of the sequential chemical purification steps investigated in this thesis.

4.3. Effect of HCl Leaching

4.3.1. Removal of Iron and Carbonate Impurities

The impacts of HCl leaching on the removal of iron and carbonate impurities are clear and consistent. Iron content was reduced in all experiments (Table 6) between about 2.6 and 22.6% relative to the initial concentration. Experiments 6 and 8 saw the biggest drops, suggesting that acid leaching is able to dissolve iron-bearing phases under the applied conditions.

Simultaneously, a show of the increased content of calcium was detected after the treatment. This decrease is not new calcium but is due to the selective removal of those gangue minerals such as calcite and iron oxides, resulting in relative enrichment of CaF_2 in the solid residue.

In contrast, silica content showed no consistent decrease after acid treatment. Minor fluctuations were observed; however, these variations fall within the expected range of analytical uncertainty and feed heterogeneity. This confirms that silica, primarily present as quartz, remains chemically stable under the applied acidic conditions.

These results demonstrate that HCl leaching is highly effective for the removal of acid-soluble impurities such as iron and carbonates but is insufficient for silica removal. Therefore, an additional treatment step is required to target quartz-associated impurities.

Order	Initial (Fe)	After HCl (Fe)	Change (%) of Fe	Initial (Ca)	After HCl (Ca)	Change (%) of Ca	Initial (Si)	After HCl(Si)	Change (%) of Si
Exp 5	0.116	0.108	-6.90%	41.14	44.28	+7.63%	2.18	2.21	+1.38%
Exp 6	0.117	0.091	-22.22%	43.79	44.60	+1.85%	2.17	2.10	-3.23%
Exp 7	0.117	0.114	-2.56%	43.79	47.82	+9.20%	2.17	2.21	+5.07%
Exp 8	0.133	0.103	-22.56%	46.17	45.81	-0.78%	3.79	3.72	-1.85%

Table 10: Result of HCl of leaching

An increase in chloride content was observed after acid leaching, indicating incomplete removal of residual acid during washing. In some cases, chloride levels exceeded 0.10%, suggesting that washing efficiency is a critical factor. Residual chloride may affect both products

quality and analytical results. Therefore, sufficient washing is necessary to ensure accurate evaluation of purification performance.

4.4. Effect of NaOH Leaching

Temperature was identified as the most important factor influencing silica removal. At 70°C, only minor, consistent changes in silica content were observed, indicating limited dissolution. At 90°C, a measurable reduction in silica content was achieved. This demonstrates that higher temperature significantly enhances the dissolution of silica. This behavior is consistent with the strong structural stability of quartz, which requires elevated temperatures to achieve sufficient reaction kinetics.

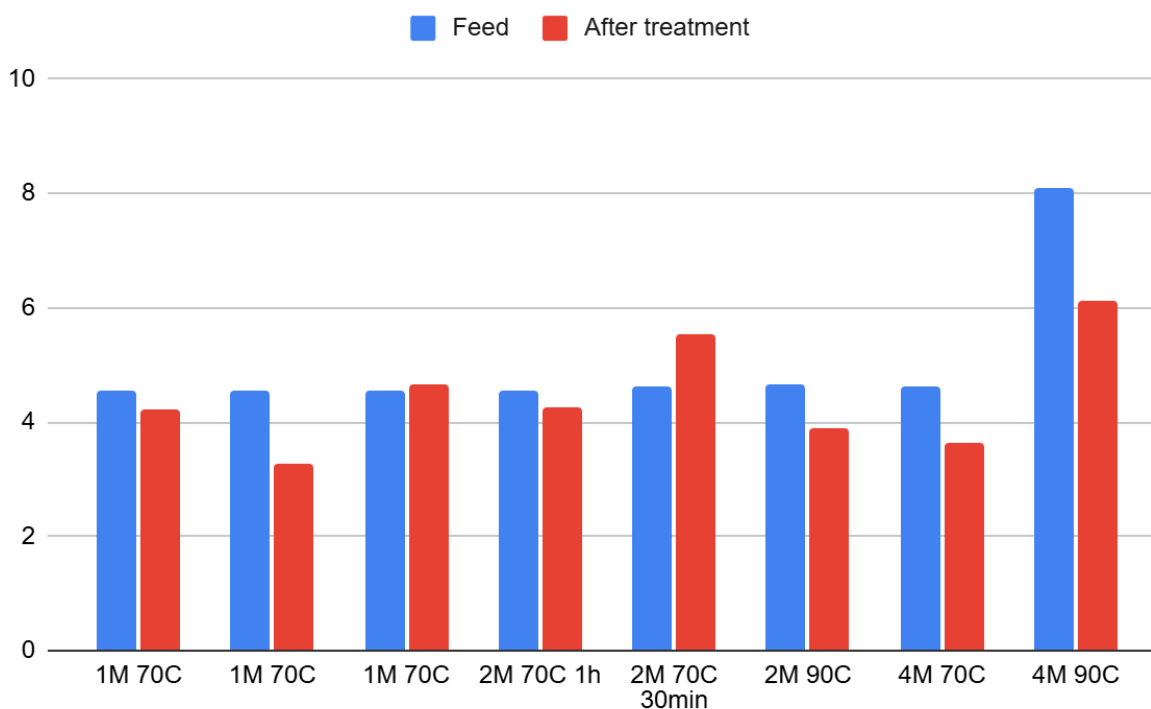


Figure 17: Result of NaOH treatment

The effect of NaOH concentration was less significant compared to temperature. Increasing concentration from 1M to 4M did not result in substantial improvement in silica removal at lower temperatures. At higher temperatures, increased concentration showed some improvement, but the overall effect remained moderate. This indicates that silica dissolution is primarily controlled by reaction kinetics rather than reagent availability.

Silica removal occurs through the reaction between SiO_2 and NaOH , forming soluble sodium silicate. This reaction involves breaking strong Si–O–Si bonds, which requires sufficient thermal energy. As a result, the dissolution of quartz is limited at lower temperatures but becomes more significant at elevated temperatures. Despite improved performance at higher temperatures, complete silica removal was not achieved. Residual silica remained in all samples, indicating that quartz dissolution was only partial under the applied conditions. This limitation may be due to the high stability of quartz, insufficient reaction time, or physical association of silica with fluorite particles.

4.5. Combined Effect of Sequential Treatment (HCl + NaOH)

The sequential application of HCl and NaOH leaching resulted in an overall improvement in fluorite purity. HCl effectively removed carbonate and iron impurities, while NaOH contributed to partial silica removal. The combination of both treatments is therefore necessary to target different types of impurities. However, the results indicate that full optimization is required to achieve acid-grade specifications.

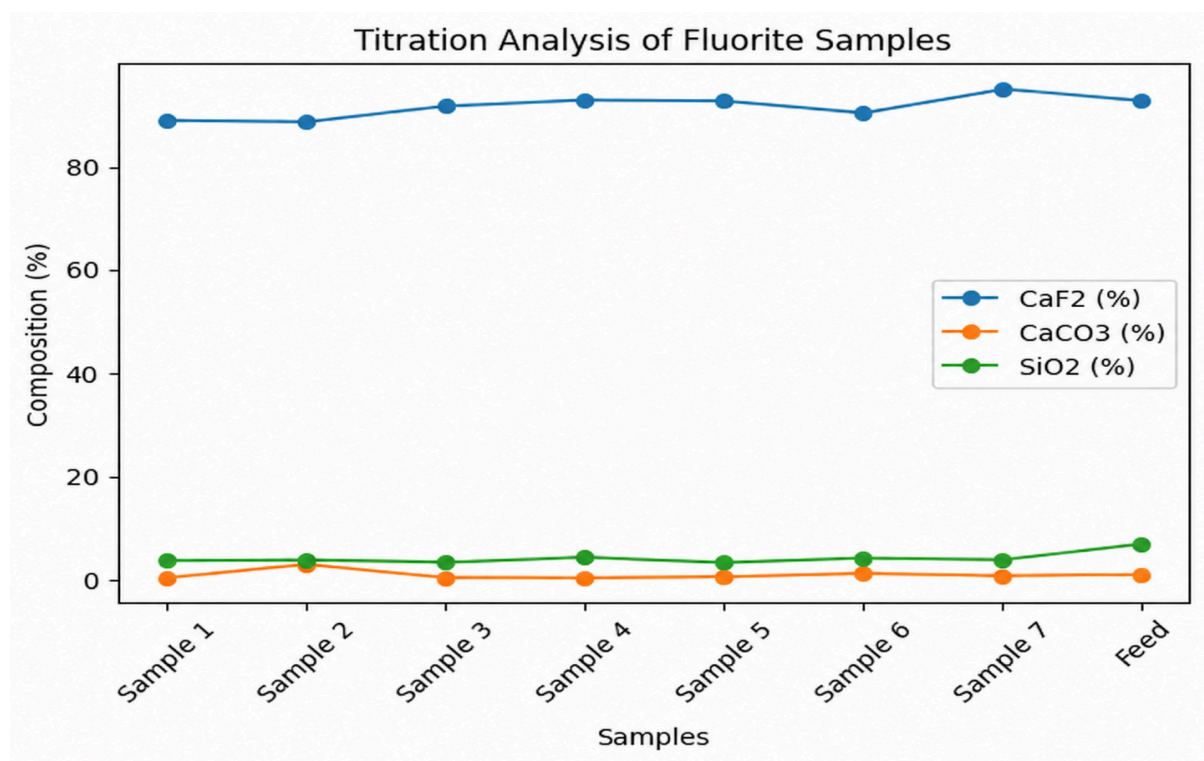


Figure 18: Titration analysis of chemically purified fluorite concentrates and the feed

4.6. Final Product Quality and Acid-Grade Evaluation

4.6.1. Achieved CaF_2 Grade

Titration results showed that CaF_2 content increased after treatment, reaching a maximum value of approximately 95.18% under the most favorable conditions. This represents a significant improvement compared to the feed material but still falls short of the acid-grade requirement of $\geq 97\%$. After treatment, silica remained the dominant impurity, with values generally between 3% and 4%. Carbonate content was effectively reduced to low levels, confirming the efficiency of acid leaching. Iron content was also reduced to acceptable levels, indicating successful removal of iron-bearing phases.

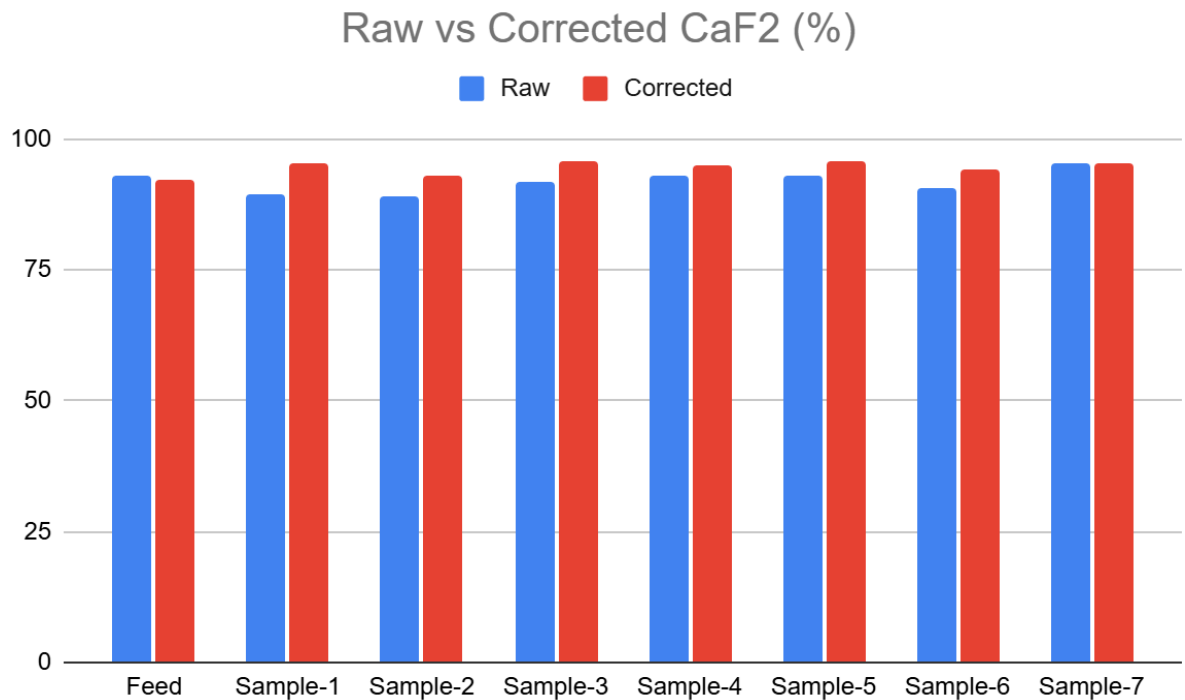


Figure 19: Raw titration vs. mass-balance-corrected CaF_2 . Correction factor = $100 \div \text{mass balance total per sample}$.

5. Conclusions and Recommendations

5.1. Main Conclusions

This study investigated the sequential chemical purification of a Mongolian fluorite flotation concentrate using hydrochloric acid (HCl) and sodium hydroxide (NaOH) leaching

under systematically varied temperature and concentration conditions. The following principal conclusions are drawn from the experimental results.

First, the flotation concentrate used as feed material contained approximately 93.02% CaF_2 , 1.06% CaCO_3 , and 6.98% SiO_2 as determined by titration and gravimetric analysis, confirming that it does not meet the acid-grade specification of $\geq 97\%$ CaF_2 without further chemical treatment. XRF analysis across four feed batches showed silicon content ranging from 2.12% to 3.79%, iron content of 0.116–0.133%, and notable aluminium content (1.50%) in Batch 4, reflecting the natural heterogeneity of the flotation concentrate and the presence of aluminosilicate minerals in some feed batches.

Second, HCl leaching at 1 M and 50°C for 15 minutes was consistently effective at removing iron oxide and carbonate impurities across all eight experiments. Iron content was reduced in every experiment, confirming the dissolution of hematite and goethite according to the reactions, $\text{Fe}_2\text{O}_3 + 6\text{HCl} \rightarrow 2\text{FeCl}_3 + 3\text{H}_2\text{O}$ and $\text{FeOOH} + 3\text{HCl} \rightarrow \text{FeCl}_3 + 2\text{H}_2\text{O}$ a concurrent increase in calcium content was observed after HCl treatment, attributed to the selective dissolution of calcite and other acid-soluble gangue minerals, which concentrates the CaF_2 fraction in the solid residue. Silica content showed no consistent reduction after acid leaching, confirming the chemical stability of quartz under these conditions.

Third, temperature was identified as the dominant variable controlling silica removal by NaOH leaching. At 70°C, NaOH leaching at 1M, 2M, and 4M produced no consistent or reproducible reduction in silicon content, regardless of concentration. At 90°C, a measurable silica reduction of approximately 16.5% was achieved with 2M NaOH (Sample-5), and the highest individual CaF_2 grade of 95.18% was produced by 4M NaOH at 90°C (Sample-7). This confirms that the activation energy required to break Si–O–Si bonds in crystalline quartz is not sufficiently overcome at 70°C and that temperatures at or above 90°C are necessary for effective quartz dissolution in this system.

Fourth, NaOH concentration had a secondary influence on silica removal. Increasing the concentration from 1M to 2M at 70°C produced no significant improvement, while increasing to 4M at 70°C showed a marginal positive effect. The combination of 4M NaOH at 90°C produced the largest absolute silica reduction and the highest CaF_2 grade in any experiment, indicating that concentration and temperature act synergistically. Nevertheless, even under the most aggressive conditions tested, the acid-grade specification of $\geq 97\%$ CaF_2 was not achieved, with the best product reaching 95.18% CaF_2 .

Fifth, carbonate removal by HCl leaching was effective in most experiments. Five of the seven product samples met the acid-grade CaCO_3 specification of $\leq 1.0\%$, confirming that 1M HCl at 50°C is adequate for carbonate dissolution under the contact times applied. The anomalous result in Sample-2 (2.96% CaCO_3) is attributed to procedural inconsistency in that experimental run.

Sixth, SiO_2 content as determined by gravimetric analysis ranged from 3.36% to 4.36% across all product samples, remaining well above the acid-grade specification of $\leq 1.5\%$ SiO_2 in every experiment. Silica removal is therefore the primary bottleneck preventing achievement of acid-grade quality under the conditions investigated in this study.

Seventh, a mass balance of the leaching process confirmed product yields of 86.1–90.5% from 100 g feed batches, with the consistently lower yield in Experiment 3 attributed to procedural deviation during that run. CaF_2 stability throughout the leaching process was confirmed by the consistent calcium content measured by XRF across all experiments, indicating that neither HCl nor NaOH leaching caused significant dissolution of the valuable CaF_2 phase.

5.2. Recommended Operating Conditions

Based on the experimental results, the following operating conditions are recommended for the chemical purification of Mongolian fluorite concentrates of similar composition to the material studied.

For the HCl leaching stage, a concentration of 1M HCl at 50°C is confirmed as appropriate for carbonate and iron removal. However, the leaching time should be extended from the 15 minutes applied in this study to 60–90 minutes to improve iron removal and bring Fe content consistently below the acid-grade specification of $\leq 0.05\%$ Fe_2O_3 . The washing protocol after HCl leaching should comprise a minimum of three counter-current wash stages with deionized water to ensure Cl^- content below 0.05% in the product.

For the NaOH leaching stage, 2M NaOH at 90°C for a minimum of 60 minutes is recommended as the starting point for further optimization. The results of this study demonstrate that 90°C is the minimum effective temperature for silica dissolution in this system,

and that extending the leaching time beyond the 30 minutes applied here is likely to produce greater silica reduction. A concentration of 4M NaOH at 90°C may be considered if further silica reduction is required, provided that the washing protocol is sufficient to prevent aluminium re-precipitation on the fluorite surface during the pH drop that occurs during washing.

5.3. Recommendations for Further Study

Several areas are identified for further experimental investigation to build on the findings of this study.

The most important single improvement is to extend the NaOH leaching time at 90°C beyond 30 minutes. Based on the Arrhenius kinetics of quartz dissolution, a contact time of 60–120 minutes at 4M NaOH and 90°C is predicted to produce significantly greater silica reduction and may bring the product closer to the $\leq 1.5\%$ SiO₂ specification. A kinetic study measuring silica dissolution as a function of time at fixed temperature and concentration would establish the optimum contact time and allow calculation of the activation energy for silica dissolution in this specific fluorite concentrate system.

Investigation of the aluminium re-precipitation phenomenon identified in Batch 4 experiments is also recommended. The application of a dilute acid rinse at pH 3–4 after NaOH leaching using a small volume of dilute HCl prior to the main water washing stage would dissolve re-precipitated Al(OH)₃ and prevent its incorporation into the dried product. Monitoring wash effluent pH during washing would help identify the pH range at which re-precipitation occurs.

Calcimetric analysis of both feed and product samples is recommended to directly quantify CaCO₃ content and confirm whether the acid-grade carbonate specification is consistently met. This would supplement the titration data already obtained and provide a more complete analytical basis for evaluating process performance.

Finally, a pilot-scale investigation using the optimal conditions identified in this study, 1M HCl at 50°C for 60–90 minutes followed by 2–4M NaOH at 90°C for 60–90 minutes, would provide data on the scalability of the process, including reagent consumption, water balance, effluent treatment requirements, and product yield at larger throughput. Such a study would establish the engineering basis for designing an industrial chemical purification circuit for Mongolian fluorite concentrate.

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Appendix

ГЕОХИМИЧЕСКАЯ ЛАБОРАТОРИЯ

Шинжилгээний үр дүн:
GA2026.0062

Г-Б-09/ИД
Хэм: 03/15.01.2023

ЗАХИАЛГА №: GA2026.0062

ШИНЖЛЭЛТЭЭ ЭХЭЛСЭН ОГНОО: 2026.04.28

ШИНЖЛЭЛТЭЭ ДУУССАН ОГНОО: 2026.04.29

ЭЛЕМЕНТ	CaF ₂	CaCO ₃	SiO ₂
Д/Д ШИНЖЛЭЛГЭЭНИЙ АРГА	Titir	Titir	GRAV
ТОДОРХОЙЛОХ ДООД ХЭВТЭЭР	1	0.25	0.1
НӨГЖ	%	%	%
1 Duk-1	89.28	0.55	3.72
2 Duk-2	88.89	2.96	3.92
3 Duk-3	91.84	0.55	3.40
4 Duk-4	93.02	0.46	4.36
5 Duk-5	92.82	0.65	3.36
6 Duk-6	90.66	1.29	4.24
7 Duk-7	95.18	0.83	3.91
8 Duk- p-CC1	93.02	1.06	6.98

ЧАНАРЫН ХЯНАЛТ

1 Method Blank	<1	<0.25	<0.1
Duk-4	93.02	0.46	4.36
2 Duk-4 Rep.	93.21	0.46	4.20
Duk- p-CC1	93.02	1.06	6.98
3 Duk- p-CC1 Rep.	92.82	1.02	7.04

Автестэглэгдсэн Стандартчилсан Зигвар

STD CGL135 Cert.	35.60	0.78	47.67
4 STD CGL135 Meas.	35.79	0.74	47.80

Хуудас 2/2

Figure 20: Titration Analysis Results of Acid and Base Leaching

Figure 21: XRD diffractogram of fluorite feed

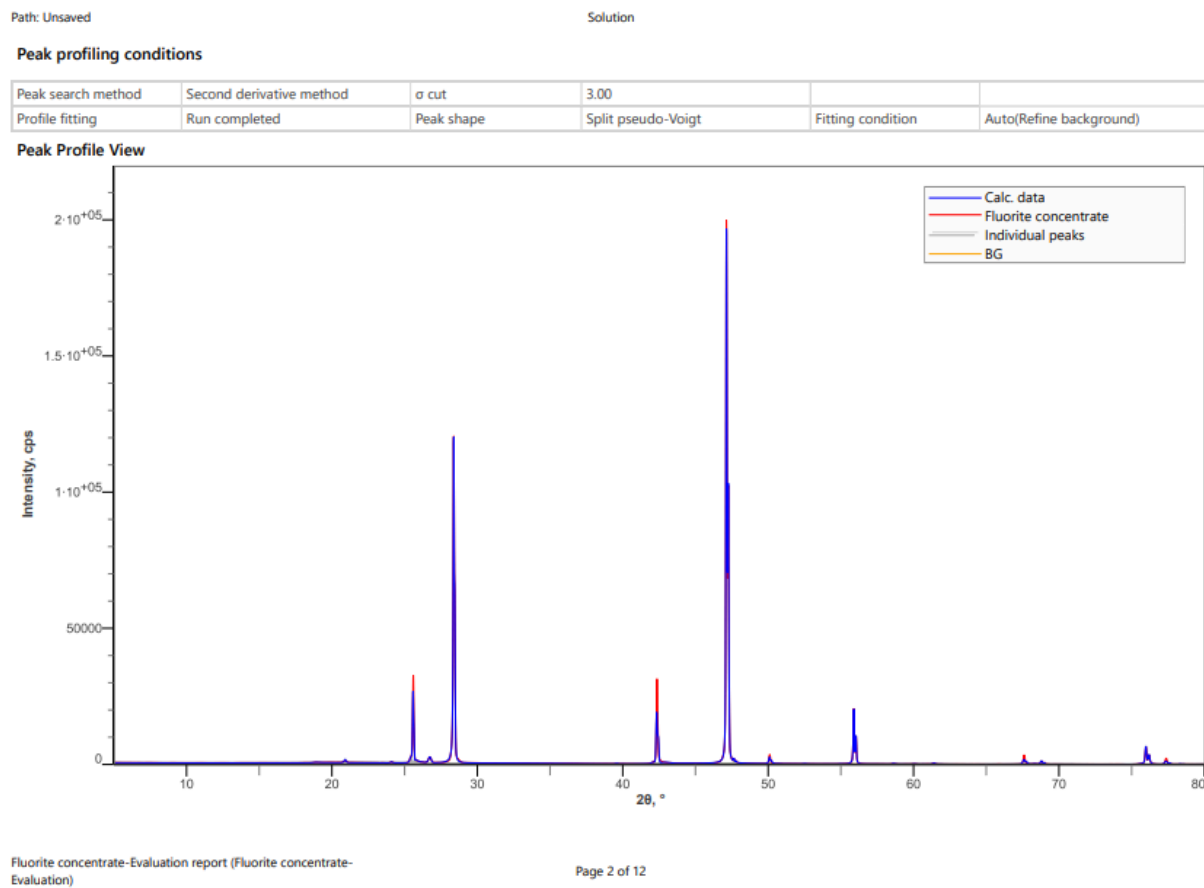


Figure 22: XRD diffractogram of Final Flotation Concentration