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Investigation on the Beneficiation of Fluorite-ore using a mixture of Oleic acid and Palmitic acid via Froth Flotation

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ABSTRACT

Fluorite (fluorspar), an important industrial mineral ore, is one of the major raw materials for the production of hydrofluoric acid. Naturally occurring fluorite ore contains gangue minerals, primarily silica (SiO₂) and calcite (CaCO₃). The beneficiation of fluorspar is needed to mitigate the severity of operational issues. Several studies on fluorspar beneficiation using the froth floatation technique have been executed, but the process is restricted by the use of mineral acids to remove calcite. In this study, a novel scheme for fluorspar beneficiation was investigated for the floatation of fluorite and depression of calcite and other gangue minerals simultaneously without the use of mineral acids. Moreover, mixtures of saturated and unsaturated fatty acids (oleic acid and palmitic acid) were used instead of mineral acids. Various parameters were investigated, such as the weight percent of the feed-slurry, feed pH, the effect of reagents on the process selectivity, and the effect of feed boiling and dilution on the up-gradation of fluorspar. The adopted methodology with tested reagents resulted a 67 wt. % reduction of CO₃²⁻ and 75 wt. % reduction of SiO₂ in gangue material at a pH 10 for the feed slurry. Fluorspar purity increased from 65-75 wt. % to 95 wt. % after the boiling and dilution steps, respectively.

Keywords: Beneficiation, Calcite (CaCO₃), Fluorspar, Fluorite, Minerals, Silica (SiO₂)



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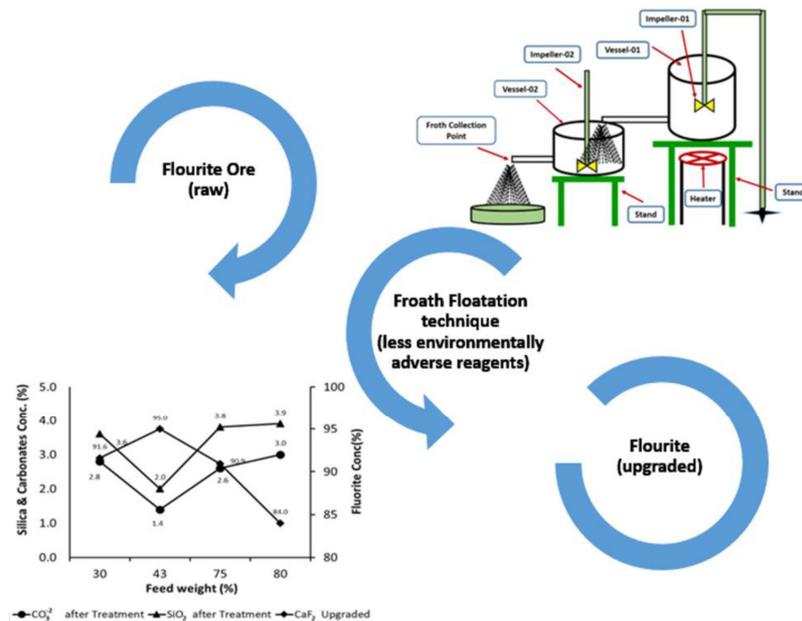
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Graphical Abstract



1. Introduction

Fluorite (CaF₂) is a declared critical non-metal material by the European Union with diverse applications because of its economic value in optical, ceramic, and metallurgical industries and sensitive transportation. It is used as a mother compound in the production of hydrofluoric acid, with further industrial applications. Such applications drive the interest towards the purification methods of fluorite because it is found as an ore in nature and co-exists with gangue materials, such as calcite (CaCO₃), barite (BaSO₄), and quartz (SiO₂) [1]. Several beneficiation techniques are used to enrich the purity of fluorite, including gravity separators, magnetic and electrostatic separators, optical sorters, and flotation devices [2]. The noticeable drawbacks of the above-mentioned techniques compared to the froth flotation technique include an imbalance between gravitational and viscous forces, diamagnetic behavior of gangue material and CaF₂, lower number of experiments on ores, sensitive handling with limited exposure of light to the ore [3]. Froth flotation exploits the plastic surface characteristics (hydrophobic or hydrophilic) to separate the target material from the rest of the ore. Different purification grades of fluorspar are required for various applications, and a variety of froth flotation techniques employing various chemicals have been developed. Xanthates, hydrochloric acid, polyaspartate, sodium oleate, sodium hydroxide, sodium carbonate, sodium silicate, organic chemicals, citric acid, sodium fluoride, sulfoleic acid, sodium naphthenate, salted copper sulfate, sulfuric acid, methyl isobutyl carbinol, ethridonic acid, hydrofluoric acid, carboxymethyl cellulose, and many other chemicals have been used as collectors, depressants, pH regulators, and frothers in different proportions and combinations in froth flotation.

The beneficiation requirement for complex ores necessitates development of environment friendly efficient depressant [4].

Similarly, some depressants for calcite inevitably result in low recovery of high-grade fluorite [5]. Furthermore, xanthates applied as flotation agents show high toxicity especially in aqueous solution [6]. In other studies, foaming agent in the gas froth flotation technique is used to provide stable gas bubbles and agitation to separate hydrophilic and hydrophobic materials [7-8]. In some cases, the attempts to understand the effects involved during the interaction, harmfulness and sensitive handling of different reagents during the flotation processes have been discussed in detail [9-13].

A variety of methods are obsolete now because of the hazards of handling inorganic acids, the use of gaseous media, and reagents being non-selective for the separation of calcite and fluorite, which forms the basis of this research. The proportions of the reagents compared to the quantities used in other extractive metallurgy fields are comparable (Table 1). In this study, the selection criteria of the reagents were set based on their recovery from wastewater effluents and low impact on the environment (Table 2). Some critical reagents, such as guar gum, quebracho, oleic acid, and palmitic acid, are extracted from guar beans, quebracho tree, palm, and olive kernels, respectively. Similarly, quebracho and silicate-based reagents can be recovered from wastewater by centrifugation/heating and chemical precipitation techniques [14–19]. The notable difference is the use of a combination of oleic and palmitic acid to collect fluorite together with guar gum as a flocculant for the flotation of fluorite with a less environmentally adverse depressant and pH regulator. Other studies included chemical flotation scheme including sodium naphthenate, fatty acids, gums, inorganic salts as depressant, collectors and frothers [20-22]. In the present work, a scheme without incorporating mineral acids for simultaneous beneficiation of fluorspar, depression of calcite and other gangue minerals has been introduced. Additionally, the novel aspect includes completion of flotation based on agitation/heating with envi-

ronmentally friendly reagents recoverable from natural or waste-water effluent sources especially without the application of air.

2. Materials and Method

Fig. 1 presents a schematic diagram of the experimental setup for fluor spar beneficiation using froth flotation. Two lab mixers (115-230 VAC, Cole-Parmer, US), two borosilicate glass beakers of 10,000 ml and 13,000 ml in volume, two tripod stands, a Bunsen burner, wire gauze, two spatulas, oven (HMF450-50/60/50, HAOYUE, China), X-ray fluorescence spectrometer (ARL OPTIM'X WDXRF, Thermo Fischer Scientific, US), thermometer, and pH meter (KL-009, Qingdao International Co, LTD, China) were used in the experiments. A 10,000 ml glass beaker was placed on a tripod stand with wire gauze for uniform heating. One of the two lab mixtures was adjusted with the whole previously set apparatus, so its impeller was inserted in a beaker up to its half depth after positioning on the tripod stand with a Bunsen burner. The other assembly was also arranged as explained above, but instead, a 13,000 ml glass beaker was used without incorporating wire gauze and a Bunsen burner.

Raw fluor spar ore samples were obtained from the Loralai District (30°20'N 69°00'E) of Balochistan, Pakistan. The feed slurry was prepared after wet grinding the fluor spar ore using a ball mill (C & M Mining Machinery) with a production capacity range of 0.65-2 tonne/h and diluted with demineralized water (DMW). The experiments were performed at various weight percentages of feed slurry, i.e., 80 wt. %, 75 wt. %, 43 wt. %, and 30 wt. %. The pH of the feed solution was adjusted to 8, 9, 10, and 11 by adding a sodium carbonate solution. Subsequently, the feed was stirred for 30 minutes to obtain a stable pH. Sodium silicate (depressant) was then added to the feed slurry to suppress the gangue material. Depressant, guar gum, quebracho, oleic acid, and palmitic acid were added to the system over 10 minutes. The slurry after the addition of all reagents was boiled for 20 min to collect froth from the first stage. Later, the boiling slurry was diluted to 25 wt. % for further froth extraction. The collected froths were dried at 400 °C and analyzed for calcium fluoride (CaF₂), carbonates (CO₃²⁻), and silica (SiO₂) by X-ray fluorescence spectrometry (XRF, ARL OPTIM'X WDXRF, Thermo Fischer Scientific, US). Fig. 2 shows the detailed methodology.

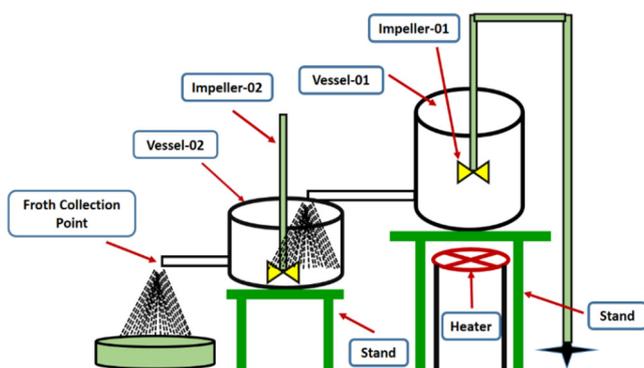


Fig. 1. Experimental setup of the froth flotation process for fluor spar beneficiation

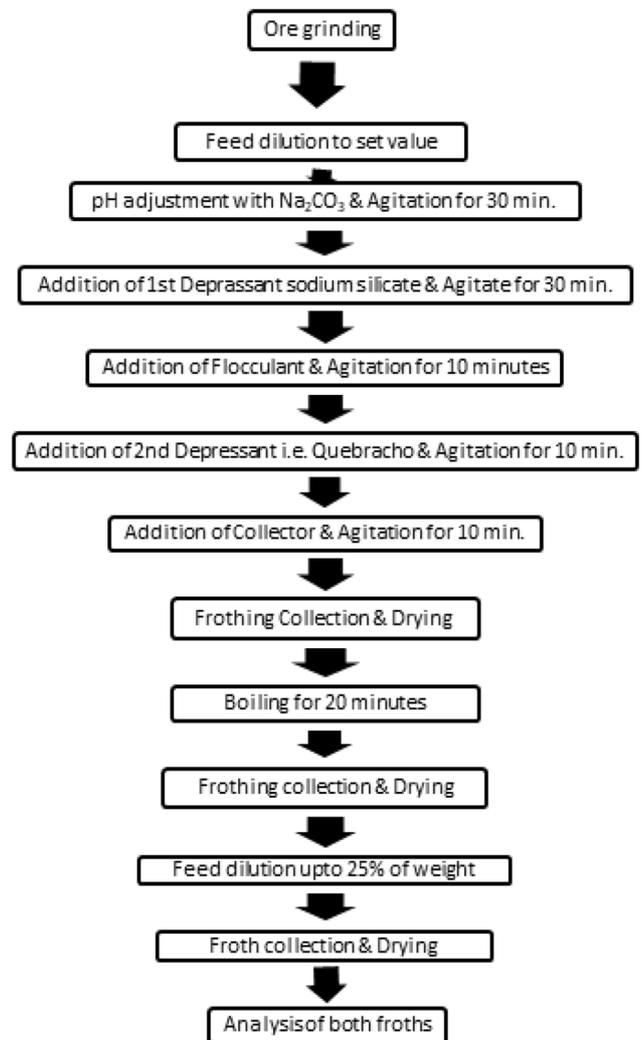


Fig. 2. Steps adopted in the froth flotation process

A total duration of 4 h on the grinding, addition of depressants-flocculants, agitation, settling, dilution, filtration and drying for the fluorite enrichment was required; this excludes time spent on the analysis of samples. Additionally, a batch and continuous comparative assessment can also be included for future studies using the same composition of chemical reagents.

The details of depressants, flocculant, collector, and chemical for pH adjustment are given below:

- **Depressants:** Commercial grade quebracho and sodium silicate (Na₂SiO₃) to suppress the gangue minerals.
- **Flocculant:** Food-grade guar gum to assist in the flotation of fluorite.
- **pH Adjustment:** Aqueous solution of sodium carbonate (Na₂CO₃).
- **Collector:** Mixture oleic acid (unsaturated fatty acid) and palmitic acid (saturated fatty acid) to collect fluorite from feed and float on the surface. In each experiment, the following quantities of reagents were used for 10 L of feed slurry, as shown in Table 1.

Table 1. Quantities of Reagents for 10 L of Feed Slurry

No.	Reagent	Quantity
1	Sodium Carbonate	pH adjustment
2	Sodium Silicate (Na ₂ SiO ₃)	4 g
3	Quebracho	0.75 g
5	Guar Gum	0.817 g
6	Oleic Acid	6.2 ml
7	Palmitic Acid	2.5 g

In the proposed method, quebracho and sodium silicate were used as depressants to suppress gangue minerals, food-grade guar gum to assist flotation of fluorite, an aqueous solution of sodium carbonate (Na₂CO₃) for pH adjustment, and a mixture of oleic acid (unsaturated fatty acid) and palmitic acid (saturated fatty acid) as a collector was used. Sodium silicate and acidified sodium silicate fall in the category of inorganic depressants. Sodium silicate has

a good depressing quality for calcite and silicate [20]. The aqueous solution of silicate compounds contained colloidal Si(OH)₄, SiO(OH)₃⁻, and SiO₂(OH)₂²⁻. At low pH, negatively charged colloidal Si(OH)₄ forms a strong bond with the silica present as gangue material, but the interactions of Si(OH)₄ with positively charged fluorite are not strong at low pH. The electrostatic forces of attraction between fluorite and negatively charged Si(OH)₄ are weak and cannot remove the water layer from the fluorite surface. Nevertheless, the adsorption layer can be removed easily, allowing fluorite to come to the surface while depressing silica. On the other hand, at high pH levels, SiO(OH)₃⁻ and SiO₂(OH)₂²⁻ form a strong bond with fluorite and result in its depression. Sodium silicate depresses silica very well at all pH ranges because of the strong chemical bonding but depresses fluorite only at high pH. Therefore, sodium silicate is considered the first choice for depressing silicate in fluorite flotation. The effective range of pH for its separation lies between 6–8 [14]. Quebracho falls in the group

Table 2. Comparative Summary to Select or Reject Specific Reagents

No.	Reagents	Reason of Rejection *	Reason of Selection
1	Citric Acid	Causes fire, Induces respiratory and skin problem, etc.	
2	Sodium Fluoride	Causes nausea, vomiting, diarrhea, abdominal pain, and loss of appetite	
3	Sulfoleic Acid	Causes shortness of breath, irritation in eyes and skin.	
4	Sodium Nephthenate	May cause eye, skin, digestive tract, and respiratory irritation.	Not applicable
5	Salted Copper Sulphate	Causes eye irritation, nausea, vomit. Damages body cells, tissues, liver, and kidney. High exposure can lead to death.	
6	Sulfuric acid	Injurious to lungs, eyes, skin, and teeth. It's a corrosive substance.	
7	Sodium Carbonate	Irritation in the respiratory tract, shortness of breath, and coughing. Causes pulmonary edema (accumulation of fluid and swelling).	For pH regulation, carbonates are preferred rather than HCl or NaOH.
8	Methyl Isobutyl Carbinol	Above 41°C, it becomes explosive.	
9	Dextrin	Its modification is sensitive and affects the process.	
10	Hydrochloric Acid	Toxic for eye, skin, and mucous membrane.	Not applicable
11	Sodium Hydroxide	Highly toxic for living organisms.	
12	Xanthate	Very toxic environmental pollutant.	
13	Quebracho/Tannin	-	It has remarkable depressing characteristics towards calcite.
14	Ethridonic Acid	Its proper cleaning is necessary before utilization. If it is not cleaned correctly, it can irritate the eyes, skin, and mucous membrane if inhaled.	Not applicable
15	Palmitic Acid	-	In a weak acidic environment, fluorite floats efficiently in the presence of Palmitic Acid.
16	Oleic Acid	-	Falls in the class of fatty acids
17	Guar Gum	-	Its colloidal properties make it prominent in the froth flotation technique.
18	Hydrofluoric Acid	If Inhaled, it can cause damage to the lungs. It also causes pulmonary edema, a condition in which fluid accumulation occurs in the lungs leads to swelling. It causes skin burns and skin ulcers.	Not applicable
19	Sodium Silicate	It is moderately toxic but there are no chronic and severe hazards.	It is used because of its exceptional depressing behavior towards silicate.
20	Sodium Oleate	Coughing, sneezing, and irritation in nose and throat.	Not applicable
21	Carboxymethylcellulose	May cause irritation on skin and eyes.	Not applicable

of organic depressants [15]. It does not break down to new compounds in acidic, basic, and enzymatic media. Tannins contain a phenolic (-OH) group and adsorb on the surface of negatively charged gangue materials by forming a chemical bond. These negatively charged gangue repels the anionic collector, and remains in solution [15]. In a weak acidic environment, fluorite floats efficiently in the presence of palmitic acid [20]. Guar gum is considered a good depressant that can form hydrogen bonds with water [16]. Sodium carbonate is used as a pH regulator because carbonates are less hazardous than acids. Fatty acid, an environmentally friendly reagent, allows the flotation of many non-sulfide minerals [20].

The reagents used in the proposed process can also be recovered from wastewater effluents or natural resources. The purification of oleic acid can be done from palmitic acid via crystallization [23]. The collector mixture (oleic acid and palmitic acid) can be used for this separation [17]. Quebracho phenolic can be recovered from tannery wastewater and be used in various industrial applications. It can be recovered by decantation, centrifugation, and heating. The compound can prevent the contamination of underground water and will contribute from an economic point of view [18]. Silicate compounds can be removed from wastewater by chemical precipitation [19]. Sodium carbonate can be used to remove the hardness of water [24]. Table 2 lists the drawback of commonly used chemicals in the froth flotation technique. The data were collected from various sources, including material safety data sheets and hazardous material fact sheets, available from public domain accessible sources.

3. Results and Discussion

In this study, the effects of various parameters such as pH, dilution, boiling, reagents, and weight of slurry were studied.

3.1. Effect of pH

Figs. 3 and 4 show the effects of pH on weight percentage concentration of fluorspar and percentage reduction in gangue, respectively. The results revealed the optimal feed pH to be 10 for the recovery of fluorite from fluorspar ore, which leads to a decrease in the recovery of calcite from fluorspar ore at pH > 10 [25]. In the range of pH from 7–11 has a relationship with the point of zero charge of fluorite [20]. The reported pH point of zero charge (pH_{pzc}) for fluorite and calcite is 9.5 [25]. The zeta-potential is an electrostatic repulsion between two similar charged particles. Smaller particles resist each other at higher zeta potential (positive or negative). At lower zeta potentials, attractive forces between particles overcome the resistive forces resulting in aggregation. Rapid coagulation occurs at zeta potentials of 0 to +5 or -5. The range of zeta potentials for fluorite lies near pH 9.5 [25]. Hence, the high recovery of fluorspar and maximum percent reduction in gangue occurred at pH 10, as shown in Figs. 3 and 4, respectively. An analysis of the froth concentrates, i.e., 95 wt. % of fluorspar corresponding to pH 10, resulted in a 67 wt. % and 75 wt. % reduction in gangue for CO₃²⁻ and SiO₂, respectively. Furthermore, among the chosen reagents, sodium silicate depresses silica very well at all pH ranges because of strong chemical bonding but depresses fluorite only at the higher pH [14].

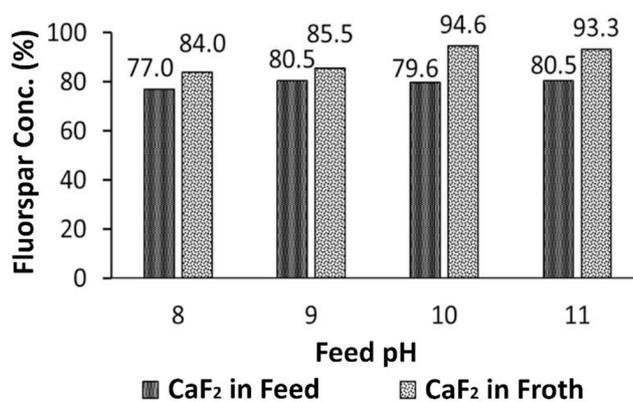


Fig. 3. Effect of pH on the weight % concentration of fluorspar

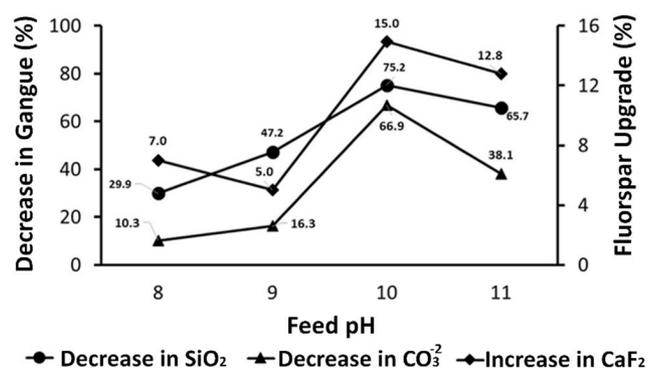


Fig. 4. Effect of pH on the weight % reduction in gangue and the upgrading of fluorspar

3.2. Effect of boiling, dilution, and weight % of slurry

Dilution took place in two stages, before and after boiling. The effects of only the first dilution were studied because most of the industrially relevant slurries result in lower removal rates upon further dilution with water. The presence of silica has undesirable results in the quick settling of slurry because of the relatively high settling velocity attributed to its high density. The removal of silica, if present in the form of finest silicate ingrowths, becomes a rather difficult problem to solve. On the other hand, in this study, the silica concentration varied from 8 wt. % to 11 wt. % with the change in concentration of feed slurry in the range of 30–80 wt. %, as shown in Fig. 5a. Furthermore, these silica concentrations were reduced by approximately 50 wt. % after boiling. For example, at 43 wt. % of the feed slurry, the silica concentration was 8.1 wt. %, indicating which reduced significantly to 3.7 wt. % after boiling. The silica concentration was reduced further after dilution. At 43 wt. % of the feed slurry, the silica concentration was 3.7 wt. % after boiling, which decreased to 2.0 wt. % after dilution. The combined effect of boiling and dilution using the adopted methodology produced a maximum silica reduction of approximately 75 wt. % in a 43 wt. % feed slurry. Similarly, a 66 wt. % reduction of CO₃²⁻ (Fig. 5b) was obtained after boiling and dilution at 43 wt. % of the feed slurry.

Boiling strongly affects fluorspar upgrading, and at high temperatures, all reagents dissolve homogeneously in the entire phase. The depressants, especially quebracho, can separate fluorite from

calcite and depress gangue, such as sodium silicate. The hydrophobicity of the collector becomes prominent with an increase in temperature, which in turn increases its floatability. Therefore, boiling for 20 minutes assisted fluor spar to float as a part of froth. An overall increase in the fluorite concentration from 13–25 wt. % was achieved for feed slurry concentration (30–80 wt. %), as shown in Fig. 5c.

The oleic and palmitic acid as a collector initiate polymerization reactions, synonymous with hydrophobicity, leading to flotation [26]. The collecting power of fatty acids increases with increasing degree of unsaturation, resulting in polymerization reactions. The expected reaction pathways start from the auto-oxidation of oleate molecules to form hydro-peroxides resulting in epoxides, which were further converted to polyethers [27]. Furthermore, the fluorite surface potentially catalyzes the oxidation and polymerization reaction of adsorbed oleyl groups, leading to a hydrophobic structure [28] and separation from the aqueous layer. The availability of CO_3^{2-} ions from the added sodium carbonate decreases the adsorption

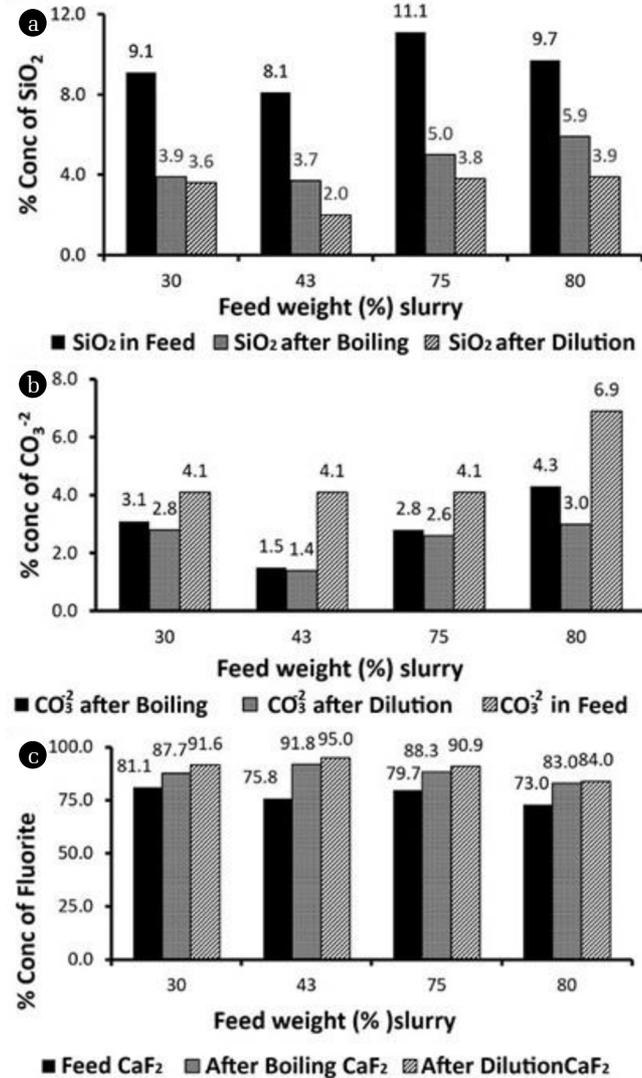


Fig. 5. Effect of dilution and boiling a) SiO₂ b) CO₃²⁻, and c) CaF₂

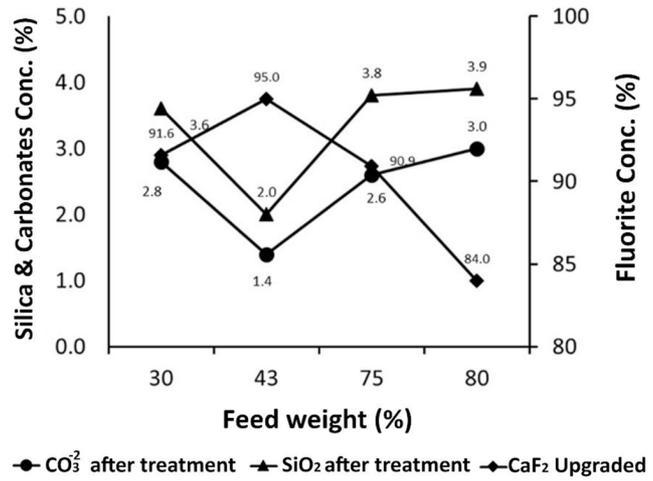


Fig. 6. Effect of feed weight % on CO₃²⁻, SiO₂, and CaF₂.

of silica onto fluorite [11], potentially due to the anion exchange reaction between carbonate and silicate ions. The other reason could be the active sites of the crystal lattice of fluor spar undergoing hydrogen bond formation with available fluoride because silica forms a bond with hydrogen and becomes more attached to the cationic sites of fluorite than calcite. This also results in the effective suppression of calcite [29]. The role of quebracho as a depressant was reported to adsorb onto the calcite surface by forming a calcite complex, especially at basic pH [15]. In this study, the maximum reduction in silica and carbonate concentration occurred at 43 wt. % of the slurry, as shown in Fig. 6. A comparison of the grade of fluorite after dilution and boiling for various feed weight percentages of the slurries, an overall 95 wt. % grade purity of fluorite at 43 wt. % of slurry was achieved. The comparison of sesbania gum [21], seed gum [30] in relative terms produced around 89.39 wt.%, 82.44 wt.% concentrated product of CaF₂ respectively, whereas, in this study a maximum of 95% concentration was achieved with guar gum. The pronounced effect of the slurry weight percent is comparable to the highest removal of carbonates and silica post boiling, dilution, and drying stages.

4. Conclusion

This study reports the overall findings of using environmentally friendly reagents in optimized combination and quantity to upgrade the concentration of fluorite ore obtained from the Loralai District (30°20'N 69°00'E) of Balochistan province in Pakistan. The process can be scaled up to treat several tons of base ore using less severe reagents towards the environment. The adopted methodology with the tested reagents (quebracho, sodium silicate, guar gum, sodium carbonate, oleic acid, and palmitic acid) yielded a 67 wt. % reduction of CO₃²⁻ and 75 wt. % reduction of SiO₂ in gangue material at a pH 10 for the feed slurry. The overall results for the upgrading of fluorite from the froth and corresponding reductions in carbonates and silica left in the gangue improved the post boiling diluted samples. An overall improvement of 25 wt. % fluorite was achieved compared to the 76 wt. % concentration of fluorite present in

the 43 wt. % feed slurry. The final concentration of 95 wt. % fluorite was achieved with the maximum removal of carbonates and silica after the treatment. Additionally, a batch and continuous comparative assessment can also be included for future studies using the same composition of chemical reagents.

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Author Contributions

A.F. (Master student), S.S.D (Ph.D.), S.I (Master Student) and Z.B.B (Ph.D.) developed the conceptualization, methodology, and wrote the manuscript. A.A. (Ph.D.) and M.Z (Ph.D.) helped in developing the conceptualization, methodology, and helped in drafting the manuscript. T.M.Q. (Ph.D.) helped in developing the conceptualization and methodology of the study. A.R. (Ph.D.) provided valuable research insights into the study and helped to review the manuscript. S.S.D (Ph.D.), M.U.R (Ph.D.), S.K (Ph.D.) and Y.K.P. (Ph.D.) provided valuable research insights into the study, review the manuscript, and helped with publishing.

Conflicts of Interest

The authors declare no conflict of interest.

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