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Flotation Concentration of a Low Grade Fluorite Ore from
Southwestern New Mexico: A Preliminary Study

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Abstract

The purpose of this study was to determine if a low grade fluorite ore could be upgraded to a commercial grade fluorite product. The initial fluorite content of the ore was six to eight percent.

In general the results of this study were favorable in that a concentrate assaying 40 percent or better fluorite with a minimum recovery of 80 percent could consistently be achieved, with the best results showing that 85 percent of the fluorite could be collected in a product which assayed nearly 55 percent fluorite. These results were achieved with a very simple flow sheet which consisted of grinding, rougher flotation and only one stage of cleaner flotation. It seems obvious that additional stages of cleaner flotation combined with depressing the gangue minerals should produce a commercial grade fluorite product.

Introduction

Fluorite (CaF_2) is a widely disseminated, mineral occurring throughout much of the southwestern United States. It is typically found in small, low grade deposits which often assay less than 10 percent fluorite. Fluorite commonly occurs with a variety of other minerals. These include calcite (CaCO_3), dolomite ($\text{CaMg}(\text{CO}_3)_2$), barite (BaSO_4), quartz (SiO_2), sphalerite (ZnS) and apatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH}, \text{F}, \text{Cl}, \text{CO}_3)$).

The United States imports the majority of the fluorite which is consumed by the country's industries each year. Major producers of fluorite in the world are Mexico, United States, South Africa, United Kingdom, U.S.S.R, France and Italy (Montgomery, 1981).

Known occurrences of fluorite in New Mexico number more than 200. Small scale mining has been done on at least 91 deposits. Since the 1880's total production of fluorite in New Mexico is estimated at 700,000 tons (McAnulty, 1978).

To be of commercial value the typical low grade fluorite material must be upgraded to meet one or more of the following specifications:

- 1). Acid grade: minimum of 97 percent fluorite with a maximum of 1.5 percent silica (SiO_2) and 0.10 percent sulfide sulfur. This grade of material is used as feed stock in the manufacture of hydrofluoric acid.
- 2). Ceramic grade: 93 to 95 percent CaF_2 with 3 percent maximum SiO_2 , 1.5 percent CaCO_3 , 0.14 percent Fe_2O_3 and no lead, zinc or sulfur. This grade of material had application in the ceramic and glass industries.
- 3). Metallurgical grade: 60 percent minimum effective

CaF₂ after subtracting 2.5 times the SiO₂ content from the CaF₂ content. This grade of material is used in the steel making process as a flux. It also is used sometimes in fluxing mixtures for fire assaying gold and silver.

General Treatment Scheme for Upgrading Fluorite Ores

Flotation is the usual method for concentrating fluorite to a commercial grade product. Due to the difficult problems encountered when trying to selectively float fluorite from its associated gangue minerals and produce high grade commercial products by flotation, the process flowsheets are complex, with many stages of grinding, conditioning and flotation, with tailings streams being recycled to earlier treatment stages. It is not unusual to have six or more stages of cleaner flotation to produce an acid grade product.

A variety of different collectors have been used with success in the flotation of fluorite. These collectors include, fatty acids, oleic acid, sodium oleate, and various soaps. Depressants are also a vital part of successfully treating fluorite. Commonly used depressants include, quebracho for calcite and lignin sulfonate and sodium fluoride for barite and other minerals.

The order of addition of the reagents can also be of importance in achieving the highest grade product possible. Small changes in the amounts of reagents added will have large effects on grade and recovery of the final product.

The classical procedure for floating fluorite used one or more fatty acids as collectors (i.e. Oleic acid, FA-1 FA-2,

etc). Treating fluorite by the fatty acid flotation method has been the subject of several USBM Reports of Investigations (Fine, Calhoun and O'Meara, 1946; Fine, O'Meara, 1947; Engel, Heinen, 1961).

Additional USBM reports describe a second system for treating fluorite by flotation based on using sodium fluoride and lignin sulfonate as the basic flotation chemistry (Browning, Eddy, McVay, 1963; Bloom, McKinney and Evans, 1963; Eddy, Browning, 1964; Eddy, Browning, Hardemon, 1967a; Eddy, Browning, Hardemon, 1967b). With this new system the results were reported to be better, with a simpler flowsheet for the ore being tested, when compared to the older fatty acid flotation procedure.

Characterization of a Typical New Mexican Fluorite Ore

The fluorite ore sample for this study was provided to the New Mexico Bureau of Mines and Mineral Resources by the Small Mines division of Phelps Dodge. It was reported to be typical of many small southwestern deposits in that it contained a small amount of fluorite (less than 10 percent). The major gangue mineral was quartz with minor gangue minerals of calcite, plagioclase, potassium feldspar and pyrite.

Purpose

The purpose of this study was to determine if the fluorite

could be upgraded by flotation to produce a commercial grade product.

The flow sheet for this test work consisted of crushing, grinding and rougher flotation followed by one stage of cleaner flotation. The variable conditions in the flotation testing were pH, temperature and various reagent combinations.

Sample Preparation

The bulk-as-received sample was dried and then crushed to a nominal 10 mesh. The crushed product was blended and then split into one kilogram samples for further test work. The one kilogram splits were stored in brown paper sacks until needed.

Grinding Studies

A one kilogram sample of nominal 10 mesh ore was ground at 5 percent solids, in a ceramic mill, with a ceramic grinding charge weighing 3200 grams, for varying periods of time. The ground slurry was then screened wet at 65 mesh and the over size was screened dry between 10 mesh and 65 mesh. The test results were used to determine the amount of grinding necessary for the flotation test work. Based on these results, a two-hour grinding time was chosen for all subsequent flotation testing.

Particle Size Distributions as a Function of Grinding Times

Mesh (tyler)	<u>Grinding Time (minutes)</u>			
	0	30	90	120
10	95.5	100.0	100.0	100.0
28	40.8	79.8	95.1	98.6
48	24.0	65.1	92.6	98.0
65	18.2	56.9	87.7	96.4

Flotation Testing

A one kilogram sample of nominal 10 mesh ore was ground for 2 hours in a ceramic mill at 50 percent solids. The ground pulp was transferred to the flotation cell and the flotation reagents were added in the following quantities:

Collector: FA-2 (0.5 lb/ton)
 Frother : Aero 65 (as needed)
 pH : 10 (sodium carbonate)

The slurry was conditioned for 10 minutes, after which air was introduced into the slurry and the fluorite containing material was floated until the froth was barren. The rougher concentrate was floated again to produce a cleaner concentrate and cleaner tail. The resulting cleaner concentrate, cleaner tail and rougher tail were analyzed for fluoride content (with a specific ion electrode) and the CaF_2 content was then calculated. The results are shown below:

Test Product	Weight %	<u>% CaF_2</u>	
		Assay	Distribution
Cleaner Concentrate	14.6	28.4	73.7
Cleaner Tail	11.0	1.0	2.1
Rougher Tail	74.4	1.8	24.3
Calculated	100.0	5.6	100.0

The conclusion from the results of the preliminary flotation test was that the fluorite content could be substantially upgraded by flotation. Therefore seven additional tests were performed using the same test procedure to determine the effect of several variables on the recovery of the fluorite. These variables included:

temperature : 40 and 70 °C
pH : 9 and 10
Reagent combinations

A short description of each test is listed below and the test conditions and results are summarized in Tables 1 and 2.

- Test 101: Establish base line response for comparison to the other tests results. Collector 0.8 lb/ton FA-2, temperature 40 C, pH 9.0 with sodium carbonate, quebracho addition 0.1 g (0.2 lb/ton).
- Test 102: Baseline with the addition of sodium silicate.
- Test 103: Increased pH with sodium silicate addition.
- Test 104: Test 102 with pine oil as frother.
- Test 105: Baseline with higher temperature (70 C)
- Test 106: Baseline with final concentrate collected at lower impellor speed (800 rpm).
- Test 107: Base line with products taken in timed intervals.

Effects of Process Variables

An analysis of the test results from these seven flotation tests leads to the following conclusions.

Table 1: Summary of Flotation Test Conditions
Phelps Dodge Fluorite

Test No	Stage	Collector FA - 2 lb/ton ⁽¹⁾	Quebracho lb/ton ⁽¹⁾	Sodium Carbonate lb/ton ⁽¹⁾	Sodium Silicate lb/ton ⁽¹⁾	Pine Oil Frother lb/ton ⁽¹⁾	Temperature °C	pH
101	Rougher Float	0.8	0.2	1.05	--	--	40	9.0
	cleaner float	--	--	1.00	--	--	40	9.0
102	Rougher	0.8	0.2	1.27	0.2	--	40	9.0
	cleaner	--	--	0.7	--	--	40	9.0
103	Rougher	0.8	0.2	?	0.2	--	40	10.0
	cleaner	--	--	?	--	--	40	10.0
104	Rougher	0.8	0.2	0.8	0.2	0.3	40	9.0
	cleaner	--	--	0.4	--	--	40	9.0
105	Rougher	0.8	0.2	3.1	--	--	70	9.0
	cleaner	--	--	--	--	--	70	9.0
106 ⁽²⁾	Rougher	0.8	0.2	1.0	--	--	40	9.0
	cleaner 1	--	--	.6	--	--	40	9.0
	cleaner 2	--	--	3.3	--	--	40	9.0
107	Rougher	0.8	0.2	1.12	--	--	40	9.0
	Concentrate 1	--	--	0.5	--	--	40	9.0
	" 2	--	--	--	--	--	40	--
	" 3	--	--	--	--	--	40	--
	" 4	--	--	--	--	--	40	--

(1) Reagent additions were calculated based on feed weight to each stage.

(2) 1st cleaner at 800 rpm; 2nd cleaner at 1200 rpm.

(3) Concentrates taken on time intervals at 30 sec, 60 sec, and 120 sec.

Table 2

Summary of Floatation Test Results
Phelps Dodge Fluorite

Test No	Product	Weight	CaF ₂ % Assay	CaF ₂ % Recovery	Calculated Grade Cumulative Product
101	Cleaner concentrate	13.0	46.2	88.4	46.2
	Cleaner tail	1.7	11.2	2.3	42.2
	Rougher tail	85.3	0.7	8.8	6.8
102	Cleaner concentrate	13.1	43.4	83.2	43.4
	Cleaner tail	1.7	7.5	1.9	39.3
	Rougher tail	85.2	1.2	14.9	6.8
103	Cleaner concentrate	17.4	40.5	92.6	40.5
	Cleaner tail	3.7	1.6	0.8	33.7
	Rougher tail	78.9	0.6	6.6	7.6
104	Cleaner concentrate	12.1	42.2	83.2	42.2
	Cleaner tail	1.7	9.4	2.6	33.7
	Rougher tail	86.2	1.0	14.2	6.2
105	Cleaner concentrate	33.8	20.5	93.4	20.5
	Cleaner tail	8.5	1.6	1.8	16.7
	Rougher tail	57.7	0.6	4.8	7.4
106	Cleaner concentrate	14.0	55.7	85.7	55.7
	Cleaner tail	1.6	38.8	6.8	54.0
	Rougher tail	84.4	0.8	7.5	9.1
107	1st concentrate	6.0	43.2	31.7	43.2
	2nd concentrate	4.9	42.9	25.8	43.1
	3rd concentrate	4.6	47.7	26.9	44.4
	Cleaner tail	2.7	23.6	7.8	41.3
	Rougher tail	81.8	0.8	7.8	8.2

1. The addition of sodium silicate appeared to have a detrimental effect on both the recovery and grade of the fluorite product. These effects can be seen by comparing the assay results of the cleaner concentrate products or the tailing products from Test Nos. 101, 102 and 104 as shown in the table below. In fact, Test Nos. 102 and 104 had the highest loss of CaF_2 in the tailings out of the seven tests performed.

2. The addition of pine oil as a frother had little effect on the flotation response as seen in the results from Test Nos 102 and 104 as shown below.

Cleaner Concentrate Results

Test No	Sodium Silicate	% CaF_2	
		Grade	Recovery
101	no	46.2	88.4
102	yes	43.4	82.8
104	yes	42.2	83.2

Tailing Results

Test No	Sodium Silicate	% CaF_2	
		Grade	Recovery
101	no	0.7	8.8
102	yes	1.2	14.9
104	yes	1.0	14.2

3. As seen from comparing the results of Test Nos 101 and 105, the effect of increased temperature (test No.105) was to increase the fluorite recovery at the expense of achieving a

substantially lower grade. Test No. 105 achieved the highest recovery of any of the seven tests, along with the lowest grade. These results are shown below.

Cleaner Concentrate Results

Test No	Temperature	% CaF ₂	
	°C	Grade	Recovery
101	40	46.2	88.4
105	70	20.5	93.4

The increased temperature obviously increased the floatability of both the fluorite and the gangue minerals. Floating this ore at an increased temperature might be acceptable in a rougher flotation stage. This would insure maximum recovery of fluorite in the rougher stage and might eliminate the need for any scavenging of the rougher tails. The rougher concentrate would be cleaned several times to make a commercial grade product. An alternative would be to carry out the rougher flotation at a lower temperature and then send the rougher tails to a be scavenged at a higher pulp temperature, with the scavenged concentrate recycled to the rougher flotation.

4. The effect of increased pH (pH 10, Test No. 103) was similar to the temperature effect except there was only a moderate drop in the grade of the concentrate. This can be seen by comparing the results from Test Nos. 102 and 103.

Cleaner Concentrate Results

Test No	pH	% CaF ₂	
		Grade	Recovery
102	9.0	43.4	83.2
103	10.0	40.5	92.6

Similar to the above argument for performing the rougher flotation at an elevated temperature, the same argument can be made for performing the rougher flotation at an elevated pH. Indeed increasing the pulp pH would be preferred to increasing the pulp temperature, due to the fact that it would be easier and cheaper, than trying to heat the pulp, and maintain the elevated temperature.

5. Collecting the cleaner concentrate under the gentler condition of a lower impellor speed produced the highest CaF₂ grade product with a minor decrease in recovery as shown below. In Test No. 106 the concentrate was floated using a lower impellor speed of 800 rpm (as opposed to the normal 1500 rpms). This test produced the best results with the highest grade concentrate (55% fluorite) and good recovery (85 % recovery).

Cleaner Concentrate Results

Test No	Impellor rpms	% CaF ₂	
		Grade	Recovery
101	1500	46.2	88.4
106	800	55.7	85.7

6. In test 107 the flotation concentrate was collected in timed intervals of 30 seconds, 30 seconds and 60 seconds and each

product was analyzed separately. Collecting the final concentrate in timed increments failed to produce a high grade product. In fact, as seen from the results of test 107 the product collected during the second minute of flotation was of higher grade than the products collected during the first minute. The test results are shown below.

Cleaner Concentrate Results

Test No	Time seconds	% CaF ₂	
		Grade	Recovery
107	0-30	43.2	31.7
	30-60	42.9	25.8
	60-120	47.7	26.9
	cumulative	44.4	84.4

Conclusions

This low grade fluorite ore (about six percent CaF_2) was successfully upgraded to make a product containing 55 percent fluorite with a recovery of 85 percent of the fluorite. Additional stages of grinding and flotation might further upgrade the concentrate to produce one of the commercial grades of fluorite. During this test work no attempt was made to depress any of the gangue minerals (SiO_2 , CaCO_3) to prevent them from floating. An investigation into this area would be the logical place for additional test work to begin. Indications are that the fluorite floats well enough to make at least a minimum grade product if the gangue minerals can be rejected.

Maximum recovery might be obtained by using a rougher-scavenger-recleaning circuit, with the scavenger operating at a higher pH (10.0) to insure maximum recovery of the fluorite bearing material.

A second line of investigation would be to test low grade fluorite ores with the sodium fluoride, lignin sulfonate system as described previously. This approach could minimize the complexity of the resulting flowsheet.

References

- Browning, J. S., Eddy, W. H., and McVay, T. L., 1963, Selective Flotation of Barite-Fluorspar Ores From Kentucky, USBM Report Of Investigation 6187, 15 pp.
- Bloom, P. A., McKinney, W. A., and Evans, L. G., 1963, Flotation Concentration of a Complex Barite-Fluorspar Ore, USBM Report of Investigation 6213, 16 pp.
- Eddy, W. H., and Browning, J. S., 1964, Selective Flotation of a Barite-Fluorspar Ore from Tennessee, USBM Report of Investigation 6491, 8 pp.
- Eddy, W. H., Browning, J. S., Hardemon, J. E., 1967a, Selective Flotation of a Fluorspar Ore from Illinois, USBM Report of Investigation 6953, 9 pp.
- Eddy, W. H., Browning, J. S., Hardemon, J. E., 1967b, Continuous Flotation of Fluorspar from a Calcareous Illinois Ore, USBM Report of Investigation 6982, 10 pp.
- Engel, A. L., and Heinen, H. J., 1961, Experimental Treatment of Nevada and California Fluorspar Ores, USBM Report of Investigation 5751, 11 pp.
- Fine, M. M., Calhoun, W. A., and O'Meara, R. G., 1946, Concentration of Fluorite from Metals Reserve Company Stock Piles, USBM Report of Investigation 3893, 13 pp.
- Fine, M.M., and O'Meara R. G., 1947, Laboratory Beneficiation of Disseminated Fluorspar Ores, USBM Report of Investigation 4158, 19 pp.
- McAnulty, W. N., 1978, Fluorspar in New Mexico, New Mexico Bureau of Mines and Mineral Resources, Memoir 34, 64pp.
- Montgomery, Gill, 1981, Fluorspar, pp 101-102, Engineering and Mining Journal VOL 182, No. 3, McGraw-Hill, N.Y., New York.