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Potential of low-grade fluorite ore of Landi Kotal, Khyber Pakhtunkhwa Province, Pakistan

M. A. Bhatti[1]*, U. Zafar[1], A. Mehmood[1], R. Mehmood[1] and S. Nasir[2]

[1]*Mineral Processing Research Centre, PCSIR, Ferozepur Road, Lahore 54600, Pakistan*

[2]*Technology Wing, Ministry of Science and Technology (MoST), Islamabad 44010, Pakistan*

Abstract

This paper describes the results of a beneficiation study conducted on low-grade fluorite ore. The study was aimed at the development of a suitable beneficiation process to produce chemical grade fluorite concentrate. The representative sample of the ore was up-graded by leaching and flotation process. The important parameters of froth flotation process were optimized to obtain highest grade and recovery of fluorite concentrate. A single-factor variation method was applied to get the optimum conditions of the process. The rougher concentrate was reground to liberate fine locked fluorite particles and two cleaning flotation were employed in close circuit to achieve higher grade concentrate. A process flowsheet was designed in the light of these tests. After optimization of process parameters, the fluorite ore containing 62.24% CaF_2 could be upgraded to a concentrate assaying 97.55% CaF_2 with an overall recovery of 92.73%. The prepared fluorite concentrate meets the specifications of chemical grade and is suitable for production of fluoride based chemicals.

Introduction

Fluorite (CaF_2) mineral is also known as fluorspar in the industry. It belongs to the family of oxygen free halide minerals. It is a colorful mineral having tint or shade of violet or green. It usually crystallizes in isometric cubic habit, sometime also in granular and columnar masses (Bide *et al.* 2011). Natural fluorite mineral has ornamental uses as the gemstone. It occurs widely and globally with major deposits in more than 9000 areas. The estimated reserves of fluorite mineral in the world are around 230 million tons. The largest deposits occur in South Africa (41 Mt) followed by Mexico (32 Mt) and then China (24 Mt). At present, China is the lead producer of fluorite in the world with annual production of about 3 Mt (Miller, 2011).

Fluorite is a commonly occurring mineral in hydrothermal ore deposits, vein deposits and replacements or metamorphic deposits. It may occur as a minor accessory mineral in igneous rocks (granite, carbonatite, and pegmatite). It is sometimes a minor component of limestone and dolostone. It also occurs in vein deposit along with other metallic minerals and may be associated with galena, sphalerite, molybdenite, hematite, barite, calcite, tourmaline and quartz (Blackburn, 1988; Jain, 2001). Fluorite ore deposits are of three main types *i.e.,* silicate, carbonate and polymetallic depending upon the type of host minerals. Fluorite ores processing flow sheets are quite complex with respect to beneficiation when associated with galena, sphalerite, molybdenite and pyrite (Peng *et al.* 2014; Lubisi *et al.* 2018; Taguta *et al.* 2020). Fluorite beneficiation is divided into two parts. In first part, high grade lumpy massive fluorite ore is separated by manual selection method. Raw ore is divided into several sizing grades by screening. The remaining part of fluorite ore is crushed, ground and floated to obtain powder fluorite concentrate (Wang *et al.* 2018).

There are three main industrial uses of natural fluorite (fluorspar) depending upon the different grades of purity (Zhang and Song, 2003; Akgun *et al.* 2006).

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*Corresponding author's e-mail: arifbhattipcsir@yahoo.com

Metallurgical grade fluorite (60–85% CaF_2) is the lowest grade that is used in metallurgy as a flux to lower the melting point of raw materials for smelting of iron ore during steelmaking as it helps to increase slag liquidity and fluidity. It also removes the impurities like sulphur and phosphorous from steel. Ceramic grade fluorite (85–95% CaF_2) is a medium grade and used in the manufacture of enamels and opalescent glasses. Acid grade fluorite (97% or more CaF_2) is the highest and the purest grade of fluorite that is used in the manufacture of hydrofluoric acid (HF) which is the primary source of fluorine based chemicals. It accounts for 95% production of HF. It is also used in the preparation of cryolite (Na_3AlF_6) and AlF_3 which are the main fluorine compounds that decrease the melting point of alumina in Hall–Heroult process from 2072°C to 960°C during the production of pure aluminum metal (99.8%). More than 95% of acid grade fluorspar is achieved by flotation process (Day, 2002; Gao *et al*. 2021).

During mining, high grade fluorite ore is sorted separately for direct use as lumpy massive fluorite ore. But low grade ore which is rejected can be beneficiated to produce a powder fluorite concentrate. These low grade ores contain various gangue minerals which need to be removed in order to obtain a product suitable for industrial applications. The present study is focused on beneficiation and utilization of low grade fluorite ore rejected as mine waste.

Materials and methods

Sample preparation

The representative sample of fluorite ore of Tirah valley, Landi Kotal area, district Khyber, Peshawar Division, Khyber Pakhtunkhwa (KPK) Province, Pakistan was provided by Al-Hamrah Fabrication Works (Pvt.) Ltd., Karachi, Pakistan. Initially, 80 kg of fluorite ore in the form of lumps, packed in two bags of 40 kg each, was supplied to Mineral Processing Research Centre of PCSIR Laboratories Complex, Lahore for laboratory scale research and development study. The ore was in the form of lumps of variable size ranging from 2 inch to 6 inches (Fig. 1a). The whole sample was mixed and crushed in jaw crusher to get a product of half inch down and then in roll crusher to get minus 4 mesh product (Fig. 1b). The crushed sample was then repeatedly riffled to reduce the sample weight up to 1 kg in order to make a representative sample for chemical analysis. It was ground in disc pulverizer (Denver, USA) to obtain minus 100 mesh size powdered sample for chemical analysis. The remaining sample (79 kg) was packed in plastic bag for further processing work.

Chemical analysis

The conventional volumetric, gravimetric and instrumental analytical techniques were used for the chemical analysis of head sample and processed products. The head sample was analyzed for CaF_2 and the associated gangue components. Dried head sample (1 g) was digested by treating the ore with a mixture of Analytical Reagent (AR) grade nitric acid (HNO_3) and perchloric acid ($HClO_4$) made by BDH. The sample solution was prepared by filtration and washing the residue with water. Total calcium in the solution was determined by EDTA titration using Murexide indicator (Merck), while calcium present in ore due to non-fluorite minerals was estimated by acetic acid leaching followed by titration using same indicator. Total calcium and magnesium were estimated by using Eriochrome Black T indicator. The calcium of fluorite was determined by the difference (ASTM E 815-17b, 2017). The finely ground ore sample (1 g) was fused with excess of AR grade sodium carbonate (Merck) in platinum crucible at 900°C in muffle furnace. Silica and aluminum oxide were estimated by gravimetric methods. Iron was found by titration method with standard potassium dichromate solution (Jeffery *et al*. 1989). Sulphur was estimated by
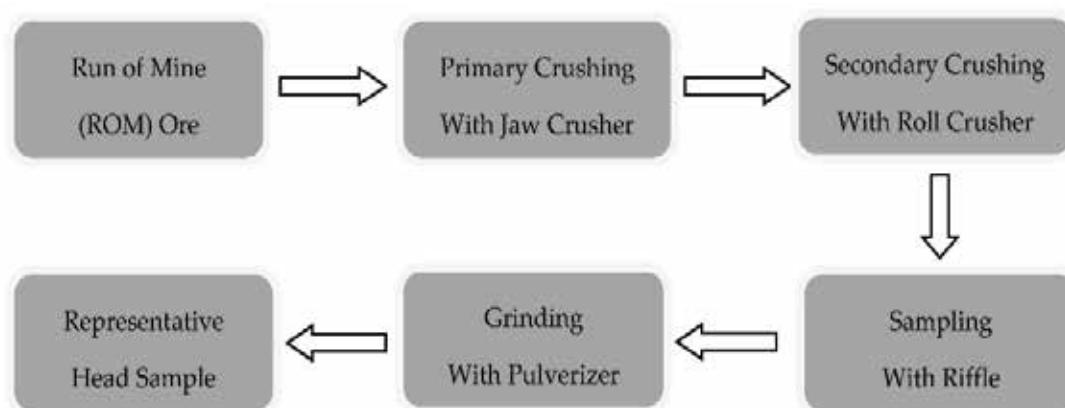
Fig. 1(a). Lumpy fluorite ore of Tirah Valley, Landi Kotal, KPK, Pakistan

Fig. 1(b). Laboratory scale jaw crusher and roll crusher used for sample preparation

Eschka mixture ($2MgO:1Na_2CO_3$) fusion method. The sample was fused with Eschka mixture at 800°C followed by leaching in hot water, filtration, acidification with HCl, precipitation with $BaCl_2$ solution and weighing as $BaSO_4$. Phosphorus was determined by spectrophotometer method by developing yellow colour complex with ammonium molybdate and ammonium metavanadate. Moisture was determined by heating the sample in electric oven for one hour at 110°C. The loss on ignition (LOI) was found out by placing the sample in electric furnace at 950°C for one hour. Alkali metals (sodium and potassium) were determined by flame photometer (PFP-7 Jenway, England). The chemical analysis of head sample is presented in Table I. The chemical analysis of processed products of flotation was also carried out by same techniques as applied for head sample of ore.

Pre-Treatment acid leaching tests

The flotation feeds were prepared by grinding the crushed fluorite ore in rod mill (6″ inner dia by 12″ inner length) made by Denver, USA to obtain flotation feed of required mesh size followed by dilute acid leaching prior to flotation. The flotation feed (ground ore) was treated with dilute (5%) commercial hydrochloric acid in stainless steel leaching tank equipped with stirring impeller to remove carbonates. The calcium carbonate present in the ore was decomposed by dilute hydrochloric acid forming calcium chloride and carbon dioxide gas. The completion of reaction was indicated by the cease in the effervescence of carbon dioxide. The slurry was allowed to settle and supernatant clear water layer was decanted. The sample was washed with water two times until the pH of slurry is slightly acidic or neutral to litmus paper.

Batch type flotation tests

The flotation experiments were performed on pretreated ground ore using Denver D-12 flotation machine (Fig. 1c). The ground washed ore was transferred to stainless steel flotation cell and mixed with water to make slurry. A number of batch type flotation tests were carried out at different set of conditions so as to investigate the effects of important parameters such as (a) grind size of the ore, (b) % solids in the pulp, (c) pH of the pulp slurry, (d) rotation speed of impeller, (e) dosage of collector, (f) dosage of frother, (g) quantity of depressant and (h) conditioning time on the grade and recovery of rougher fluorite concentrate. The ore was ground to almost 100% passing (minus) 70, 100, 150, 200 and 250 mesh sizes. The pulp density was studied at 20%, 25%, 30%, 35% and 40% solids in the slurry adjusted with water. The impeller speed (agitation) was varied from 700 to 1100 rpm. The pH of the pulp was investigated from natural 7 to alkaline range 11 and it was maintained with commercial grade soda ash Na_2CO_3 (ICI, Pakistan). The pure oleic acid (China) was applied as collector for fluorite mineral and its dosage was varied from 20 to 100 g/ton of ore. Polypropylene glycol (China) was employed as frother and its concentration was changed from 10 to 50 g/ton. The commercial grade sodium silicate Na_2SiO_3 was added to the feed as depressant for siliceous gangue material. The quantity of depressant was studied in the range of 200 to 600 g/ton. The commercially available starch was employed as iron oxide depressant. Its quantity was studied using 50, 75, 100, 150, and 200 g/ton. The slurry was conditioned with flotation reagents from 4 to 12 min. A series of flotation tests comprising of one roughing and two cleaning flotation were performed. The flotation products were dried in electric oven. The optimized conditions of flotation parameters are presented in Table II. The material balance of a typical flotation test

is presented in Table III. The chemical analysis of final fluorite concentrate is given in Table IV. The results of various flotation tests are presented in Fig. 2 to 10. The flow-sheet of a process developed for the beneficiation of a low grade fluorite ore is shown in Fig. 11.

Fig. 1(c). Denver D-12 flotation machine used for flotation of fluorite ore

Evaluation of the flotation process

In order to investigate the influence of flotation reagents on the performance of flotation process and consequently the recovery of fluorite in the concentrate was calculated using the following formula described by Wills and Napier-Munn (2006):

$$\% \ Recovery \ (R) = \frac{C \times c \times 100)}{(C + T) \times f}$$

Where R is % recovery of valuable mineral, C is dry weight of concentrate, c is % grade of concentrate, T is dry weight of tailing and f is % grade of feed.

However, there is a complexity in quantitatively assessing the technical performance of a floatation experiment when the results of two similar tests are compared. If both the grade and recovery are greater for one case than the other then the situation is simple, but if the results of one test show a higher grade but a lower recovery than the other and vice versa, then the choice is no longer simple. The recovery and grade have been combined into a single index defining the efficiency of the separation by Schulz as follows:

$$Separation \ Efficiency \ (S.E.) = Rm\text{-}Rg$$

Where Rm is the recovery of the valuable mineral and Rg is the recovery of the gangue into the concentrate. Therefore separation efficiency (S.E.) was calculated by applying the following formula:

$$Separation \ Efficiency \ (S. \ E.) = R \ \times \ [1 - \frac{F \ (Cm\text{-}C)}{C \ (Cm\text{-}F)} \ ]$$

Where R is the recovery of mineral, F is the feed grade, C is the concentrate grade and Cm is the theoretical maximum concentrate grade (Kallio *et al.* 2021).

Results and discussion

Chemical analysis

The chemical analysis of head sample (Table I) indicates that the calcium fluoride (CaF_2) content in the ore is 62.24%. It is sufficient grade for the up-gradation and commercial exploitation of the ore. The main undesirable impurities are calcium carbonate (10.57%), silica (13.35%), alumina (11.72%) and iron oxide (1.90%) which can be minimized by flotation process. The sulphur and phosphorus were not detected in this ore which indicates that sulphur containing minerals (sulphide or sulphate) and phosphorus bearing minerals (apatite) are not present in this ore. For industrial utilization of fluorite, the impurity content of SiO_2, S, P, should be accorded with the standard. It is apparent from the result that the ore is medium grade and is not suitable for final application until beneficiated.

Table I. Chemical analysis of representative head sample of fluorite ore

Constituents	Percentage
Fluorite (CaF_2)	62.24
Calcium Carbonate ($CaCO_3$)	10.57
Silica (SiO_2)	13.35
Iron Oxide (Fe_2O_3)	1.90
Aluminum Oxide (Al_2O_3)	11.72
Magnesium Oxide (MgO)	0.05
Sodium Oxide (Na_2O)	0.13
Potassium Oxide (K_2O)	0.014
Sulphur (S)	Not detected
Phosphorous (P)	Not detected

In order to produce a commercial grade fluorite concentrate, some kind of beneficiation work is necessary for further up-gradation of this ore. The froth flotation technique was selected to attain the desired grade.

Effect of acid leaching Pre treatment

It is found that the calcite (calcium carbonate) and fluorite (calcium fluoride) minerals show similar behavior toward flotation with oleic acid collector i.e. both are floated under same conditions. Although some plants use tannin and quebrachoo under strongly alkaline conditions (pH 10–11) to depress calcite mineral but it requires multiple cleanings to minimize calcite and clean the fluorite (Lin *et al*. 2016). Therefore, it was decided to decompose calcite before the flotation of fluorite mineral. For this purpose, a dilute (5%) solution of hydrochloric acid (HCl) was employed to prepare calcite free flotation feed. It was added in the ground ore until the cease of effervescence of CO_2 gas which indicates the complete decomposition of all the carbonates in the flotation feed. It was noticed that dilute hydrochloric acid solution helps to control the effervescence of carbon dioxide released from the solution as well as negligible quantity of fluorite dissolve in dilute acid solution (Gohar *et al*. 2002). In present investigation dilute HCl was found suitable to decompose all calcite (calcium carbonate) present in the ore. The calcium carbonate free slurry was used for subsequent flotation tests. The advantage of dilute HCl pretreatment is that there is no need to increase the pH beyond 10 to depress calcite with quebrachoo as reported by some researchers (Raju and Prabhakar, 2000). Moreover, less quantity of flotation reagents is required for flotation of fluorite mineral due to absence of calcite.

Effect of grind size of ore

The different feed sizes of ore were prepared in order to study the influence of grind size on the flotation of fluorite mineral. As a fact, the crushed ore is generally ground to a size at which valuable mineral grains are liberated from the associated gangue minerals at the coarsest possible size avoiding over grinding to reduce slimes production (Liu *et al*. 2013). In order to determine the optimum mesh of grinding, the raw ore was ground in rod mill to different mesh sizes and flotation tests were performed after pretreatment with dilute hydrochloric acid (HCl). The results of flotation tests showing the effect of grind size on the grade and recovery of fluorite concentrate are presented in Fig. 2. This figure clearly depicts a gradual increase in the grade and recovery of concentrate with the decrease in particle size up to 200 mesh (75 μm). Separation efficiency of flotation test performed at 200 Mesh was found to be 59.71 as compared to 58.94 at 250 Mesh size. So, this feed size was considered as optimum and

selected for onward tests. It was noticed that as the grind size became fine to finer i.e., from 200 to 250 mesh size, the grade improved a little from 82.54% to 83.07% but the recovery decreased from 91.68% to 88.76% . It could be explained that additional grinding generated more slimes which actually lowered the recovery of concentrate during flotation tests at rougher stage. Fluorite ores usually require coarse grinding from 70 to 100 mesh to liberate the fluorite from associated gangue minerals. But in this particular ore grinding up to 200 mesh produced highest grade and recovery which shows that ore is fine-grained in nature (Yao *et al*. 2020).
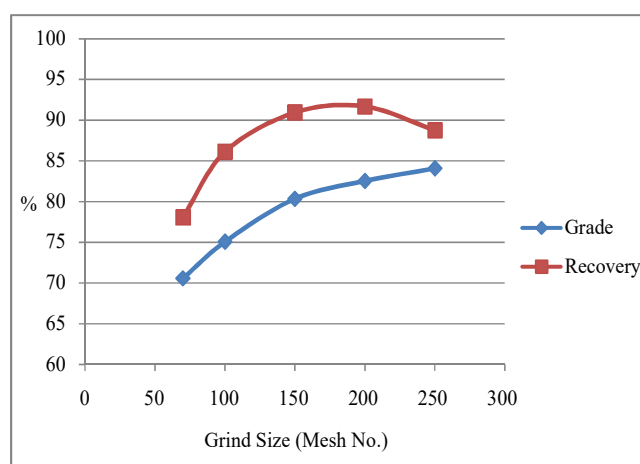
Fig. 2. Effect of grind size on the grade and recovery of fluorite rougher concentrate

Effect of pulp density

In order to investigate the effect of pulp density on the flotation behavior of the fluorite ore, the experiments were conducted at 20%, 25%, 30%, 35% and 40% solids in the slurry. Initially, slurry was conditioned at a higher pulp density of 40% solids which was then reduced to desired level by dilution with water. The test results of pulp density variation are shown graphically in Figure 3. It can be noticed from the graph that as the pulp density is increased from 20% to 30% solids, the grade and recovery improved greatly. But when it is further increased, the recovery increased slightly from 92.83% to 93.11% but a decrease in the grade of concentrate from 82.95% to 81.78% was resulted. Separation efficiency of flotation test performed at 30% solids was found to be 61.38 while it was measured to 58.92 at 35% solids. This behavior may be due to fact that higher pulp densities produce thick froth layer which is difficult to wash in order to drain out the entrapped gangue particles (Li *et al*. 2015). Accordingly, in the later experiments, the pulp density was set at 30% solids.
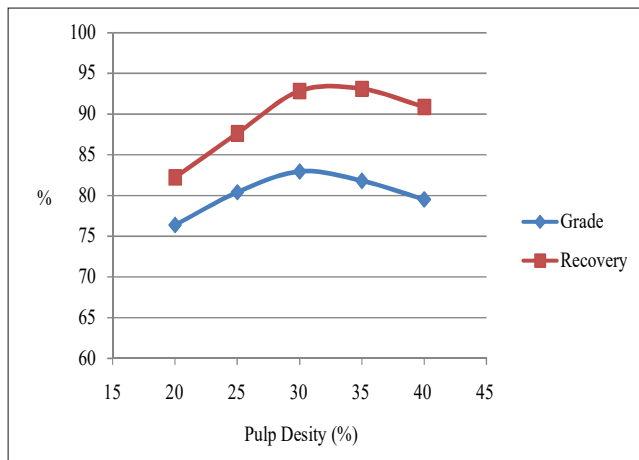
Fig. 3. Effect of pulp density on the grade and recovery of fluorite rougher concentrate

Effect of pH of the pulp

In a set of flotation experiments, pH of the pulp was varied from natural (7) to alkaline (11) to investigate the role of pH on fluorite ore flotation. The pulp was conditioned with soda ash (Na_2CO_3) as pH modifier to achieve required pH of slurry. The results obtained at different pH values of pulp are shown in Figure 4. The plot of grade and recovery versus pH showed that as the pH of pulp was increased from 7 to 10, both grade and recovery were increased but after that a slight decline in grade and recovery was noted. This indicates that around pH 10, the collector-mineral bond is much more stable leading to optimum recovery of 93.02% (Zhao *et al.* 2012; Corpas-Martinez *et al.* 2019). So, for the subsequent flotation trials, the pH of pulp was maintained at 10.
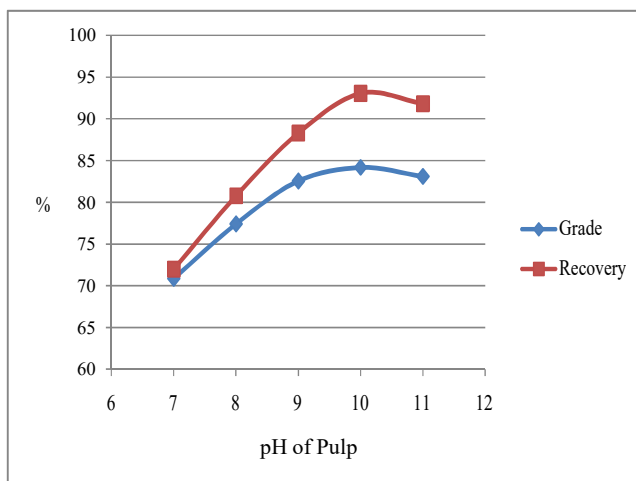
Fig. 4. Effect of pulp pH on the grade and recovery of fluorite rougher concentrate

Effect of impeller speed (Agitation)

A few flotation tests were performed by varying the impeller speed from 700 to 1100 rpm in order to examine the effect of agitation on the grade and recovery of fluorite concentrate. The plot of percentage grade and recovery against agitation speed is shown in Figure 5. This figure elucidates that recovery of fluorite concentrate increases with agitation speed up to 900 rpm beyond which grade of concentrate decreases. It is clear from this figure that impeller speed of 900 rpm yielded the best grade concentrate (85.62% CaF_2) along with 94.02% recovery indicating the adequate mixing and aeration in the pulp. It was observed that at lower impeller speed, the surface is quite low so that froth height and its removal were improper leading to lower recovery. On the other hand, higher impeller speed (1000 rpm) spilled the pulp along with froth into the launder resulting in lower grade (84.96%). Moreover, the separation efficiency index of flotation test performed at 900 rpm was calculated to 67.99 and flotation test performed at 1000 rpm showed 67.54. Therefore, impeller speed was set at 900 rpm for optimum agitation.
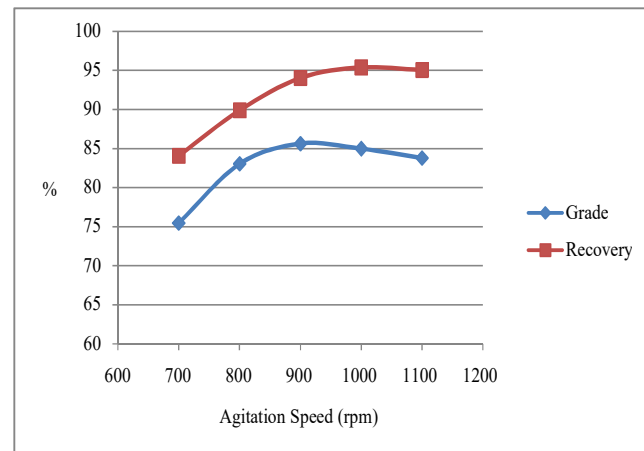

Fig. 5. Effect of agitation speed on the grade and recovery of fluorite rougher concentrate

Effect of collector dosage

The anionic collectors, mainly fatty acids or their salts are employed for the flotation of fluorite mineral (Souvannavong *et al.* 2020)). Pure oleic acid was selected as thestandard collecting agent for fluorite mineral along with such modifying agents as sodium carbonate, sodium silicate and starch. The oleic acid collector was applied within arange of 20 to 100 g/ton of ore. As flotation response of calcite and fluorite is similar with fatty acid collectors, the separation from these minerals presents some problems. Therefore, dilute hydrochloric acid was used to remove calcite prior to flotation.

The results of flotation tests at different dosage of collector are presented in Fig. 6. It can be noticed from this figure that with increase in concentration of collector from 20 g/ton to 100 g/ton, recovery of fluorite improved with a slight change in its grade. The collector yielded the best metallurgical performance (86.05% grade and 94.34% recovery) at a concentration of 80 g/ton and therefore it is the optimum value. This quantity shows the starvation level i.e. the concentration required to make a monomolecular layer of collector on the mineral surface. Excessive dosage of collector tends to reduce the selectivity by collecting the other minerals (Wills and Napier-Munn, 2006).
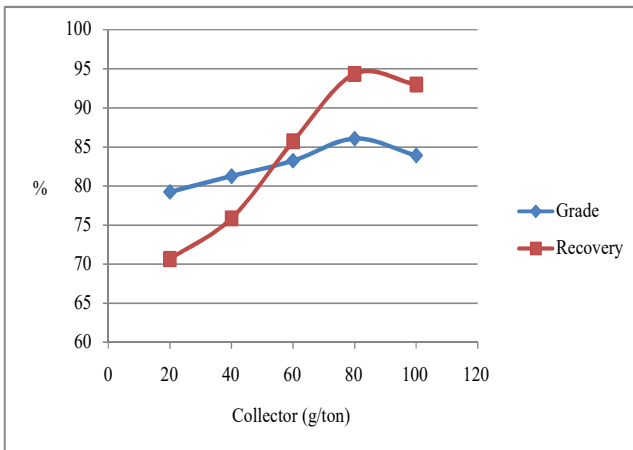
Fig. 6. Effect of collector dosage on grade and recovery of fluorite rougher concentrate

Effect of frother dosage

In few preliminary experiments pine oil, cresol and methyl isobutyl carbinol were tried as frother in combination with oleic acid collector, but no significant effect in froth stability was observed. Then in another experiment polypropylene glycol (polyglycol-400) was used as frother along with oleic acid collector. It helped to produce a thick and stable froth with dense small size bubbles. The further flotation tests were performed by varying frother concentration from 10 to 50 g/ton. The effect of frother dosage on the flotation of fluorite ore is shown in Fig. 7. The figure elucidates that the best grade of concentrate(86.12% CaF_2) and recovery (95.15%) was obtained when 30 g/ton of polyglycol-400 was used as frother. Further frother dosage (40g/ton) did not improve the grade and recovery significantly. The separation efficiency index of flotation test performed using 30 g/ton and 40 g/ton of frother was found almost similar being 69.87 and 69.82 respectively.
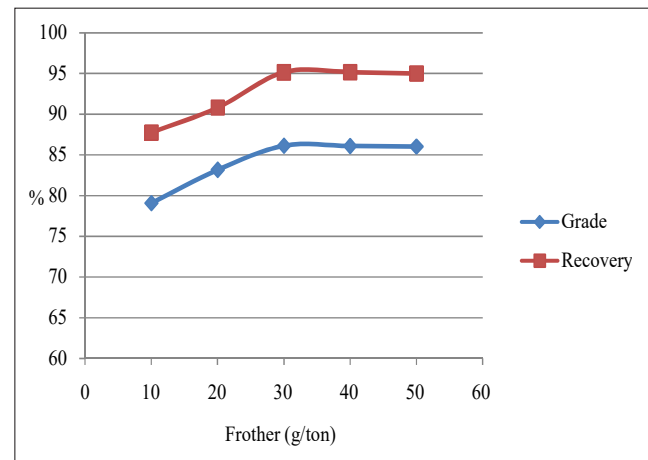

**Fig. 7. Effect of frother dosage on the grade and recovery of fluorite rougher concentrate**

Effect of depressant quantity

The various types of gangue minerals present in fluorite ore were quartz, silicates, hematite and aluminum oxides. In order to depress these gangue minerals, two different types of depressants were employed (Zhou *et al.* 2013). These were sodium silicate (Na_2SiO_3) and starch. Trials were continued using sodium silicate and starch as regulator. The results obtained using different quantities of sodium silicate depressant is shown graphically in Fig. 8. It is apparent from this graph that the best recovery 95.63% of fluorite concentrate was obtained at concentration of 500g/ton sodium silicate depressant. After that value the grade improved a little from 86.88% to 87.25% but the recovery was decreased significantly from 95.63% to 93.22%. The higher separation efficiency 71.83was achieved using 500g/ton sodium silicate depressant as compared to 70.77 using 600g/ton depressant. This effect can be explained that sodium silicate efficiently depresses the gangue minerals (quartz and other silicate minerals) with in proportion amount but excessive amount decreases the recovery due to an over coating of some middling particles (Zhang *et al.* 2017).

Starch solution (10%) was added to depress iron oxide and aluminum oxide minerals. The results of starch depressant on the flotation performance of fluorite are shown in Fig. 9. It can be noted that the most effective quantity of starch depressant for hematite and aluminum oxides was 100 g/ton of ore. Further quantity of starch could not improve the grade and recovery.
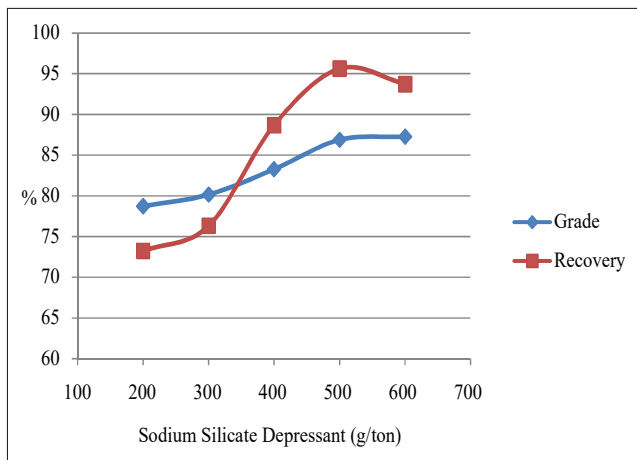
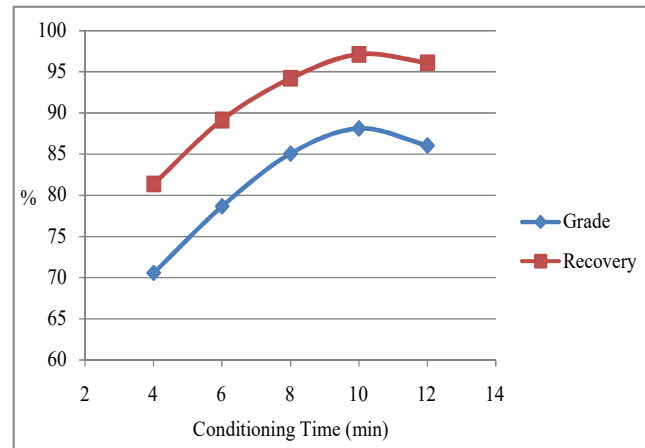**Fig. 8. Effect of sodium silicate depressant quantity on the grade and recovery of fluorite rougher concentrate**
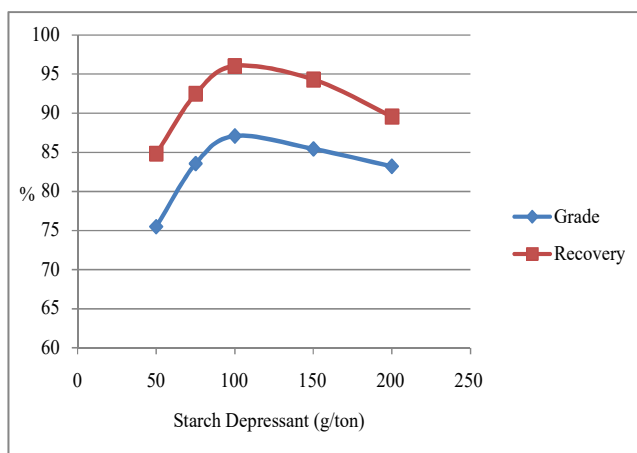
Fig. 9. Effect of starch depressant on grade and recovery of fluorite rougher concentrate

Effect of conditioning time (Stirring)

In order to determine the optimum conditioning time for the flotation reagents, it was varied from 4 to 12 min with increment of 2 min. The results of these tests are shown in Figure 10. It can be seen from the graph that both grade and recovery of rougher concentrate increased with increase in conditioning time and maximum grade (88.12%) and recovery (97.14%) could be obtained in rougher flotation at a conditioning time of 10 min. So, it was established that conditioning time of 10 min was sufficient for the coating of minerals by all the reagents added. It is also obvious from this graph that increasing the conditioning time beyond this period reduced the grade as well as recovery to some extent. This may be due to shearing of collector layer initially deposited on the particle's surface due to reverse process of desorption

of the collector molecules from the surface of the fluorite particles (Song *et al.,* 2006; Corpas-Martinez *et al.*, 2020).

Fig. 10. Effect of conditioning time on the grade and recovery of fluorite rougher concentrate

Optimized flotation conditions

The details of flotation reagents and their optimum quantities are given in Table II. It can be seen from this table that addition of flotation reagents (collector, frother and depressant) is required at each stage of flotation for the maximum output of the product (concentrate). The amount of flotation reagents is decreased step by step in cleaning stages. The pH of pulp, impeller speed (agitation), and conditioning time were remained constant throughout in all the operations (roughing, cleaning and recleaning). Moreover, the best recovery of concentrate is achieved at optimized conditions of flotation parameters. Regrinding of the rougher concentrate prior to cleaning steps is helpful in production of acid grade concentrate.

Material balance

Table III presents the material balance of an optimum fluorite ore flotation test. This particular ore produced an acid grade concentrate of 97.55% CaF_2 with 92.73% recovery after acid leaching followed by one rougher and two cleaning flotation operations. The rougher tailing was discarded due to low CaF_2 content while cleaning tailings were circulated and added in grinding mill for regrinding and flotation. Two stages of cleaning flotation brought the final flotation product (concentrate) up to acid grade and at the same time retained a high weight recovery with a minimum circulating load (Souvannavong *et al.* 2020). This was made possible when the cleaning tailings collected from cleaning steps were diverted to the proper part in the milling circuit for most economical and efficient retreatment as shown in flow-sheet (Fig. 11).

Table II. Optimum conditions of fluorite ore flotation parameters

Parameter/Condition	Rougher Flotation	Cleaner Flotation	Re-Cleaner Flotation
Grind Size of Ore	Minus 200 #	Minus 250 #	Minus 250 #
Pulp Density	30%	20%	15%
Agitation (Impeller) Speed	900 rpm	900 rpm	900 rpm
pH of the Pulp	10	10	10
Oleic Acid Collector	80 g/ton	50 g/ton	25 g/ton
Polypropylene Glycol Frother	30 g/ton	20 g/ton	10 g/ton
Sodium Silicate Depressant	500 g/ton	250 g/ton	100 g/ton
Starch Depressant	100 g/ton	80 g/ton	50 g/ton
Conditioning Time	10 min	10 min	10 min

Note:# Indicates Mesh Number

Table III. Material balance of a typical fluorite ore flotation test

Products of Flotation	Weight %	Grade % CaF_2	Recovery % CaF_2
Re-Cleaner Concentrate	59.16	97.55	92.73
Re-Cleaner Tailing	2.89	45.44	2.11
Cleaner Concentrate	62.05	95.13	94.84
Cleaner Tailing	6.56	21.82	2.30
Rougher Concentrate	68.61	88.12	97.14
Rougher Tailing	20.64	8.59	2.85
Leached Concentrate	89.25	69.73	99.99
Filtrate Solution	10.75	0.06	0.01
Head Sample	100.00	62.24	100.00

Chemical analysis of final fluorite concentrate

Chemical analysis of final flotation concentrate (Table IV) shows that acid grade fluorspar assaying 97.55% CaF_2 with 1.2% SiO_2 and 0.35% Fe_2O_3 could be produced by one rougher and two cleaning flotation. There was no effervescence observed in the final concentrate when acetic acid was added during analysis which indicates the absence of calcium carbonate (calcite). The chemical and aluminum making industries have a great demand of acid grade fluorspar concentrate with less than 1.5% SiO_2. The silica content is usually limited to less than 1.5% with penalty starting from 1.0% SiO_2. These limitations on grade of fluorite content and impurities level need careful control of flotation conditions when high purity and recovery is requirement (Crozier, 1992). More than 95% of acid grade fluorspar is achieved by flotation process (Kienko *et al.* 2010).
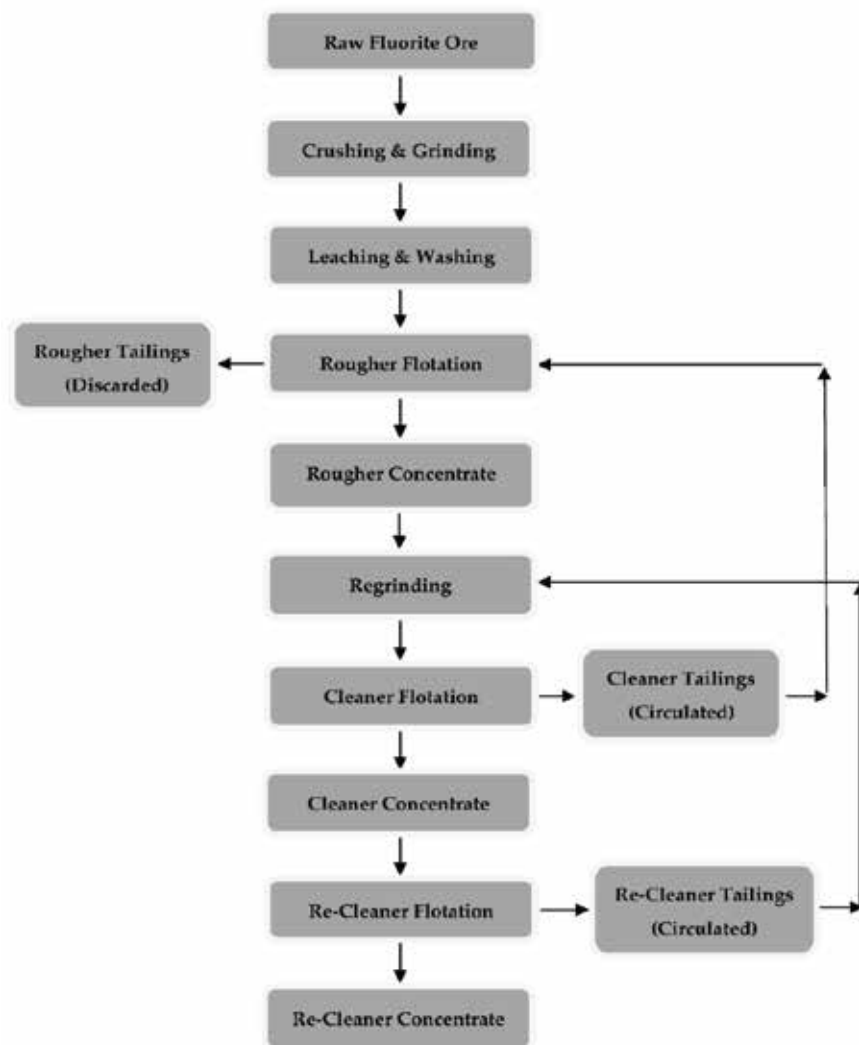
Fig. 11. Flow-sheet for the beneficiation of a low-grade fluorite ore of Tirah Valley

Table IV. Chemical analysis of final re-cleaner flotation fluorite concentrate

Constituents	Percentage
Moisture	0.23
Fluorite (CaF_2)	97.55
Calcium Carbonate ($CaCO_3$)	0.00
Silica (SiO_2)	1.20
Iron Oxide (Fe_2O_3)	0.35
Aluminum Oxide (Al_2O_3)	0.86
Magnesium Oxide (MgO)	traces
Sodium Oxide (Na_2O)	traces
Potassium Oxide (K_2O)	traces
Sulphur (S)	Not detected
Phosphorous (P)	Not detected

Conclusion

The froth flotation technique was found suitable to produce fluorite concentrate of desired grade and specification from this ore. Calcium carbonate, silica, iron oxide and alumina were the major impurities in this particular ore which were minimized. Dilute hydrochloric acid leaching prior to flotation was found helpful in removing all the calcium carbonate in the flotation concentrate. Multiple cleaning (cleaning and re-cleaning) of rougher flotation concentrates with addition of sodium silicate depressant at each stage minimized the silica content to less than 1.2% which is required for production of acid grade concentrate. Use of starch depressant helped to control the amount of iron and aluminum minerals present in the ore. After optimization of process parameters, the provided fluorite ore containing around 62.24% CaF_2 could be beneficiated and upgraded to a chemical grade flotation concentrate containing 97.55% CaF_2 content with an overall 92.73% recovery.

Acknowledgment

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