

## IMPROVEMENT IN BENEFICIATION OF LOW GRADE FLUORITE ORE FROM KALAT MARAN RANGE

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This paper describes a bench scale investigation on the preparation of metallurgical and chemical grade fluorspar concentrate from a low-grade fluorite ore from Kalat Maran Range. A combination of chemical treatment and flotation techniques has been applied to fluorite ore. The ore initially containing 36.5% calcium fluoride has been processed and beneficiated to produce calcium fluoride concentrate containing 98.7% calcium fluoride with 99.8% recovery.

**Key words:** Metallurgical grade, Fluorite concentrate, Chemical grade fluorite concentrate, Chemical treatment, Flotation parameters.

### Introduction

Fluorite or Fluorspar ( $\text{CaF}_2$ ) is used as a flux in making steel glass, enamelling of utensils and making of hydrofluoric acid. Small reserves of fluorite ore has been reported in Chitral, Dir and Hazara Districts. The significant deposits are found in Kalat Division. Most of the fluorite are milky but other colors are also found.

The fluorite deposit (Zaki Ahmad 1978) occur in the Northern part of the Kohi-Maran Range in Baluchistan Province, about 40 miles by road south from Kolpur Railway station, which is 20 miles from Quetta. The known deposits of fluorite are in the eastern slope of the Kohi-Maran Range, the crest of which is roughly parallel with the axial trace of a major northtrending anticline. The Veins are in dark grey massive limestone of the Chiltan limestone formation of Jurassic age. The calcite-fluorite Veins have formed as hydrothermal filling and replacement in the limestone. Most of the fluorite is milky, but those of other colors are also present.

The processing of a Kalat Maran Range low grade fluorite ore aims at developing a process to produce a minimum of 85% fluorite concentrate for metallurgical use etc.

In 1967 Whang and Ki-up stated that by adjusting the pulp pH to 9.5 with sodium carbonate and adding about 700g of sodium silicate and 500g of oleic acid per ton of ore at first and second conditioning stages respectively, a fluorite concentrate assaying more than 97% calcium fluoride was obtained at 40°C with a recovery of 95-96%.

According to Kogan and Eidelman (1972) at a pH of 7.0 and an ambient temperature of 35°C the quantity of concentrate is decreased. The only satisfactory results were obtained

when 200g per ton of K-soap as a collector was used. The time of agitation of the pulp was ten min. A concentrate grade of (94-96%) calcium fluoride was obtained during the 1st stage of flotation. They concluded that at a grind size of 74 microns fluorite can be beneficiated by normal flotation.

Robert Dominigue (1983) used sodium alginate as effective depressant in froth flotation of an ore with a gangue comprising of calcite, dolomite, talc, chlorite and barite present as ultra fine slime particles under 80 microns size, in flotation of an ore containing 80% calcium fluoride and 20% calcite ground to 200. He used 1 kg per ton sodium silicate as depressant and 250g per ton anionic fatty acid as collector, a fluorite concentrate containing 84% calcium fluoride was obtained. Replacement of the silicate depressant by 200 g per ton ore solubilized soberagene, a powder algae containing alginic acid gives a concentrate of 94% calcium fluoride.

Nesterova and Magda (1983) produced high purity calcium fluoride 99.98% from ores containing fluorite (63.3-66.1) and quartz 13-22% by flotation, leaching the flotation concentrate in 20% hydrochloric acid, roasted at 700°C for the removal of sulphur and flotation reagents, magnetic separation and sintering with ammonium fluoride for the removal of silica and then repeated leaching, washing with water for the removal of chloride ion and drying at 150°C to 180°C.

Streat and Elwali (1983) studied the solubility of calcium fluoride in acid sandy soils via  $\text{Ca}^{++}$  and  $\bar{\text{F}}$  activity measurements. Calcium fluoride was added to the three acid sandy soils previously limed to various pH between (4.0 and 7.8). The equilibrium  $\text{Ca}^{++}$  and  $\bar{\text{F}}$  activities in soil water suspensions were determined and compared that  $\text{CaF}_2$  was the solid phase controlling  $\bar{\text{F}}$  activity in suspension pH range of

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(5.5 to 7.0), however, below 5.0 the  $\bar{F}$  activity indicated suspension with respect to  $\text{CaF}_2$ . The  $\text{pksp}$  for calcium fluoride precipitated in the laboratory was calculated to 10.5. The result revealed that liming fluoride contained sandy soils may reduce fluoride ion in soil solution by precipitation.

Kumar in 1974 studied various parameters like grind size (-100 mesh) on the low grade fluorite ore and then floated with sodium oleate as collector and (1% terpineol in MeOH) as frother and depressor 20% sodium silicate, the pH of 8.5, the conditioning time for 15 min, air was bubbled through the slurry. The fluoride concentrate obtained 80% calcium fluoride through flotation.

Linke in 1958 studied the solubility of calcium fluoride in aqueous solution of hydrochloric acid stated that of (0.01 to 1.0) normality of the aqueous hydrochloric acid dissolves (0.00087 to 0.028) g moles per liter of calcium fluoride.

The flotation of fluorite ore using a new collector oleoyl sarcosine (OS) for upgrading the ore. They achieved to get a concentrate assaying 92.17%  $\text{CaF}_2$  with 80.1% recovery from an ore containing 51.85%  $\text{CaF}_2$  and high contents of calcite, quartz and iron oxide.

## Experimental

**Mineralogy.** Mineralogical studies on the ore showed that besides fluorite, the other predominant mineral was calcite.

The gangue mostly consisted of Quartz and varying amounts of iron oxides.

X-ray diffraction (Siemens D-5000) studies on ground ore showed the presence of fluorite, calcite, quartz, and other minerals of iron. A qualitative diffractographic scan shown the 2 $\theta$  and d values for different minerals species. The diffractogram obtained is presented in Fig 1. The average mineralogical composition of head sample is given in Table 1.

**Chemical analysis.** The ore was analysed using conventional technique of chemical analysis. The major and minor elements in the ore were confirmed by X-ray fluorescence (JSX-603, Fig. 2) followed by atomic absorption spectrophotometry (Hitachi Z-8000). The average chemical analysis is given in Table 2.

**Sample preparation.** The ore weighing about 130 kg was received in the form of lumps, measuring 30mm to 100mm in size. The ore samples for testwork were prepared by subjecting about half of the lump ore to primary and secondary crushing to a product size (3-4 mm). The rolls mill product was screened and the results are presented in Table 3. A 100 kg sample of Rolls mill products was divided by splitting for the determination of "Bond Work Index". Rest of the Rolls mill product was ground in the Rod mill to obtain product 100% passing 74 microns as already indicated in the mesh of liberation studies to prepare feed for the further processing work.

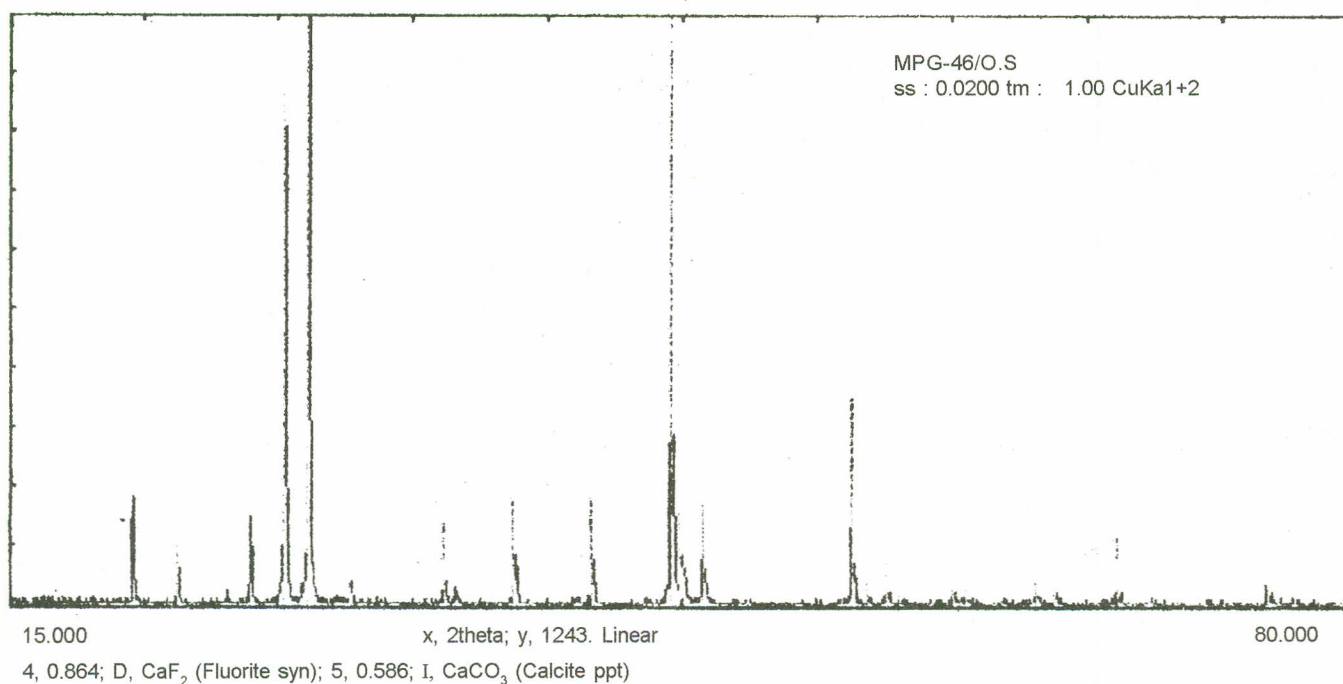


Fig. 1 Qualitative diffractogram for different minerals.

**Mesh of liberation.** Mesh of liberation study was carried out by grinding rolls mill product in a rod mill and screening the ground material. The screen analysis of the rod mill product has been shown in Table 4. The various size fractions obtained as above were subjected to mineralogical examination under microscope for counting the number of liberated and interlocked mineral particles. The results of mesh of liberation study are presented in Table 5. The Table 5 shows that the calcium fluoride is liberated from gangue to the extent of about 100% if ground to 74 microns.

**Bond work index.** The Kalat Maran Range low grade fluorite is calcareous in nature and breaks easily during grinding large amount of fines were generated. The "Bond Work Index" as determined by using the procedure described by

Diester 1987 comes out to be 7.398 kw h per ton of the ore. The graphical presentation of "Bond Work Index" is shown in Fig.3.

**Processing. Acid Treatment Tests:** The calcite in the ore is about half of the total amount of material, a series of acid treatment tests were conducted to separate the calcite. In these tests fluorite ore ground to minus 74 microns size was used. The ore was ground in a laboratory rod mill and then subjected for acid treatment. Various solid to liquid ratios using hydrochloric acid were used. The solid to liquid ratio is presented in the Table 6. At the end of the acid treatment operation, the undissolved residue was separated and washed to the neutral pH, dried, weighed and stored for flotation tests. The analysis of fluorite after hydrochloric acid treatment is given in Table 7.

**Flotation Tests:** The residue assaying 74% calcium fluoride obtained as above after leaching with hydrochloric acid was subjected to flotation in half kg batches. The flotation was carried out in a Denver (Model D-12) flotation machine. The effect of flotation parameters such as pH, percent solids feed size, the impeller speed and reagents were studied to obtain optimum grade and recovery of calcium fluoride. The various parameters optimized are given in Table 8. The rougher concentrate obtained assayed 89.92% calcium fluoride with a recovery of 99.96% in the optimised condition. It was then subjected to cleaning operation which yielded a concentrate 99.7% calcium fluoride with a recovery of 99.8%. The metallurgical balance obtained under the optimum operating parameters is given in Table 9. The chemical analysis of the cleaner concentrate is given in Table 10.

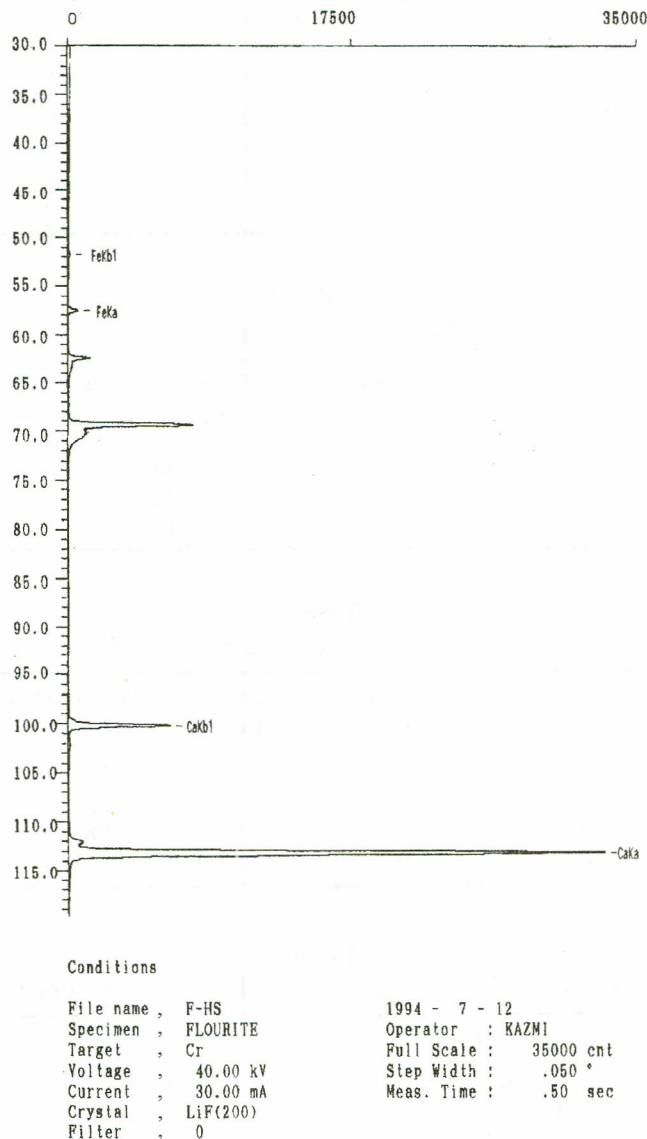
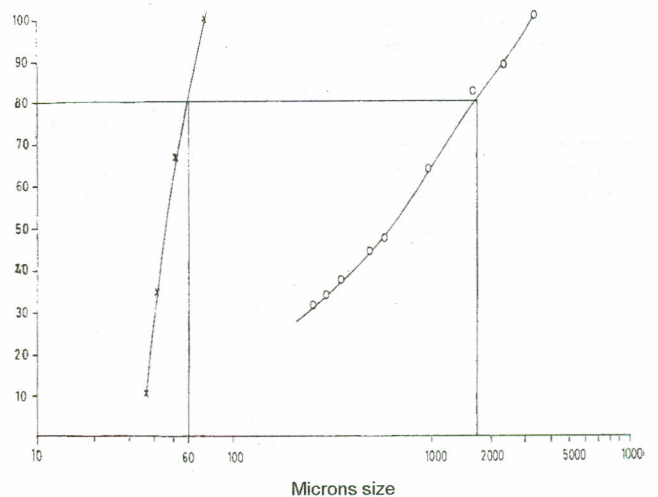


Fig 2. Chemical analysis of the elements by X-ray fluorescenes.



F<sub>2</sub>, 1750 μ; G<sub>bp</sub>, 2.51 g, rev; P<sub>1</sub>, 74 μ; P<sub>2</sub>, 60 μ; W<sub>i</sub>, 7.398 Kw. hr./5 Ton

Fig 3. Bond Work Index of Fluorite.

## Results and Discussion

Mineralogical composition of fluorite is shown in Table 1. The calcium fluoride is associated with approximately an equal amount of calcite. The next major constituents in the fluorite ore are the iron mineral limonite and quartz. Minor quantities of goethite, hematite and magnetite are also present. The hydrated oxides of iron like limonite, goethite are combined with calcium fluoride grains but hematite and magnetite are partially combined with calcium fluoride grains. Calcite was removed from the ore by leaching with hydrochloric acid prior to flotation. The remaining impurities like silica and iron oxides are removed by flotation.

**Table 1**

Mineralogical composition of head sample of fluorite ore

Minerals	Percent (%)
Fluorite	36.46
Calcite	37.99
Quartz	8.50
Limonite	12.77
Goethite	2.29
Hematite	0.92
Magnetite	1.04

**Table 2**

Chemical analysis of fluorite ore

Constituents	Percent (%)
Calcium carbonate	38.00
Silica	8.50
Iron oxide	17.00
Calcium fluoride	36.50

**Table 3**

Sieving analysis of rolls product of fluorite ore

Sieve size (Microns) $\mu$	Percent weight (+ mesh)	Cumulative % wt (+ mesh)	Cumulative % wt (- mesh)
33.27	19.75	19.75	80.25
1615	21.68	41.43	58.57
991	15.23	56.66	43.34
701	7.06	63.72	36.28
590	5.77	69.49	30.51
350	5.10	74.59	25.41
295	1.85	76.44	23.56
246	1.94	78.38	21.62
175	3.07	81.45	18.55
147	1.66	83.11	16.89
124	1.27	84.38	15.62
104	1.38	85.78	14.22
74	2.24	88.12	11.88
-74	11.88	100.00	00.00

Table 1-5 shows the results of the mineralogical composition, chemical analysis and mesh of liberation studies analysis. It may be concluded that calcium fluoride grains are liberated at 74 microns size. Table 6 shows the effect of hydrochloric acid on fluorite ore. Commercially available acid having 32% strength was used after dilution because concentrated acid reacted spontaneously with calcite. The dilution was studied from (340 g l<sup>-1</sup> to 355 g l<sup>-1</sup>) HCl. It was observed that 100% calcite was removed with an acid concentration of 355 g l<sup>-1</sup> HCl at a liquid to solid ratio of (1.8). A reaction time of one hour was found to be satisfactory at room temperature. Table 7 shows the analysis of the residue obtained after the

**Table 4**

Sieving analysis of rod mill product of fluorite ore

Sieve size (Microns) $\mu$	Percent weight retained	Cumulative % wt (+ mesh)	Cumulative % wt (- mesh)
124	1.52	1.52	99.48
104	1.84	3.36	96.64
74	3.35	6.71	93.29
-74	23.29	100.00	00.00

**Table 5**

Mesh of liberation study

Sieve size (microns) $\mu$	Percent free calcium fluoride grains
149	94.0
104	98.0
74	100.00

**Table 6**

Effect of hydrochloric acid on fluorite

HCL (g l <sup>-1</sup> )	Ratio of solid to liquid	Weight of residue (g)	Percent calcite dissolved
340	1.700	552.0	96.91
345	1.725	546.4	97.96
350	1.750	540.9	98.99
355	1.775	535.50	100.00

**Table 7**

Analysis of fluorite after hydrochloric acid treatment

Constituents	Percent (%)
Calcium fluoride	74.18
Silica	17.27
Iron oxide	8.55
Calcium carbonate	Nil

**Table 8**  
Optimum flotation parameters

Parameters	Rougher	Cleaner
Grain size	74 m	74 m
Pulp density	30%	20%
Conditioning time	5 min	5 min
Flotation time	15 min	15 min
Speed of impeller	1200 rpm	1050 rpm
<i>Reagents:</i>		
Collector (Oleic acid)	100 g t <sup>-1</sup>	50 g t <sup>-1</sup>
Frother/Promoter (Sodium dodecyl sulphate) (SDS)	25 g t <sup>-1</sup>	10 g t <sup>-1</sup>
<i>Depressant:</i>		
Sodium silicate	200 g t <sup>-1</sup>	100 g t <sup>-1</sup>
Starch	40 g t <sup>-1</sup>	25 g t <sup>-1</sup>

acid treatment. As a result of this treatment the calcium fluoride increases from 36.5% to 74.18%, silica from 8.5% to 17.27%, while iron minerals and calcium carbonate decreases from 17.0% to 8.55% and 38% to zero% respectively.

Table 8 shows the optimum flotation parameters for rougher and cleaner flotations. The pH of the pulp was 9.5 in both flotations. 100 per ton of oleic acid as collector was used in rougher and 50g per ton in the cleaner flotation respectively. Similarly 25g per ton of sodium dodecyl sulphate (S.D.S.) as frother/promoter was used in rougher and 10g per tone in cleaner flotations respectively. The sodium silicate and starch were used as sodium silicate and starch has been indicated in Table 8. Conditioning time of 5 min was found satisfactory in both flotations for coating on surfaces of minerals and 15 min was found sufficient for finishing the flotation process. The speed of the impeller was found best at 1200 rpm in rougher and 1050 rpm in cleaner flotation.

Table 9 shows metallurgical balance for calcium fluoride. The grade of calcium fluoride increases from 74.18 to 89.97% in the rougher flotation with the recovery of 99.96% in the cleaner flotation the grade of calcium fluoride increases from 89.97 to 98.7% with a recovery of 99.8%. It has been observed from the results obtained that chemical treatment of the ore prior to the flotation gives better results and is a proper processing technique than conventional flotations. It has also been indicated that simple flotation without acid treatment gives concentrate assaying 85% calcium fluoride with a recovery of 76%. The chemical treatment of the

**Table 9**  
Metallurgical balance for CaF<sub>2</sub> flotation

Products	Wt (%)	Grade (% CaF <sub>2</sub> )	Distribution
Cleaner concentrate	75.0	98.7	99.80
Cleaner tailing	7.42	1.60	0.16
Rougher concentrate	82.42	89.97	99.96
Rougher tailing	17.58	0.14	0.04
Heads	100.00	--	100.00

**Table 10**  
Chemical analysis of final concentrate

Constituents	Percent (%)
Calcium fluoride	98.7
Silica	0.7
Iron oxide	0.6
Total	100.0

ore and flotation gives final concentrate assaying 98.7% calcium fluoride and a recovery of 99.8% is achieved as is indicated in Table 10.

### Conclusion

The laboratory scale beneficiation studies on Kalat Maran Range low grade fluorite ore has indicated that it is possible to upgrade the fluorite ore from 36.5% CaF<sub>2</sub> to 98.7% CaF<sub>2</sub> leading to good recoveries. High grade calcium fluoride (98%) finds many useful applications in chemical and metallurgical industries.

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