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Recovery of Ultrafine Barite From Mill Wastes

By W. E. Lamont and G. V. Sullivan

UNITED STATES DEPARTMENT OF THE INTERIOR

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RECOVERY OF ULTRAFINE BARITE FROM MILL WASTES

By W. E. Lamont[1] and G. V. Sullivan[2]

ABSTRACT

The Bureau of Mines conducted flotation tests on a mixture of barite waste materials from Nevada in which essentially all of the barite values were finer than 20 micrometers. Flotation variables investigated in these tests were the effects of (1) sodium silicate as a pulp dispersant, (2) sodium hydroxide as a pH modifier, (3) increased amounts of sodium cetyl sulfate, (4) conditioning time and (5) solids content during conditioning. The optimum flotation conditions were achieved by adding 2.5 pounds of sodium silicate and 10 pounds of sodium cetyl sulfate per ton of feed and conditioning the pulp for 20 minutes at a 35-percent solids content. Using these conditions, a concentrate was produced that contained 94.7 percent $BaSO_4$, with an attendant recovery of 90.9 percent of the barite in the feed.

In addition to the flotation tests, a selective barite flocculation process was developed to treat extremely fine barite. A barite concentrate containing 96.5 percent $BaSO_4$ with an attendant recovery of 82.1 percent of the barite was produced by selective flocculation. A process patent application has been filed based on this process.

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INTRODUCTION

A major goal of the Bureau of Mines is resource conservation, which includes (1) maximizing mineral recovery from domestic resources and (2) recovering mineral values currently lost in scrap and waste materials. To help meet this goal, the Bureau of Mines has been investigating the recovery of various potentially valuable minerals from mineral-processing wastes.

One of the more promising areas of these studies is the recovery of extremely fine barite from mill waste materials. Wharton[3] determined the amount of barite contained in some Missouri waste ponds, and Brobst[4] includes barite in old waste ponds in reserves data.

Barite is used in well-drilling muds, paint, glass, rubber, plastics, and barium chemical manufacture. The United States, while producing about 30 percent of world supply, still imports about 40 percent of its barite consumption. U.S. reserves of barite have historically been considered sufficient in the long term; however, Haines[5] has suggested that U.S. reserves are inadequate to meet expected demand through the year 2000.

Domestic barite production increased from 1.1 million tons in 1974 to 1.7 million tons in 1978; however, during the same period, consumption increased from 1.7 to 2.8 million tons.[6] The major factor in the increased barite consumption was the increase in oil- and gas-well drilling. Barite is an important ingredient in well-drilling fluids because of its high specific gravity, chemical inertness, and softness or nonabrasiveness.

In fiscal year 1979, the Bureau's Tuscaloosa Research Center initiated a study to devise methods to recover barite previously lost in milling and to prevent such losses in the future. Flotation tests were conducted using waste materials from Georgia, Missouri, and Nevada.[7] Results of these tests indicated that barite concentrates that met oil well drilling-mud specifications could be produced from these sources. Further studies are continuing.

During these studies, three small samples of extremely fine barite waste materials were received from a barite mining company in Nevada. Flotation tests of these samples indicated that it was possible to produce barite concentrates meeting oil well drilling-mud specifications from waste materials of such fine-size distribution; however, the amount of barite recovered, using similar flotation conditions, varied between the samples.

The inconsistency in barite recovery prompted a decision to study the effects of a number of flotation variables on barite recovery from waste materials of such fine-size distribution. Tested were various amounts of (1) sodium silicate as a pulp dispersant, (2) sodium hydroxide as a pH modifier, (3) sodium cetyl sulfate as the collector, (4) conditioning time, and (5) solids content during conditioning.

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[3] Wharton, H. M. Barite Ore Potential of Four Tailings Ponds in the Washington County Barite District, Missouri. Mo. Geol. Survey Water Res., RI 53, 1972, 91 pp.

[4] Brobst, D. R. Barite. Ch. in U.S. Miner. Res., U.S. Geol. Survey Prof. Paper 820, 1973, pp. 75-84.

[5] Haines, S. K. Barite. BuMines Mineral Commodity Profile, February 1979, 13 pp.

[6] U.S. Bureau of Mines. Barite. Mineral Commodity Summaries, 1979, pp. 16-17.

[7] Lamont, W. E., E. G. Davis, and G. V. Sullivan. Retreatment of Tailings To Recover Barite. Proc. 7th Miner. Waste Utilization Symp., sponsored by the BuMines and IIT Res. Inst., Chicago, Ill., Oct. 20-21, 1980, pp. 26-33.

ACKNOWLEDGMENT

Valuable contributions to the success of this research were made by J. E. Hardemon, physical science technician (retired). He observed, noted, and reported unique conditions for selective flocculation that later proved to be the basis for the separation of ultrafine barite. Based on these Bureau studies, he has been designated a coinventor of the selective flocculation process.

DESCRIPTION OF SAMPLE

The three small samples of barite waste materials were air-dried, crushed to pass 20 mesh, and thoroughly mixed. Chemical analysis of the mixture showed that it contained 42.2 percent $BaSO_4$, 26.2 percent SiO_2, 10.8 percent Al_2O_3, and 7.7 percent Fe_2O_3. Loss on ignition at 1800° F was 8.2 percent. Chemical analyses from earlier studies indicated that there was less than 1 percent combined CaO and MgO present. X-ray analysis of the mixture showed the presence of the following, in order of decreasing quantities: barite, quartz, goethite, and illite. A representative sample of the mixture was disaggregated and dispersed in a Minerals Separation[8] batch flotation cell using sodium hydroxide as the pH modifier and sodium silicate as the dispersant. Particle sizing of this sample was conducted to determine the distribution of the barite values.

Stokes' law and the specific gravity of quartz (2.65) were used to calculate the particle sizes on a quartz basis (table 1) for both the centrifugation and the sedimentation techniques. The specific gravity of barite (4.5) was used to calculate the size of particles on a barite basis. Centrifugation was used to isolate the minus 1-micrometer fraction, and sedimentation was used to separate the 5- and 20-micrometer fractions. In each case, the separation was repeated until a clear effluent was obtained, indicating effective separation on a size basis. The plus 20-micrometer fraction was screen-sized at 38 micrometers (400 mesh); however, no barite was found in the plus 38-micrometer fraction. Table 1 shows that 87 percent of the barite was finer than 13.7 micrometers in equivalent barite diameter.

TABLE 1.- The calculated barite particle sizes and distribution of sample based on the specific gravities of barite and quartz

Barite[1] particle size, µm	Particle size distribution, pct	$BaSO_4$, pct	
		Analysis	Distribution
Plus 13.7 (plus 20)......................	6.6	79.9	12.6
Minus 13.7 plus 3.4 (minus 20 plus 5).....	31.0	73.5	54.5
Minus 3.4 plus 0.7 (minus 5 plus 1).......	29.2	41.3	28.9
Minus 0.7 (minus 1)......................	33.2	5.1	4.0
Composite or total..................	100.0	41.8	100.0

[1] The equivalent quartz particle sizes are given in parentheses.

FLOTATION TESTS

Tests were conducted to determine the effects of sodium hydroxide and sodium silicate on flotation. Earlier studies of fine barite samples indicated that a pH range of 10.0 to 10.5 yielded the most effective flotation results. The test results (fig. 1) indicated that the sodium silicate alone, which had a

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[8] Reference to specific equipment or trade names does not imply endorsement by the Bureau of Mines.

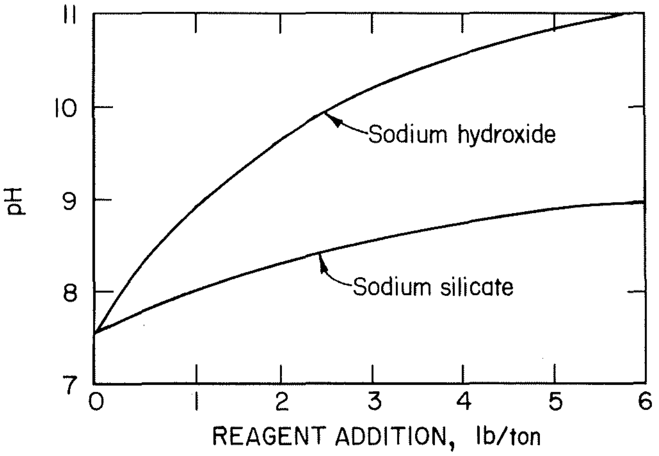


FIGURE 1. - Effect of reagent additions on pH.

sodium-to-silica ratio of 1.8, would not yield the desired pH range. Hence, subsequent pH adjustments were made using sodium hydroxide.

A series of rougher flotation tests was conducted to determine the effects of various amounts of sodium silicate on the pulp. The pH of the pulp was adjusted to 10.0 using 2.6 pounds of sodium hydroxide per ton of feed, and preliminary tests indicated that at least 4 pounds of sodium cetyl sulfate per ton of feed was required to yield effective flotation of the fine barite. Figure 2 shows the results of these tests.

Figure 2A shows the effect of sodium silicate on the $BaSO_4$ content and distribution in the rougher concentrate and on the total amount of waste material recovered from the feed; figure 2B shows the effect on the composite rougher tailings. In each of these flotation tests, and all other tests, the rougher flotation tailings were partitioned by centrifugation and sedimentation at 20, 5, and 1 micrometer as in the original particle sizing. The effects of various amounts of sodium silicate on the $BaSO_4$ content of the four size fractions are shown in figure 2C.

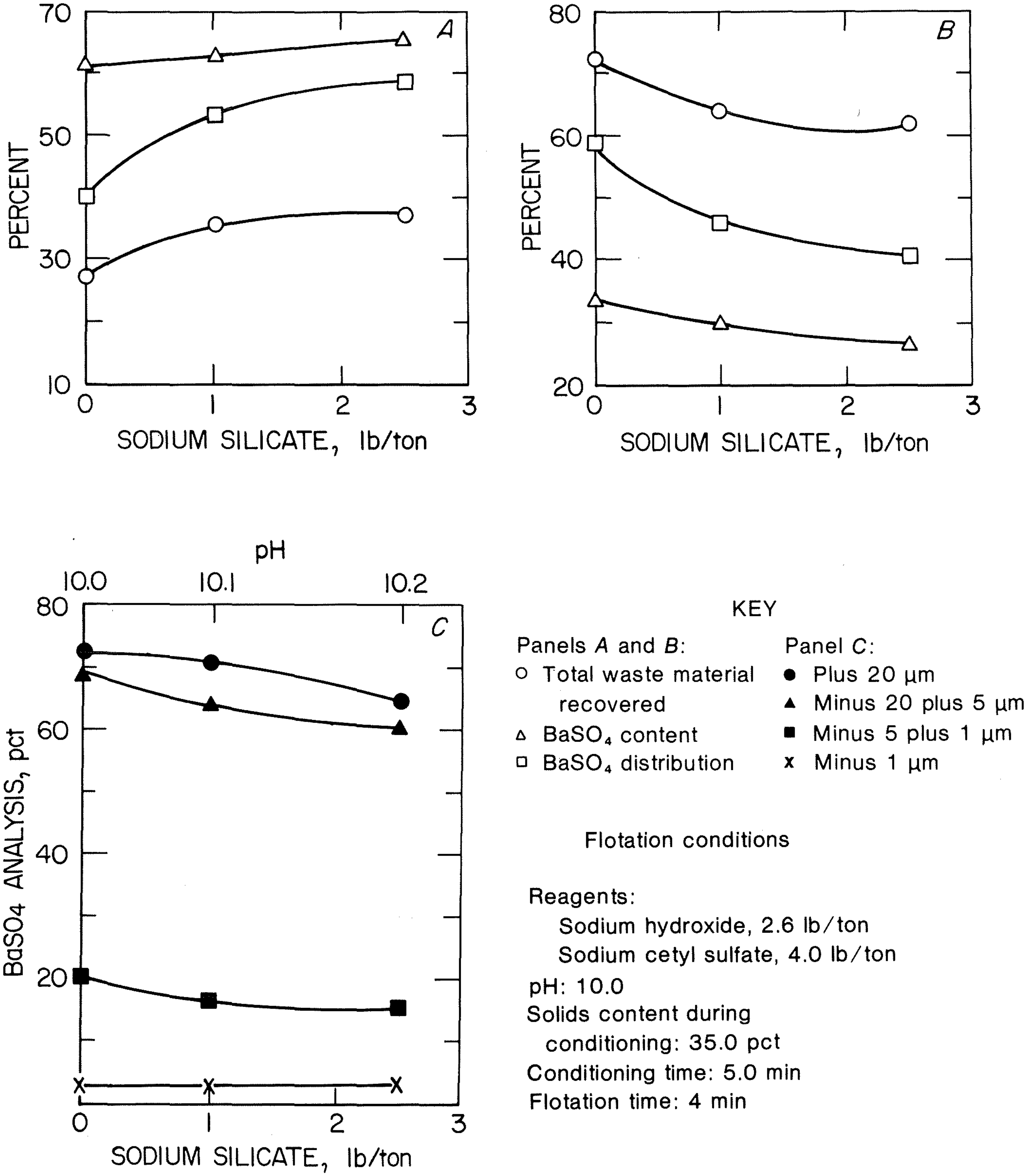
Figure 2A shows that sodium silicate has a beneficial effect in the pH range of 10.0 to 10.2. Both the $BaSO_4$ content of the concentrate and the attendant barite recovery improved with increased amounts of sodium silicate, indicating (1) better dispersion and/or cleaner mineral surfaces and/or (2) the effect of a slight increase in pH from 10.0 to 10.2 because of the added sodium silicate. Data in figure 2C indicate that sodium silicate has a greater effect on the barite in the plus 1-micrometer fraction than on the barite in the minus 1-micrometer fraction.

To determine the effect of pH on flotation of the pulp, tests were conducted in which the quantities of sodium silicate and sodium cetyl sulfate were held constant while the pH was varied using sodium hydroxide as the pH modifier. In these tests, 6.0 pounds of sodium cetyl sulfate per ton was used since data in figure 2A indicated that 4.0 pounds per ton was not sufficient for high barite recovery. Results of these tests are shown in figure 3.

Data in figure 3A indicates that the optimum pH is somewhere around 10. No effort was made to better define the optimum pH. The $BaSO_4$ content of the rougher concentrate decreases with either higher or lower pH. Figure 3B shows the effect of pH on barite losses in the rougher tailings. Figure 3C shows that the effect of pH on the $BaSO_4$ content of the tailings is a function of particle size. Possibly, when the pH is higher than 10, there is incipient flocculation of the fine gangue minerals, leading to unclean barite particle surfaces.

Figure 4 shows that increased conditioning time has a beneficial effect on barite recovery even in the minus 1-micrometer fraction of the rougher tailings. Of the five parameters investigated in this study, conditioning time was the only one showing continuous beneficial effect on barite recovery from each of the size fractions of the rougher tailings.

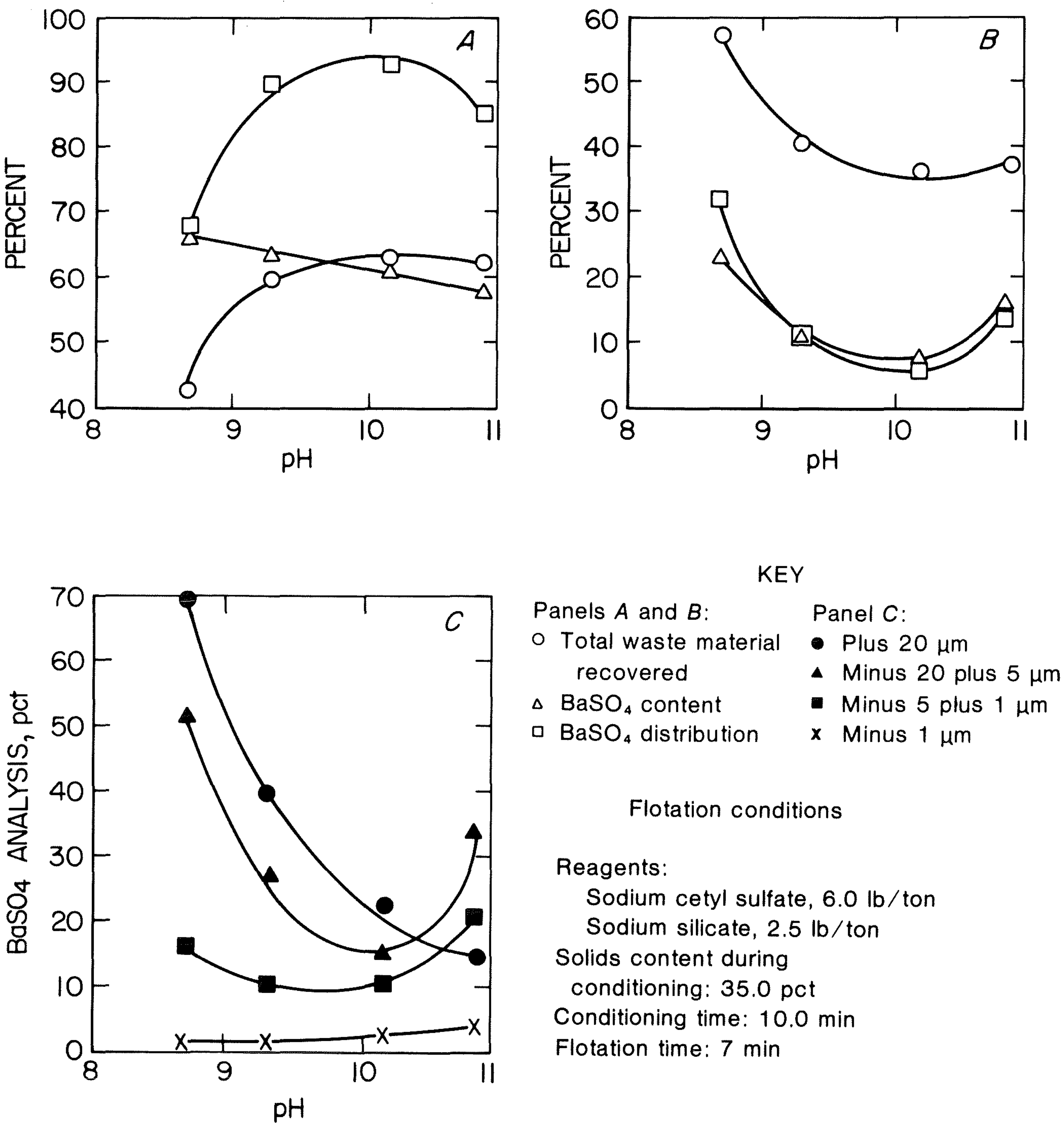
The effects of various amounts of sodium cetyl sulfate are shown in figure 5. There is a significant depressing effect on the barite coarser than 5 micrometers when using more than 8.0 pounds of sodium silicate per ton;



Flotation conditions

Reagents:
Sodium hydroxide, 2.6 lb/ton
Sodium cetyl sulfate, 4.0 lb/ton
pH: 10.0
Solids content during conditioning: 35.0 pct
Conditioning time: 5.0 min
Flotation time: 4 min

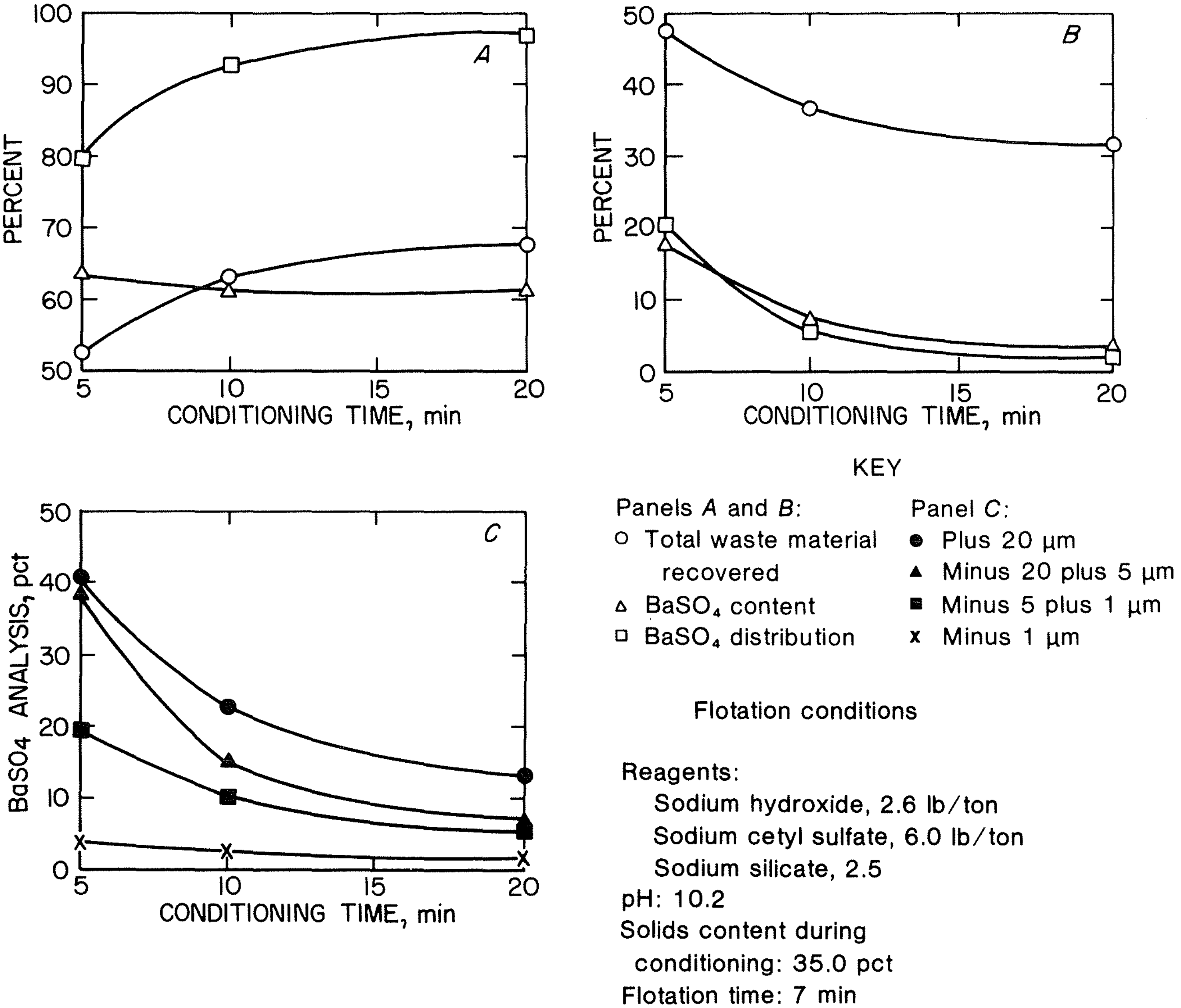
FIGURE 2. - Effects of various amounts of sodium silicate on barite recovery and $BaSO_4$ content and distribution. *A*, Rougher concentrate; *B*, rougher tailings; *C*, four size fractions of the rougher tailings.



Flotation conditions

Reagents:
Sodium cetyl sulfate, 6.0 lb/ton
Sodium silicate, 2.5 lb/ton
Solids content during
conditioning: 35.0 pct
Conditioning time: 10.0 min
Flotation time: 7 min

FIGURE 3. - Effects of varying pH and/or amounts of sodium hydroxide (used to adjust pH) on barite recovery and $BaSO_4$ content and distribution. *A*, Rougher concentrate; *B*, rougher tailings; *C*, four size fractions of the rougher tailings.



KEY

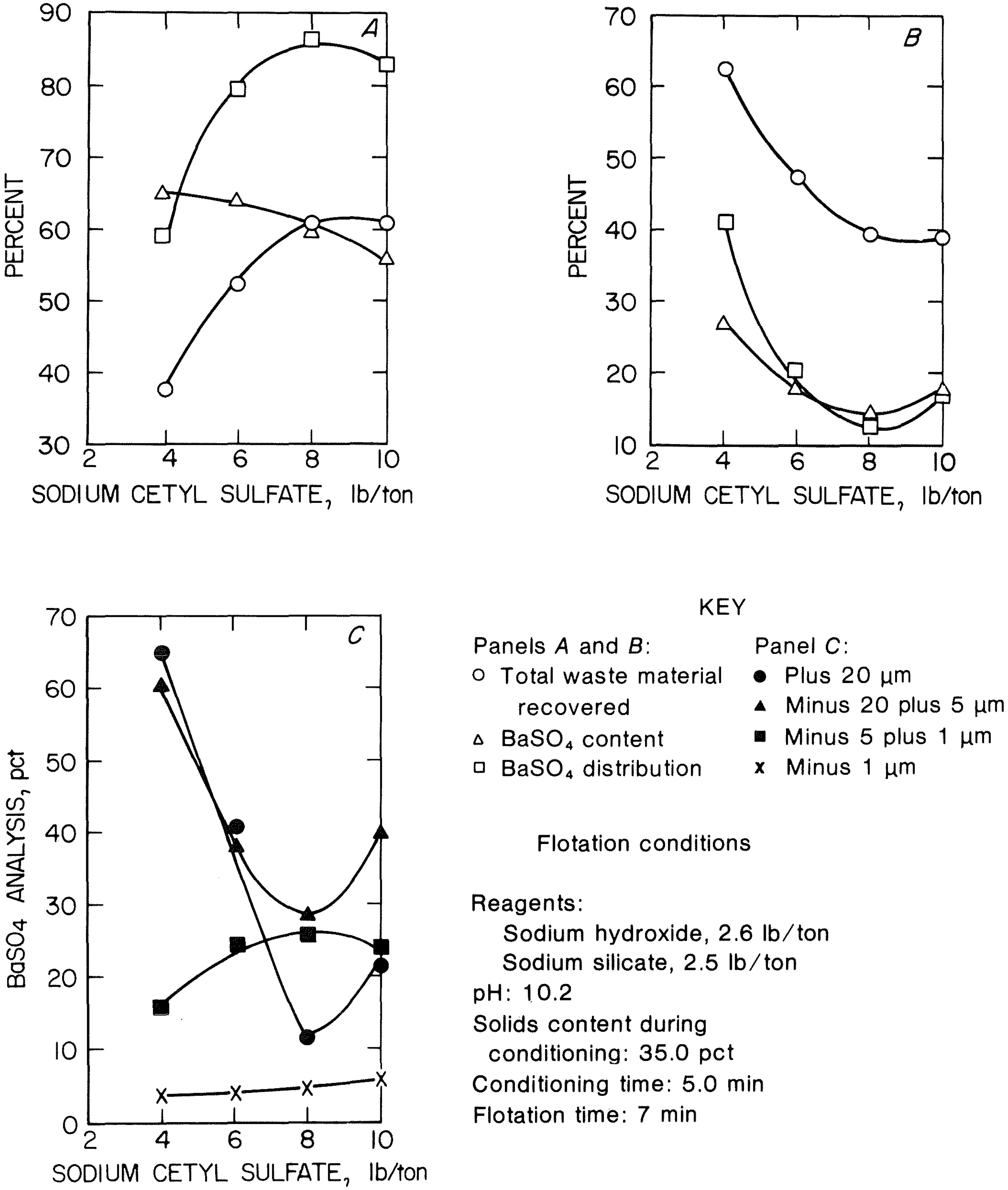
Panels *A* and *B*:
- ○ Total waste material recovered
- △ $BaSO_4$ content
- □ $BaSO_4$ distribution

Panel *C*:
- ● Plus 20 µm
- ▲ Minus 20 plus 5 µm
- ■ Minus 5 plus 1 µm
- x Minus 1 µm

Flotation conditions

Reagents:
Sodium hydroxide, 2.6 lb/ton
Sodium cetyl sulfate, 6.0 lb/ton
Sodium silicate, 2.5
pH: 10.2
Solids content during conditioning: 35.0 pct
Flotation time: 7 min

FIGURE 4. - Effects of various conditioning times on barite recovery and $BaSO_4$ content and distribution. *A*, Rougher concentrate; *B*, rougher tailings; *C*, four size fractions of the rougher tailings.



Flotation conditions

Reagents:
  Sodium hydroxide, 2.6 lb/ton
  Sodium silicate, 2.5 lb/ton
pH: 10.2
Solids content during
  conditioning: 35.0 pct
Conditioning time: 5.0 min
Flotation time: 7 min

FIGURE 5. - Effects of various amounts of sodium cetyl sulfate on barite recovery and $BaSO_4$ content and distribution. *A*, Rougher concentrate; *B*, rougher tailings; *C*, four size fractions of the rougher tailings.

however, the depressing effect on barite finer than 5 micrometers is evident throughout the entire range of amounts of sodium cetyl sulfate used.

Figure 6 shows the effects of varying the solids content during conditioning. Rougher flotation was performed at the same solids content as used in conditioning. These data indicate that the solids content has little effect on barite recovery. However, there was a definite decrease in the total amount of waste material reporting to the concentrate and in the $BaSO_4$ content of the concentrate produced at the higher solids content, indicating more entrapment of the gangue minerals with increased solids content. Optimum solids content for conditioning and flotation appears to be about 35 percent.

Based on these tests, the optimum conditions for recovering ultrafine barite appear to be--

1. A solids content of about 35 percent.

2. The use of 2.5 pounds of sodium silicate per ton.

3. A pH of about 10.2.

4. A conditioning time of 20 minutes.

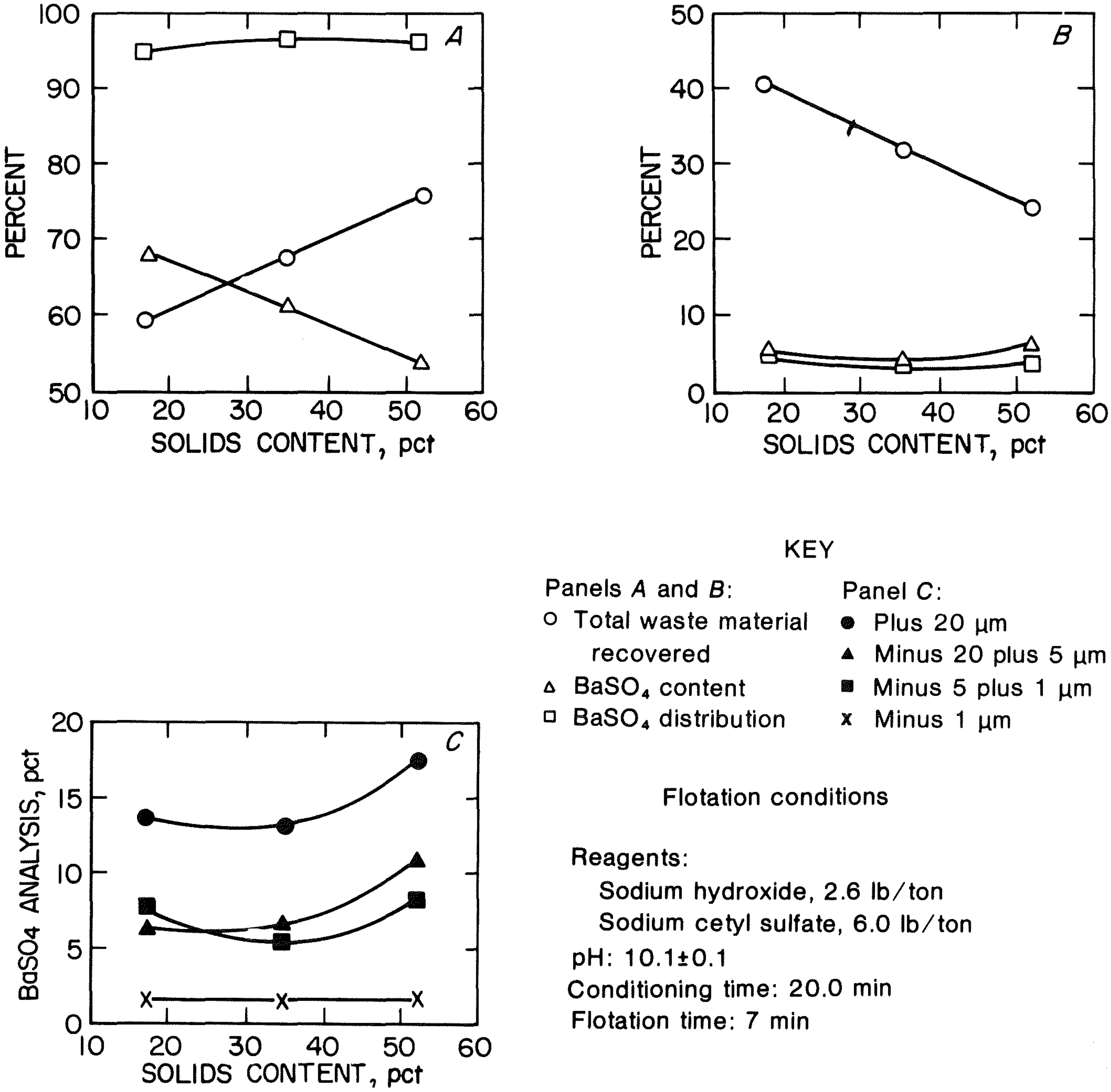
5. About 8 pounds of sodium cetyl sulfate per ton.

Using these conditions, a test was conducted wherein the rougher concentrate was cleaned three times to determine if high-grade $BaSO_4$ concentrates, with attendant high barite recovery, could be produced from this material. Because of anticipated losses during the cleanings, 10 pounds of sodium cetyl sulfate per ton was used instead of 8 pounds per ton. A concentrate containing 94.7 percent $BaSO_4$ was produced while recovering 90.9 percent of the barite in the feed. Table 2 lists the products obtained and their $BaSO_4$ content and distribution.

TABLE 2. - Flotation of barite using the optimum conditions

Product	Product distribution, pct	$BaSO_4$, pct	
		Analysis	Distribution
Rougher concentrate:			
Cleaning 3 concentrate	39.9	94.7	90.9
Middlings:			
1	20.6	6.4	3.2
2	29.5	8.2	1.9
3	33.6	19.2	1.6
Composite or total	73.6	55.1	97.6
Rougher tailings:			
Plus 20 µm	.9	1.7	<.05
Minus 20 plus 5 µm	4.8	3.3	.4
Minus 5 plus 1 µm	8.5	6.4	1.3
Minus 1 µm	12.2	2.3	.7
Composite or total	26.4	3.8	2.4
Composite or total feed	100.0	41.6	100.0

NOTE.--Flotation conditions were (1) a solids content of 35 percent, (2) 2.5 pounds of sodium silicate per ton, (3) pH about 10.2, (4) conditioning time of 20 minutes, and (5) 8 pounds of sodium cetyl sulfate per ton.



Flotation conditions

Reagents:
Sodium hydroxide, 2.6 lb/ton
Sodium cetyl sulfate, 6.0 lb/ton
pH: 10.1±0.1
Conditioning time: 20.0 min
Flotation time: 7 min

FIGURE 6. - Effects of varying solids content (during conditioning) on barite recovery and $BaSO_4$ content and distribution. *A*, Rougher concentrate; *B*, rougher tailings; *C*, four size fractions of the rougher tailings.

SELECTIVE FLOCCULATION TESTS

The results of the flotation tests showed that selective flotation was being accomplished in size ranges normally considered much too fine for effective separation. It was speculated that the results were obtained by the flotation of floccules rather than individual particles. To determine the mechanism for flotation of such fine barite, a selective flocculation test was conducted using the optimum flotation conditions with an additional 2 pounds of sodium cetyl sulfate. However, in the selective flocculation test, rather than floating the conditioned pulp, the pulp was removed from the conditioner and placed in a glass beaker. Immediately, the barite was selectively flocculated and the remainder of the pulp was dispersed.

The conditioned pulp was diluted with tap water so that sedimentation sizing could be performed. However, it was determined visually that essentially all of the flocculated barite had settled out within 2 minutes, aproximately one-third the time required to settle the plus 20-micrometer quartz or 13.7-micrometer barite used in the initial particle sizing (table 1).

The dispersed phase of the slurry was removed by siphoning after a 2-minute settling period, and the flocculated phase was repulped again with tap water. This sequence was repeated a total of four times until essentially all of the dispersed phase was removed as four separate slime products. Results of the selective flocculation test (table 3) can be compared with the original sizing data (table 1) for particle size calculated on the basis of the specific gravity of barite. The calculated equivalent particle size of the barite settling in 2 minutes was 23.4 micrometers. This test (table 3) produced a concentrate containing 96.5 percent $BaSO_4$ with an attendant recovery of 82.1 percent of the barite in the feed.

TABLE 3. - $BaSO_4$ analyses and distribution in selectively flocculated pulp

Product	Product distribution, pct	$BaSO_4$, pct Analysis	$BaSO_4$, pct Distribution
Flocculated pulp (Plus 23.4 µm)............	35.9	96.5	82.1
Slimes (Minus 23.4 µm):			
1....................................	51.7	10.4	12.8
2....................................	9.6	12.6	2.9
3....................................	2.0	26.0	1.2
4....................................	.8	52.1	1.0
Composite or total....................	100.0	42.2	100.0

A second selective flocculation test was run using the same conditions except that no sodium cetyl sulfate was added to the pulp. The results of this flocculation test (table 4) show that, when no sodium cetyl sulfate is used, the barite particles do not agglomerate and virtually all of the barite is removed in the four slime fractions.

TABLE 4. - $BaSO_4$ analyses and distribution in dispersed pulp without sodium cetyl sulfate

Product	Product distribution, pct	$BaSO_4$, pct	
		Analysis	Distribution
Sand fraction (Plus 23.4 µm)............	1.6	70.4	2.7
Slimes (Minus 23.4 µm):			
1....................................	82.4	40.3	79.0
2....................................	12.4	45.3	13.4
3....................................	2.8	55.6	3.7
4....................................	.8	63.6	1.2
Composite or total.................	100.0	42.0	100.0

A comparison of the data in tables 3 and 4 shows the effect of the sodium cetyl sulfate. The sodium cetyl sulfate apparently coats the majority of the barite particles and yields agglomerates of barite considerably larger than the original particles shown by the data in table 1.

As a result of these selective flocculation tests, a process patent application has been filed based on the potential use of the selective flocculation process. A simple conditioning-and-washing system could be used to recover barite from waste materials of similar fine-size distribution, thus obviating the requirements for flotation cells and the attendant large froth volumes inherent in flotation. When used to selectively remove a barren slime prior to flotation, the process may be applicable to treating materials much coarser than ultrafine barite waste materials.

DISCUSSION AND CONCLUSIONS

The production of high-grade $BaSO_4$ concentrates from extremely fine barite mill wastes with high recovery of the barite values has been shown to be technically feasible by either flotation or selective flocculation. The pulp was treated by (1) adjusting the pH to about 10.2 with 2.6 pounds of sodium hydroxide per ton, (2) adding 2.5 pounds of sodium silicate and 10 pounds sodium cetyl sulfate per ton, and (3) conditioning the pulp for 20 minutes at 35 percent solids. Flotation of the conditioned pulp produced a barite concentrate containing 94.7 percent $BaSO_4$ while recovering 90.9 percent of the barite. Desliming the pulp four times at an equivalent barite particle size of 23.4 micrometers produced a concentrate containing 96.5 percent $BaSO_4$ while recovering 82.1 percent of the barite. Both processes for recovering ultrafine barite from waste materials have the potential to increase the barite reserve base significantly and to reduce the volume of storage area required for barite mill wastes.

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