EXPERIMENTAL TREATMENT OF NEVADA AND CALIFORNIA FLUORSPAR ORES

By A. L. Engel and H. J. Heinen

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by

A. L. Engel[2/] and H. J. Heinen[2/]

INTRODUCTION AND SUMMARY

This report is a compilation of preliminary and, in some cases, more extensive concentration experiments by the Federal Bureau of Mines on low- and medium-grade fluorspar ores from three localities in Nevada and one in California. The work was done on samples obtained from Shoshone mine, Nye County, Valery mine, Pershing County, and the Broken Hills mine, Mineral County, all in Nevada, and Dirty Weather mine, Inyo County, Calif.

These investigations were made to aid in the development of domestic fluorspar resources, in line with the Bureau's long-established program of conservation of mineral resources.

The treatment methods employed in the experimental work described included simulated or "heavy-liquid" gravity concentration of coarse minerals and comparatively fine-grained minerals, and flotation concentration of finely-ground minerals. These methods were attempted in order to beneficiate the ores and produce concentrates which could be marketed readily, with as high a recovery rate as possible, while using simple treatment methods suitable for small-scale operation.

As shown in table 1, concentrate grades varied inversely with recoveries, and where concentrates of nearly Acid-grade were produced, as by the flotation treatment of Shoshone or Valery ore, recoveries were comparatively low. It is probable that by treating of any of these ores, some Acid-grade concentrate could be made, representing a partial recovery, and secondary concentrates of lower grade could also be made, if marketing economics indicated that such procedures would be profitable. Likewise, in the case of the Broken Hills ore, some Acid-grade concentrate could be recovered by gravity treatment, and further recovery could be made of a lower-grade product.

Market specifications of various grades of fluorspar are shown in the appendix for comparison with the data in this report.

1/ Work on manuscript completed May 1960.

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TABLE 1. - Summary of experimental results

Source of ore	Sample No.	CaF_2, percent	Treatment method	Recovery, percent	Concentrate grade CaF_2, percent
Shoshone mine, Nye County, Nev....	-	47.0	Flotation	93.2	90.1
			do.	81.0	96.3
Valery mine, Pershing County, Nev.....	1	72.0	Gravity (simulated)	80.0	89.0
	2	29.0	do.	79.0	94.0
	3	21.0	do.	71.1	87.2
	3	21.0	Flotation	84.6	89.8
	3	21.0	do.	68.5	96.9
Broken Hills mine, Mineral County, Nev.....	-	38.0	Gravity (simulated)	85.4	95.5
Dirty Weather mine, Inyo County, Calif.	-	20.0	Flotation	79.5	95.0

SHOSHONE FLUORSPAR ORE, NYE COUNTY, NEV.

The ore contained 47.5 percent CaF_2, 44.4 percent SiO_2, 4.6 percent $CaCO_3$, 2.90 percent Fe_2O_3, 0.56 percent Al_2O_3, and 0.06 percent Mn_3O_4. The fluorspar occurs as cementing material in a siliceous breccia and also penetrates the silica. The deposit is described as a large, long outcrop, of which the sample is representative in grade and texture; but with areas of higher-grade ore.

Simulated Gravity Concentration

A preliminary gravity concentration experiment was made on a portion of the sample crushed to minus 10-mesh. The ore was screened into several fractions and each separated into three products--concentrate, middling, and tailing--by successive treatment in two heavy liquids (acetylene tetrabromide, either pure or diluted with benzol) of 2.95 and 2.75 specific gravity, respectively. The sink products in 2.95 specific gravity were concentrates; the sinks in 2.75 specific gravity were middlings; and the corresponding float products were tailings. This experiment was made to simulate on a "beaker-size" scale what might be expected of gravity concentration on a shaking table. The results of the experiment showed that it would be necessary to grind the ore to at least minus 100-mesh to obtain optimum liberation and recovery of fluorspar, and that it might be necessary to grind the ore to a much finer mesh to produce Acid-grade concentrate. Detailed data of this experiment are shown in table 2.

Since fine grinding was indicated by the preliminary experiment described, gravity concentration was not considered further, and all subsequent experiments were in flotation treatment.

TABLE 2. - Heavy-liquid separation, Shoshone ore

Product size, mesh	Sink, 2.95 specific gravity			Sink, 2.75 specific gravity			Float, 2.75 specific gravity		
	Weight-percent	CaF_2, percent	Distribution, percent	Weight-percent	CaF_2, percent	Distribution, percent	Weight-percent	CaF_2, percent	Distribution, percent
-10+20.....	19.0	83.8	33.6	9.5	47.3	9.4	26.9	9.9	5.6
-20+28.....	5.0	86.9	9.1	1.9	48.0	1.9	5.1	7.3	.8
-28+35.....	3.5	87.3	6.4	.9	45.3	.9	2.6	8.0	.4
-35+48.....	3.5	87.9	6.5	.7	41.9	.6	3.0	7.1	.4
-48+65.....	2.3	90.3	4.4	.4	47.1	.4	1.5	8.6	.3
-65+100.....	3.2	90.3	6.0	.4	53.2	.5	1.6	6.6	.2
-100+150.....	2.1	91.8	4.0	.2	43.8	.2	.8	4.4	.1
-150+200.....	1.7	92.1	3.3	.2	61.3	.3	.6	5.9	.1
Total.....	40.2	86.5	73.3	14.3	47.4	14.2	42.1	9.0	7.9
-200 (untreated)	3.4	64.4	4.6						

Flotation, Minus 100-Mesh Ore

Cold Pulp

Ore ground to minus 100-mesh was floated in a laboratory cell at room temperature, with the following reagents:

Na_2CO_3 (pH 8.1, pulp dispersed)	pounds per ton of ore	1.0
Na_2SiO_3	do.	.25
Quebracho (10 minutes conditioning)	do.	.1
Oleic acid (3 increments, 0.7 each)	do.	2.1
Dowfroth	do.	.06

The rougher concentrate was cleaned three times, using the following reagents:

Na_2CO_3 (pH 8.1, first cleaning)	pounds per ton of ore	1.0
Na_2SiO_3 (first cleaning)	do.	.25
Quebracho (10 minutes conditioning, first cleaning)	do.	.1
Na_2CO_3 (pH 8.4, second cleaning)	do.	1.0
Na_2SiO_3 (10 minutes conditioning, second cleaning)	do.	.25
Na_2SiO_3 (pH 7.8, third cleaning)	do.	.25

The final concentrate contained 90.1 percent CaF_2, representing 93.2 percent recovery in 48.0 percent of the original weight of ore.

Heated Pulp

Ore ground to minus 100-mesh was floated in a laboratory cell at 140° F. with the following reagents:

Na_2CO_3	pounds per ton of ore	2.5
Na_2SiO_3 (pH 9.0)	do.	1.0
Quebracho (10 minutes conditioning)	do.	.25
Oleic acid	do.	2.0
Dowfroth (10 minutes conditioning)	do.	.12

The rougher concentrate was cleaned in four stages, each time with ten minutes conditioning, with the following reagents:

Na_2CO_3	pounds per ton of ore	1.0
Na_2SiO_3	do.	.5
Quebracho	do.	.2

The final concentrate contained 87.6 percent CaF_2 representing 97.3 percent recovery in 51.5 percent of the original weight of ore.

Flotation, Minus 200-Mesh Ore

A flotation experiment similar to the last one described was made with ore ground to minus 200-mesh and the same amounts of reagents, but with the

pulp heated to 140° F. Results were similar to those obtained from treatment of unheated pulp.

Further experiments were made, using reduced amounts of oleic acid collector, still using hot pulp at 140° F. The oleic acid was eventually reduced to 0.1 pound per ton of ore. The entire suite of reagents was:

Na_2CO_3	pounds per ton of ore	1.0
Na_2SiO_3 (pH 8.5)	do.	3.0
Quebracho (10 minutes conditioning)	do.	.35
Oleic acid	do.	.1
Dowfroth (10 minutes conditioning)	do.	.2

The rougher concentrate was cleaned twice at 140° F. with no additional reagents, then twice again with the pulp at boiling temperature (201° F.) and no reagents. The final concentrate contained 94.2 percent CaF_2, representing 86.5 percent recovery in 45.8 percent of the original weight of ore.

After more experimentation to improve the concentrate grade by variations in reagents and procedure, grinding the ore to minus 325-mesh was tried.

Flotation, Minus 325-Mesh Ore

Using ore stage-ground to minus 325-mesh, several flotation experiments were made with variations in reagents and procedure. The best concentrate grade was obtained with the following procedure: The ore was floated at 95° F. with the following reagents.

Na_2CO_3	pounds per ton of ore	2.5
Na_2SiO_3 (pH 8.9)	do.	1.0
Quebracho (conditioned 10 minutes)	do.	.35
Oleic acid (conditioned 10 minutes)	do.	1.0

The rougher concentrate was cleaned twice at 95° F. with no reagents, then cleaned twice again at 201° F.; it was boiled 10 minutes each time, with no reagents.

The final concentrate contained 96.3 percent CaF_2, representing 81.0 percent recovery in 40.2 percent of the original weight of ore.

It is possible that higher grade concentrate can be made from this ore, with higher recovery of fluorspar. The evidence observed in making a large number of experiments is that any improvement in concentrate grade will be accompanied by lower recovery. It is believed that much of the fluorite mineral in the ore contains small amounts of silica, which is not liberated by grinding, even to minus 325-mesh.

VALERY FLUORSPAR ORE, PERSHING COUNTY, NEV.

Three samples of ore from this property were investigated to determine the best method of treatment for recovering fluorspar as a Metallurgical-grade

concentrate containing at least 85 percent CaF_2. The samples varied in grade and texture. The fluorspar varied from coarsely crystalline to disseminated fine grains. The gangue included calcite, carbonaceous shale, siliceous minerals, and clay.

Simulated Gravity Concentration

Sample 1

This sample contained 72 percent CaF_2, mostly in coarse particles. The ore was crushed to pass a 1-inch screen and sized into several portions. Only preliminary experiments in gravity concentration were made, to simulate the results of treatment with jigs and shaking tables. Separation into sink products or concentrates and float products or tailings was made in a heavy liquid (acetylene tetrabromide) at 2.95 specific gravity. The combined concentrate contained 89.2 percent CaF_2, representing 80.7 percent recovery in 65.3 percent of the weight of original ore. Detailed results of this experiment are shown in table 3.

Most of the fluorspar in the tailing products was fined grained and could only be treated by fine grinding and flotation. No great amount of this type of ore occurs at the mine; but this treatment could be applied to ore which is mined selectively.

TABLE 3. - Heavy-liquid separation, Valery ore, sample 1

Product size, mesh	Sink			Float		
	Weight-percent	CaF_2, percent	Distribution, percent	Weight-percent	CaF_2, percent	Distribution, percent
-1+1/2.....	16.3	82.7	18.7	12.1	48.5	8.1
-1/2+1/4....	23.3	89.5	29.0	11.7	41.5	6.7
-1/4+10.....	14.0	92.7	18.0	5.3	32.1	2.4
-10+20.....	5.7	93.8	7.4	1.9	25.3	.7
-20.....	6.0	90.7	7.6	3.7	27.9	1.4
Total..	65.3	89.2	80.7	34.7	40.1	19.3

Sample 2

This ore contained 29.5 percent CaF_2, coarse grained enough to permit satisfactory liberation by crushing to minus 1/2-inch. The crushed ore was sized into several portions and separated by simulated gravity concentration in heavy liquid (acetylene tetrabromide) at 2.95 specific gravity. Results of the experiment were much the same as those obtained by similar treatment of sample 1.

The concentrate contained 94 percent CaF_2, representing 79 percent recovery in 25 percent of the weight of original ore. The fluorspar lost in the tailing was mostly disseminated and would require fine grinding and flotation treatment for recovery. This type of ore could be treated with jigs and shaking tables.

Sample 3

This sample contained 20.9 percent CaF_2, and was stated to be representative of the entire ore body. Large quantities of nearly barren calcite were present. The siliceous material was altered and included more clay than the other samples. Much of the fluorspar was fine grained.

Simulated gravity concentration experiments were made on ore from this sample, using heavy liquid (acetylene tetrabromide) at 2.95 specific gravity to produce concentrates. Middlings and tailings were produced by separations in heavy liquid (acetylene tetrabromide diluted with benzol) at 2.7 specific gravity. The middlings were retreated by crushing in several stages and separation in the heavy liquids. The final concentrate contained 87.2 percent CaF_2, representing 71.1 percent recovery in 17.1 percent of the original weight of ore. This procedure roughly corresponded to treatment of ore crushed primarily to minus 1-inch for treatment in jigs, and with middling products stage-crushed to minus 10-mesh for treatment on shaking tables.

Flotation

The fine-grained texture of the fluorspar mineral in sample 3 required grinding the ore to minus 150-mesh for optimum liberation before flotation. When the ore was ground, much clayey material was produced, including some very fine-grained calcite. This was about 20 percent of the original weight of ore. The pulp was agitated with 1.5 pounds of sodium silicate per ton of ore to deflocculate this clayey material, which was then removed by settling and decantation from the granular portion of the ground ore.

After this desliming treatment, the pulp was conditioned for 10 minutes with 1.0 pound of quebracho per ton of ore to depress the remaining calcite. Then, 2.0 pounds of anhydrous sodium carbonate were added to adjust the pH of the pulp to 8.6. Oleic acid was used as collector reagent, to float the fluorspar in three increments of 0.4 pound per ton of ore with 0.1 pound frother B-23.

The rougher concentrate was cleaned once with 0.5 pound quebracho and again with 0.25 pound quebracho per ton of ore. The final concentrate contained 96.9 percent CaF_2, representing 68.5 percent recovery in 13.7 percent of the original weight. With only the first cleaning, the concentrate contained 89.7 percent CaF_2, representing 84.6 percent recovery in 18.3 percent of the original weight.

The discarded, deflocculated slime contained 2.6 percent CaF_2, representing 2.8 percent of the total fluorspar content of the ore in 21.2 percent of the original weight.

BROKEN HILLS FLUORSPAR ORE, MINERAL COUNTY, NEV.

The sample investigated was a composite, representative of the deposit as a whole. The ore contained 38 percent CaF_2. Much of the fluorspar was coarse grained and liberated from the gangue by crushing to minus 1-inch.

The remaining fluorspar was fine grained and disseminated in the gangue. The latter was a mixture of calcareous and siliceous minerals, with a small amount of hornblende.

Simulated Gravity Concentration

The investigation was limited to treatment of ore crushed to minus 1-inch. The crushed ore was screened into several portions, each of which was separated into concentrates or sink products and tailings, or float products in a heavy liquid (acetylene tetrabromide) with 2.95 specific gravity. This separation roughly corresponded to results obtainable by concentrating the plus 10-mesh portion of the crushed ore in jigs and the minus 10-mesh ore on shaking tables.

The combined concentrate contained 95.5 percent CaF_2, representing 85.4 percent recovery in 34.1 percent of the original weight of ore. Detailed data of this experiment are shown in table 4.

TABLE 4. - Heavy-liquid separation, Broken Hills ore

Product size, mesh	Sink			Float		
	Weight-percent	CaF_2, percent	Distribution, percent	Weight-percent	CaF_2, percent	Distribution, percent
-1+1/4.....	10.2	96.8	25.9	26.3	1.4	3.6
-1/4+10.....	6.2	97.5	15.8	14.3	.5	1.4
-10+48.....	10.8	97.1	27.5	12.2	3.1	1.0
-48+100.....	4.4	92.3	10.7	3.1	10.5	.9
-100+200....	2.5	83.8	5.5	1.7	34.5	1.5
Total..	34.1	95.5	85.4	57.6	5.6	8.4
-200 (untreated)	8.3	28.4	6.2			

DIRTY WEATHER FLUORSPAR ORE, INYO COUNTY, CALIF.

A composite sample representing the ore deposit was investigated. The sample contained 20.1 percent CaF_2. Gangue minerals included epidote, chlorite, quartz, minor amounts of calcite, pyrophyllite, and sericite, also some iron-stained clay. The fluorspar occurred in crystalline grains, mostly in the finer-size ranges, it also occurred locked with gangue minerals and in very fine grains in clay. Since most of the fluorspar was fine-grained, the ore was ground to minus 100-mesh for flotation.

Flotation

Most of the fluorspar was liberated by grinding to minus 100-mesh, but between 10 and 15 percent was extremely fine grained and was not liberated.

The best flotation results were obtained by the following procedure. The pulp was conditioned with:

Sodium carbonate.....pounds per ton of ore		1.0
Sodium silicate.....do.		1.0
Quebracho.....do.		.15
Oleic acid.....do.		1/.3

1/ 3 increments.

The rougher concentrate was cleaned in two stages without additional reagents. Concentrates from two charges of ore were combined and cleaned once more without reagents. The product was then boiled at 201° F. and again floated. The final concentrate contained 95.0 percent CaF_2, representing 79.5 percent recovery in 16.8 percent of the original weight of ore.

APPENDIX.--MARKET SPECIFICATIONS, FLUORSPAR GRADES

Acid-grade:	97 percent CaF_2 minimum; 1.1-1.5 percent SiO_2 maximum; no sulfides, to 0.10 percent maximum sulfide sulfur.
Ceramic-grade:	Not standardized. 93-95 percent CaF_2; 2.5-3.0 percent SiO_2 maximum; 1.0-1.5 percent $CaCO_3$ maximum; 0.12-0.14 percent Fe_2O_3 maximum; no lead, zinc, or sulfur.
Metallurgical-grade:	Gravel, lumps, pellets, or flotation concentrate, 60 percent minimum effective CaF_2, after subtracting two and one-half times the SiO_2 content from the actual CaF_2 content. For example, 90 percent actual CaF_2 minus two and one-half times 10 percent SiO_2, or 25, would be 65 percent effective CaF_2.

REFERENCES

ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY. Interscience Encyclopedia, Inc., New York, N. Y., vol. 6, 1951, p. 690.

ENGINEERING AND MINING JOURNAL Metal and Mineral Market: Weekly Market Information, Nonmetallic Minerals Prices and Specification Section, New York, N. Y.

HOLTZINGER, J. E. Mineral Facts and Problems. Fluorine: Bureau of Mines Bull. 556, 1956, p. 285.

McDOUGAL, R. B. Mineral Facts and Problems. Fluorine: Bureau of Mines Bull. 585, 1960, pp. 305 to 315.

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