CONCENTRATION OF BARIUM SULPHATE IN BARITE ORE BY FLOTATION METHODS

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INTRODUCTION

Barite is a naturally occurring ore having a specific gravity of 4.3 to 4.6, and whose main constituents are iron, silica, barium sulphate and aluminum. Before the World War Germany controlled the world market, and most of our barite was imported. The raw products mined in the United States sold at $3.37 per ton in 1914; however after our supply from Germany was cut-off the price of the ore rose to $6.20 per ton. Necessity caused us to open up our own barite deposits and the increased need for this ore in the industrial world has resulted in an ever increasing and profitable market for barite ore. The average price of barite ore today is $7.00 per ton of crude ore.

Barite is mined in about twenty states but the principal producers in the rank of their importance are Missouri, Tennessee, Georgia, North Carolina, Virginia, South Carolina, Alabama, and Kentucky. The principal use for barite is the manufacture of lithopone but other less important uses are listed below.

1. In pigments.
2. As a base for colored pigments.
    a. Printers ink.
    b. Aniline dyes, etc., for postage stamps, etc.
3. In putty.
4. In rubber goods (to give weight).
5. In linoleum (weight).
6. In oilcloth.
7. In enamel, in pottery and porcelain manufacture.

8. In jasper ware (abroad).
9. In making chemical reagents.
10. In enameling iron.
11. In refining sugar, especially beet sugar.
12. In tanning leather (to give weight).
13. In manufacture of hydrogen peroxide.
14. In dressing calicoes.
15. In finishing wall paper.
16. In pyrotechnics.
17. In paper collars.
18. In insecticides.
19. In artificial ivory.
20. In sealing wax.
21. In artificial stone.
22. In manufacture of alumina.
23. In asbestos cement.
24. In preparation of fertilizers.
25. In boiler compounds.
26. In paper chips.
27. In loading ropes.
28. In dressing for surface of asphalt pavement.
29. In roofing.
30. In various glasses, as rolled glass, hollow ware, crystal and table ware. Jena phosphate crown glass contains 28% BaO and 60% P_2O_5.

This long list shows the many uses to which this material is put. Many of these uses are merely to give weight to a product which is ordinarily light. Such cases are in the manufacture of paper, fabrics, rubber,

insecticides, fertilizers, ropes, and etc. In other instances, it is because the mineral takes a color stain uniformly, and this makes a small quantity of dye cover a large surface. Its use in the paint industry has been known for fifty years or more. Barium salts in glass increases the specific gravity, tenacity, elasticity and refractive index.

PURPOSE OF THIS INVESTIGATION

To be of commercial importance barite ore must contain from 96% to 98% of barium sulphate after washing and should contain 90% $BaSO_4$ in the crude. Many mines could utilize the waste products or low grade ores if there was some means of concentrating the percentage of $BaSO_4$ to the desired figure. Many deposits of barite--good ore but of a low grade--are lying idle and unworked because they are useless in their natural state.

Therefore, it is the purpose of this investigation to study one of these low grade ores having an original $BaSO_4$ content of 80% and to determine if it could be concentrated by ore dressing methods to a product of commercial value.

There are several deposits in eastern Tennessee and the ore is also found in Knox dolomite. The workable deposits are residual, but possibly the veins have been found along fault zones. They are nearly vertical and are from one to six feet wide. The barite in Cooke County has been followed down for one hundred and fifty feet.

The ore used in this investigation was obtained by Mr. J. A. Young, Tennessee Valley Authority Geologist, at Jamestown, Tennessee.

As has already been pointed out there are innumerable deposits of low grade barite faults in Tennessee, especially East Tennessee. The deposits taken singularly do not warrant mining, but taken collectively, and with a centrally located concentration plant in operation they would not only warrant mining but would undoubtedly prove a valuable investment.

The mechanical preparation of an ore for the market is accomplished by one or the other of the following processes:

1. Gravity concentration.

2. Flotation.

3. Magnetic and Electrostatic Separation.

Each process includes the three principal operations of crushing, grading, and concentrating or separating.

Gravity and magnetic methods are not satisfactory owing to the intimate relation of the barite minerals and gangue even down to a fine degree of subdivision.

Previous work indicated that flotation methods would be most feasible and that type of concentration was selected for investigation.

Flotation is the process of separating mineral sulphides from dirt, sand and gangue by beating up a foam with the aid of certain reagents. This foam floats the desired minerals away and leaves the undesirable gangue.

Although the art of flotation has reached a high state of technical perfection, thanks to skilful manipulation on the part of experienced operators, there is yet no theory, if by that is meant a complete knowledge of the forces, and the part they play, individually and collectively in bringing about the phenomenon called flotation. In a general resume of the work already accomplished, we know that in froth flotation (used in this investigation) the metallic sulphide minerals attach themselves to rising bubbles of air, while the gangue minerals settle to the bottom. We know also that certain oils aid this phenomenon, and that various reagents cause improvements in the "quality" of the foam. No set rule has been found which will apply to the flotation of all metallic sulphide minerals. The best results are sought by trial and error. All oils may be designated as either frothers or collectors.[7] Good frothers are oils, more or less soluble, that make quantities of bubbles and much froth, but evaporate quickly, causing the bubbles to burst more readily. Good collectors are oils that are practically insoluble in water and form a film not easily evaporated. This causes the bubbles to be more persistent and better able to hold the attached minerals. Pine oils are good frothers; coal tar and its sub-divisions are good collectors. Some oils combine both properties. With certain ores crude pine tar

may serve both as a frother and collector. Oils are used with all types of ores because they give an added affinity to the ore for the rising air bubble.

Oils mixed with watery pulp render the froth more permanent. This is due largely to a resulting decrease in the surface tension of the water, this tension being a contractile force.

Another puzzling feature of flotation is the fact that water shows an enhanced attraction for the gangue materials, and a lack of such attraction for the sulphide minerals. On the other hand oils show a great affinity for the sulphide minerals, but repulse the gangue materials.

Flotation of barite has been tried successfully as far back as 1928. It is yet a comparatively new idea and not very much is known about it.

At Barstow, California, Cooper Shapley[15] and his associates have treated barite bearing tailings by flotation. The tailings come from the Waterman silver mine, which was worked about forty years ago. The vein contains about 25% barite, and about 45,000 tons of tailing out of 70,000 tons originally milled is available. At present the plant consists of a double spitz K and K flotation machine 10 ft. long, of a capacity of 125 tons daily. A single spitz K and K machine 10 ft. long is used as a cleaner. The ore is mixed with water and sent to the elevated rougher machine then to cleaner machine. The specific gravity of the original tailing is 2.95; of the finished concentrate, 4.36. The latter gives the following analysis: Barium sulphate 94%; silica 1.5%; calcium carbonate .4%; and iron oxide 0.6%. Concentrate varies in fineness from minus 80 to minus 300 mesh, and averages 65% past 200 mesh.

R. G. O'Meara[5] and G. D. Coe have recently published a paper on Froth Flotation of Southern Barite Ores in which they used five types of ores A, B, C, D, and E. Ore A is mainly barite and iron oxide; ore B, barite, iron oxide and fluorite; ore C, barite and quartz; ore D, barite calcite and fluorite; and ore E, barite fluorite and galena. Ore E contains only 32.45 percent $BaSO_4$, 5.3 percent PbS and the balance is mainly fluorite.

The samples were ground to a minus 65 mesh and two reagents charges were used; one for ores A and C (not containing fluorite) and the other for ores B and D (containing fluoride) as follows:

	Pounds Reagent for Ores A & C	Per Ton Feed Ores B & D
Sodium Silicate	1.0	1.0
Sodium Oleate	0.3	
Oleic Acid	0.5	
Emulsal X.		0.5

Ore A (high in iron) yields 85.3% $BaSO_4$. Ore A (mill concentrate) yields 92.4% $BaSO_4$. Ore B yields 86.9% $BaSO_4$. Ore C yields 73.8% $BaSO_4$ and ore D yields 81.6% $BaSO_4$.

EXPERIMENTAL PROCEDURE

A. Raw Material.

The barite ore used in this investigation was obtained from Mr. J. A. Young at Jamestown, Tennessee.

The screen analyses on the raw product as shipped to the laboratory were as follows:

Mesh	Percent
+ 48	12%
-48 + 65	7.5
-65 + 80	3.5
-80 + 100	10.0
-100 + 150	20.5
-150 + 200	18.5
-200	28.5

The original ore before concentration analyzed as follows:

Constituent	Percent
Fe_2O_3	1.22
SiO_2	11.50
$BaSO_4$	80.43
Al_2O_3	2.80
Moisture	.12

B. Flow of Material.

In the Wilfley table experiments the ore and water was mixed thoroughly, after being weighed, and fed directly on to the table. The amount of wash water was not measured. The concentrate was collected, weighed, dryed and analyzed.

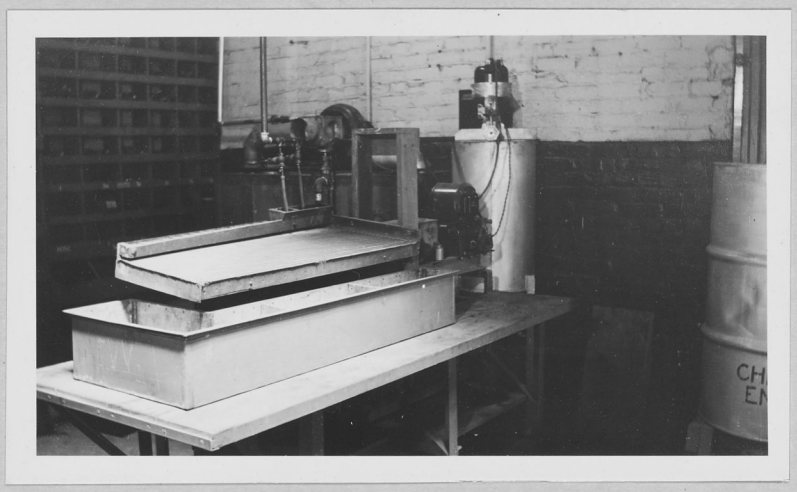

Figure 1. Wilfley Table



Figure 2. D.F.C. Flotation Cell

In the flotation runs the reagents were dissolved in water or alcohol. The sample was weighed and the water added by means of a graduated cylinder. The ore, water and reagents were added directly to the cell. It was then conditioned, floated, and the discharge collected, dried, weighed, and analyzed.

C. Apparatus.

Flotation cell No. I was purchased from the Denver Fire Clay Company. It has a capacity of 500 grams of ore with a 4:1 pulp ratio. It is driven by a 1/6 H. P. adjustable speed motor, and is mechanically agitated.

Flotation cell No. II (See drawing) has a capacity of 50 grams and is driven by a 1/8 H. P. motor. This flotation cell was built in the laboratory to be used in connection with flotation of manganese.

The Wilfley table (see Figure 2.) was purchased from the Mine and Smelter Supply Company. It is of a standard size laboratory table having a deck 40 inches long and 18 inches wide. It is driven by a 1/4 H. P. motor.

D. Operation.

From the experience of Vance[12] on manganese ores the operation was standardized to give the best results.

The Wilfley table was operated with ore feed, water flow, inclination and amplitude of jerking set to give a smooth flow over the surface of the table.

In the operation of the flotation cells, the ores, reagents, (other than collectors and frothers), and one half of the water were charged into the cell and conditioned for two minutes. Then the other half of the water, the collectors, and frothers, were added and floated for

ten minutes. The speed of the No. I cell used in this investigation was 3060 R.P.M.

E. Control.

The time for the various operations was determined by an Eastman Interval Timer.

The wet material was dried at 110° C, weighed and then analyzed. The procedure for the determination of the $BaSO_4$ was as follows:

A one gram sample of finely pulverized ore is placed in a platinum dish. 15 cc of H.Cl is added, then 10 cc of H.F is carefully added. The mixture is evaporated down to about 5 cc. This is usually accomplished by heating on a low temperature hot plate. Add 10 cc of H_2SO_4 and evaporate down to fumes of SO_2. Cool and add 100 cc of H_2O. Boil for two minutes (gently) and let stand for five minutes. Filter with a weighed Gooch crucible, and burn at a low temperature. Weigh as $BaSO_4$.

Using the large flotation machine a number of runs were made with samples of the ore screened out to a fineness in one case of minus 60 mesh, and in another minus 100 mesh. The following reagents were tried, separately and in combination, with varying results:

1. Pine oil.
2. Barrett Flotation Oil No. 4.
3. Hercules Tarol No. 1.
4. Hercules Tarol No. 2.
5. Hercules Yarmor F.
6. Sodium Oleate.
7. Oleic Acid.
8. Hydrochloric Acid.
9. Sodium Hydroxide.
10. Sodium Silicate.
11. Oxalic Acid.

A collector and a frother were added to the watery pulp in each case and in some runs two collectors and a frother, or two frothers and a collector. In other runs reagents such as sodium hydroxide were added to strengthen the foam and to depress the gangue.

Using minus 100 mesh samples of 500 grams each and a water ratio of 4 to 1, the best results were obtained with the following combination:

Reagent	Amount (grams)
Sodium Hydroxide	6.0
Oleic Acid	0.25
Pine Oil	0.25

The concentrate analyzed 93.57% $BaSO_4$, however, the recovery was low--29.4% of original barite.

The sodium hydroxide was used to strengthen the foam. The pine oil is a collector which forms a thin screen of oil over the sulphide minerals and prevents the water from "wetting" thereby increasing the flotability. The oleic acid is a frothing agent which produces a good foam when mixed with air and water.

In the runs which were ten minutes in duration it was noticed that the maximum foam was produced at the five minute mark and that the addition of sodium hydroxide produced a remarkable change in the quality of the foam. The best foams are produced when the system was slightly alkaline.

The fineness of the sample was studied with the result that the finer the sample of ore the better recovery of ore and also $BaSO_4$ was obtained. Using two samples of minus 60 mesh and minus 100 mesh respectively, it was found that the percent increase of $BaSO_4$ of the minus 100 mesh over the minus 60 mesh was approximately 10%.

In all cases the percent recovery of the original material was low, but at the same time the best recovery of original material was obtained along with the greatest concentration of $BaSO_4$.

The Wilfley table was used without very great success. The percent recovery was very good, but the percent $BaSO_4$ was lower than in the original sample. Evidently the sand was washed over the concentrate end of the table, and the SiO_2 was concentrated instead of the $BaSO_4$.

The main mining centers are located near the crude barite markets of the three principal marketing districts--the Pacific coast, the mid-western area, and the Eastern area.[5] The Pacific coast is supplied entirely by California, Nevada, and Arizona. The midwestern areas use most of the Missouri crude and a small amount from the southern states. The eastern market is the chief competitive area. Practically all of the imported crude is marketed there; also the bulk of the southern crude and ground barite. In addition this area absorbs a small part of the Missouri crude and 80 percent of the ground barite.[5]

Besides the advantage of low delivered costs and purity of product, the imported barite has commanded a price differential because it is soft rather than hard, like many of the domestic ores. The inherent physical properties of the southern ores remain, but the purity can be controlled to a great extent by beneficiation. Simple washing or gravity concentration has sufficed in the past, but in many cases a more efficient process now becomes imperative to remove impurities not amendable to these methods.[5]

An ore which can be concentrated to 90 percent will have the same market as the original raw material of that percent although there will be the added cost of purification to be considered. On the other hand if the ore is not purified it will be a total loss. Then, too, ores concentrated to 90 percent, or above, will find their place on the market. The many uses of barite will naturally demand an ore of this type for certain products.

As stated before the industry has continued to expand because of

the increasing use of lithopone. In 1914 the sales of domestic crude barite was 52,919 tons and in 1934 it was 209,850 tons.

CONCLUSIONS

To determine whether or not it would be profitable to concentrate barite on a commercial scale one must take into consideration several factors. First whether or not the ore can be found in sufficient quantities to warrant commercial scale flotation since it is known that the percent recovery is low. If the deposits are small and fairly closely grouped a central concentration plant would solve the problem.

Since it is now known that the ore can be concentrated to 93%, and that the crude salable ore which is mined in East Tennessee runs approximately 90% $BaSO_4$, and has a wide field of usefulness and a good market it follows that a thorough investigation of the possibilities of a concentration plant is warranted. This statement takes into consideration the fact that concentration plants have been operated at a price range of $4.00 per ton crude, and that the present price of the ore is $7.00 per ton crude and $23.00 to $24.00 per ton after it has been water ground, bleached and floated.

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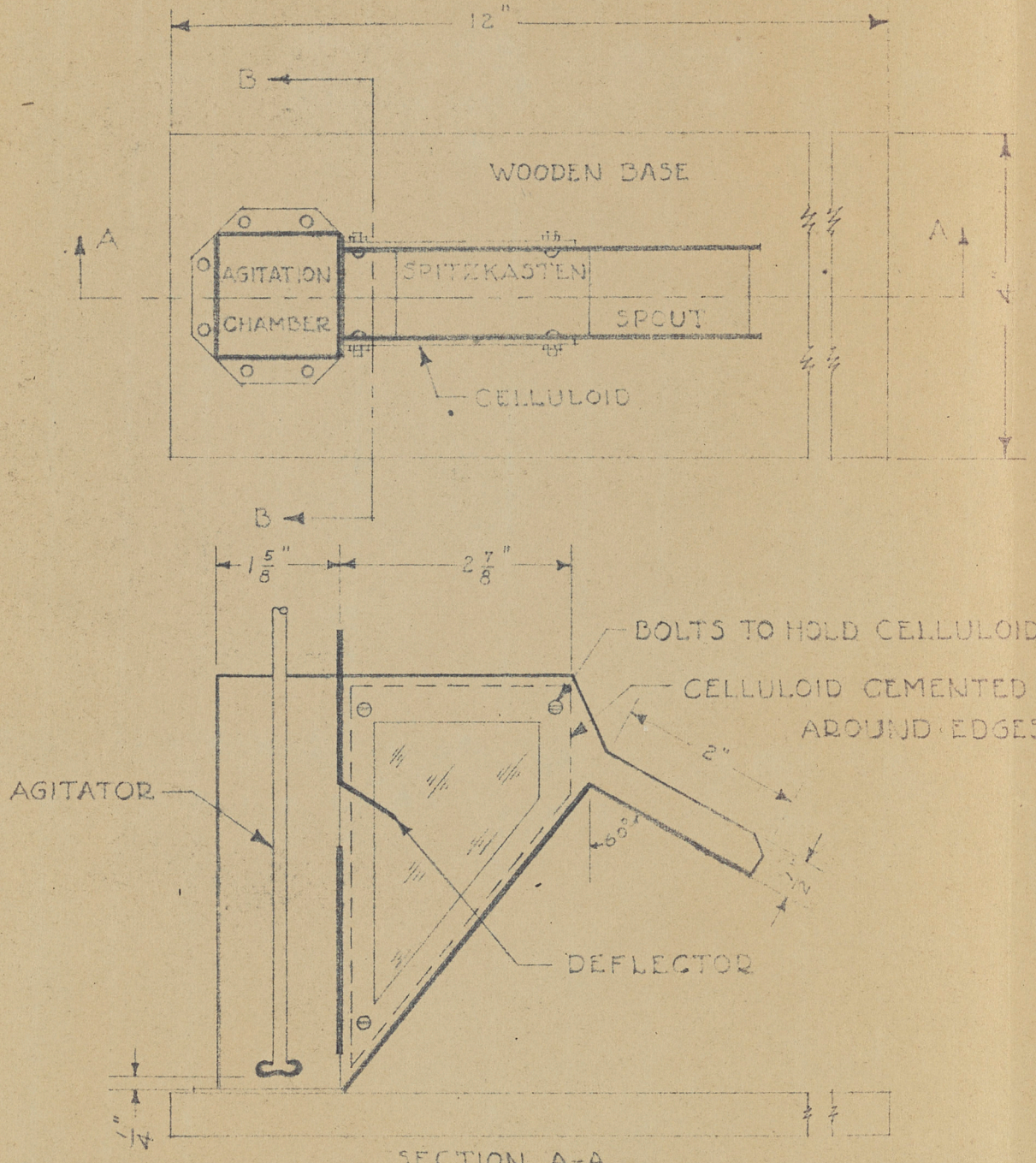
FLOTATION CELL

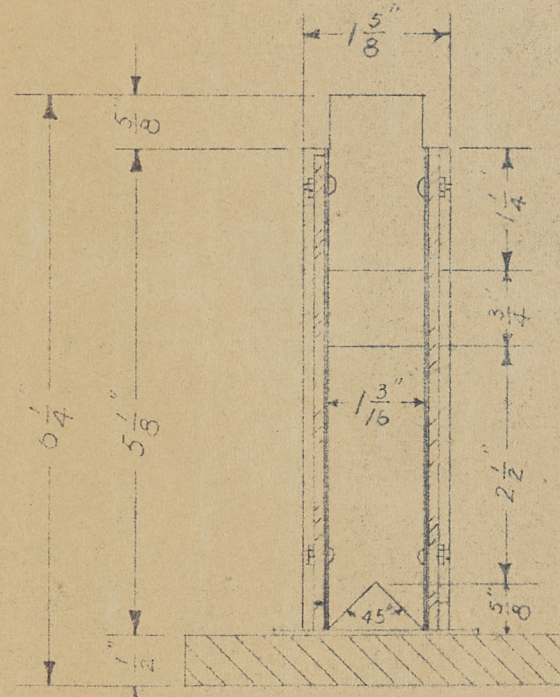
FIG. 4.

SCALE: 6" = 1'

SHEET METAL CONSTRUCTION



SECTION A-A



SECTION B-B

APPENDIX

The chemical analysis of the raw ore and the screen analysis of the same has been given under the heading "Raw Material" under "Experimental Procedure".

The ore was of such fineness that it was not necessary to grind it. Two samples were screened, one passing a 60 mesh screen and the other passing a 100 mesh screen. 1. designates the 60 mesh sample and 2. the 100 mesh sample. As sample 1-A-I. A-I indicates the specific sample and the preceding 1 the quality of fineness.

Screen analysis of No. 1, the pass 60 mesh, is as follows:

Mesh	Percent
+ 48	—
-48 + 65	2.0
-65 + 80	2.0
-80 + 100	9.5
-100 + 150	25.0
-150 + 200	25.5
-200	35.5

Screen analysis of No. 2, the pass 100 mesh, is as follows:

Mesh	Percent
48	—
-48 + 65	—
-65 + 80	—
-80 + 100	—
-100 + 150	18.5
-150 + 200	34.0
-200	47.5

EXPERIMENTAL DATA

Water Ratio 4:1
Sample 1-A-I; 500 grams

Reagents	Amounts
Oleic Acid	0.25g
Pine oil	0.15g
NaOH	0.8 g
Sodium Silicate	0.5 g

Wt. of dry conc.---:	38g
% recovery:	7.6%
% $BaSO_4$:	89.4%
%SiO_2:	0.12%

Water Ratio 4:1
Sample 2-A-2: 500 grams

Reagents	Amounts
Oleic Acid	0.25g
Pine Oil	0.15g
NaOH	0.8 g
Sodium Silicate	0.5 g

Wt. of dry conc.---:	54g
% recovery:	10.8%
% $BaSO_4$:	89.93%
%SiO_2:	1.26%

Water Ratio 4:1
Sample 1-B-1: 500 grams

Reagents	Amounts
Tarol	0.234g
Oleic Acid	0.234g.
Yarmor	0.234g
Sodium Hydroxide	2.4 g

Wt. of dry conc.---:	77g
% recovery:	15.4%
%$BaSO_4$:	81.94%
%SiO_2:	7.83%

Water Ratio 4:1
Sample 2-B-2: 500 grams

Reagents	Amounts
Tarol	0.234g
Oleic Acid	0.234g
Yarmor	0.234g
Sodium Hydroxide	2.4 g

Wt. of dry concn.--:	71g
% recovery:	14.2%
% $BaSO_4$:	93.52%
% SiO_2:	0.89%

Water Ratio 4:1
Sample 1-C-1: 500 grams

Reagents	Amounts
Pine Oil	0.12g
Sodium Oleate	0.5 g
Sodium Silicate	0.2 g
HCl	0.06 g

Wt. of dry concn.--:	46g
% recovery:	9.2%
% $BaSO_4$:	80.96%

Water Ratio 4:1
Sample 1-D-1: 500 grams

Reagents	Amounts
Sodium Silicate	0.25g
Sodium Oleate	0.07g
Oleic Acid	0.12g

Wt. of dry concn.--:	None
% Recovery:	No foam
% $BaSO_4$:	—

Water Ratio 4:1
Sample 1-E-1: 500 grams

Reagents	Amounts
Sodium Silicate	0.5g
Sodium Oleate	0.07g
Oleic Acid	0.12g

Wt. of dry concn.--:	None
% Recovery:	No foam
% $BaSO_4$:	—

Water Ratio 4:1
Sample 1-F-1: 500 grams

Reagents	Amounts
Oxalic Acid	0.15g
Sodium silicate	0.5 g
Sodium Oleate	0.07 g

Wt. of dry conc.:-- 34g
% recovery: 6.8%
% $BaSO_4$: 84.05%

Water Ratio 4:1
Sample L-G-1: 500 grams

Reagents	Amounts
Pine Oil	0.125g
Oleic Acid	0.0625g

Wt. of dry conc.:-- 52g
% recovery: 10.4%
% $BaSO_4$: 86.27%

Water Ratio 4:1
Sample 1-H-1: 500 grams

Reagents	Amounts
NaOH	6.0g
Oleic Acid	0.25g
Pine Oil	0.25g

Wt. of dry conc.:-- 121g
% Recovery: 24.2%
% $BaSO_4$: 83.30%

Water Ratio 4:1
Sample 2-H-2: 500 grams

Reagents	Amounts
NaOH	6.0g
Oleic Acid	0.25g
Pine Oil	0.25g

Wt. of dry conc.:-- 147g
% Recovery: 29.4%
% $BaSO_4$: 93.57%

Water Ratio 4:1
Sample 1-J-1: 500 grams

Reagents	Amounts
Flotation Oil No. 4	0.5g
Oleic Acid	0.5g
Sodium Silicate	0.2g

Wt. of dry conc.:-- 54g
% Recovery: 10.8%
% $BaSO_4$: 82.4%

Water Ratio 4:1
Sample 1-K-1: 500 grams

Reagents	Amounts
Tarol No. 1	0.5g
Sodium Oleate	0.5g
Yarmor Oil	0.2g

Wt. of dry conc.: -- 83g
% Recovery: 16.6%
% $BaSO_4$: 80.86%

Water Ratio 4:1
Sample 1-L-1: 500 grams

Reagents	Amounts
Tarol No. 2	0.5g
NaOH	0.1g
Sodium Oleate	0.5g

Wt. of dry conc.:-- 75g
% Recovery 15%
% $BaSO_4$: 84.08%
% SiO_2:

Water Ratio 4:1
Sample 1-M-1: 500 grams

Reagents	Amounts
Pine Oil	0.3g
Sodium Oleate	0.5g
Oxalic Acid	0.2g

Wt. dry conc.:-- 77g
% Recovery: 15.4%
% $BaSO_4$: 80.98%
%SiO_2

Wilfley Table

Sample 1-N-1: 2000 grams

Water Ratio 1 1/2 gal. H_2O/2000 grams

Wash water not measured

Wt. of dry conc.:--	327 grams
% Recovery:	16.35%
% $BaSO_4$:	73.68%

Wilfley Table

Sample 1-O-1: 2000 grams

Water Ratio--same

Wash water not measured

Wt. of dry conc.:--	309 grams
% Recovery:	15.45%
% $BaSO_4$:	74.42%

ACKNOWLEDGMENTS

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CRANES
JAPANESE LINEN
MADE IN U.S.A.

APPROVAL

The foregoing thesis is hereby approved as a creditable study of an engineering subject, carried out and presented in a manner sufficiently satisfactory to warrant its acceptance as a prerequisite to the degree for which it has been submitted. It is to be understood that by this approval the undersigned does not necessarily endorse or approve any statement made, opinions expressed, or conclusions drawn therein, but approves the thesis only for the purpose for which it is submitted.

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