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CONCENTRATION OF NONMETALLIC MINERALS

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The present invention relates to a concentration of so-called non-metallic minerals from ores containing them in association with silicious matter, the term "non-metallic" being used herein to refer to those minerals which are not used in the metallurgical industry as a source of metal contained therein, but which are used for some other purpose. Among these minerals are included phosphates, calcite, barite, and fluorspar, the invention being herein described in connection with the examples given as applied to all four of these minerals.

The general object of the invention is to provide an improved process for concentrating minerals of the character stated from ores in which the gangue is at least in part silicious.

In accordance with the invention, a pulp of suitably divided particles of the non-metallic mineral ore to undergo treatment is agitated in the presence of a substantially insoluble and unsaponifiable oil, a lower fatty acid or lower fatty acid soap to cooperate with said oil in effecting collection of the non-metallic mineral values, and an activating agent causing said fatty acid or fatty acid soap to have a preferential affinity for said values, said activating agent consisting of a soluble salt of a metal whose oxide does not exert an alkaline reaction when added to water. Thereafter, a concentrate is separated from the pulp by froth flotation or in other manner known in the art. By such procedures it has been found that excellent results may be obtained with relation to both recovery of the non-metallic mineral values and content of said values in the concentrate. The lower fatty acid or lower fatty acid soap employed as a cooperating collector may be any one of the fatty acids or fatty acid soaps having a carbon content of less than thirteen atoms, satisfactory results having thus been obtained with caprylic acid, heptylic acid, capric acid, caproic acid, pelargonic acid, and lauric acid, as well as with the soaps of these acids. In certain cases the addition of an alkali, such as caustic soda, has been found to improve the concentration or to reduce the quantity of activating metallic salt necessary.

It is already known that phosphate minerals may be successfully concentrated with the aid of fatty acids in conjunction with fuel oil and alkali, or with the aid of fatty acid soaps in conjunction with fuel oil, but it has hitherto been supposed that the only fatty acids or fatty acid soaps capable of successful use were those containing more than twelve carbon atoms. The successful use of the lower fatty acids or lower fatty acid soaps according to the present invention is due fundamentally to the employment of soluble metallic salts therewith. The presence of the metallic salt, with or without addition of alkali, may not only have the effect of considerably improving the results of concentration, but may also have the effect of considerably decreasing the quantity of the lower fatty acid or lower fatty acid soap required. The metallic salt may even enable concentration to be effected where none whatever can be practicably obtained without it, regardless of the amount of fatty acid or fatty acid soap employed.

In most forms of the invention herein described in connection with the examples given, the pulp containing the ore of the mineral to be concentrated is of an acid character subsequent to mixing with the reagents employed; that is, the pH of the pulp is less than the index number 7, corresponding to a neutral condition. This acid character of the pulp is obtained with the lower fatty acids employed in a free state or added to the pulp uncombined with other substances, and is due to the solubility of such acids in water, it being observed that solubility of the fatty acids of carbon content of less than thirteen atoms is much greater as compared with the fatty acids of carbon content of more than twelve atoms. It should also be noted that the acid character of the pulp is in general not nullified by the use of alkali in conjunction with the metallic salt; that is, the pH of the pulp is still below 7 even after the addition of alkali in the quantity determined to be suitable for maximum concentration.

In preparing the ore for treatment by the process of the present invention, it is in general desirable that it be comminuted to a particle size most suitable for efficient operation and that it be largely deslimed, its desliming greatly minimizing the consumption of the reagents. Ordinarily, the crude ore is first subjected to a preliminary grinding operation and thereafter screened or classified to remove all particles other than those desired. The undersize may then be deslimed, and the oversize reground, deslimed, and added to the deslimed undersize; or the oversize may be reground, added to the undeslimed undersize, and the whole then deslimed.

Although the procedures described in the following examples are flotation procedures, it is known that satisfactory results may in many

cases be obtained by effecting the concentration on a shaking table, as in the patent to Chapman and Littleford No. 1,968,008, of July 24, 1934.

Example 1

Deslimed phosphate feed to the flotation concentration plant of the Phosphate Recovery Corporation in Mulberry, Florida, consisting mainly of calcium phosphate and silica and of a particle size to pass through a screen of 28 meshes to the lineal inch, was made up with water to a thick pulp of 70% solids.

To this pulp were added during agitation in an impeller-type mixer, 2 pounds of lead nitrate, 6 pounds of fuel oil, 36.9 pounds of caproic acid, and 0.14 pound of a frothing agent consisting of 3 parts of crude rosin residue dissolved in 1 part of kerosene oil, the reagent amounts stated all referring to proportions figured on the basis of the dry weight tonnage (2,000 pounds) of material treated. This addition of reagents required about one minute, subsequent to which agitation was continued for two more minutes. After this mixing the pulp was transferred to a laboratory subaeration flotation machine, where it was diluted and agitated for a period of less than two minutes, during which a rougher concentrate was separated. Upon removal of the tailing, the rougher concentrate was refloated without further addition of reagents, a final concentrate being thus obtained. The tailing of this cleaning was assayed separately and was found to constitute a middling, which in commercial operation would be returned to the flotation cells for further extraction of values. The results of the test are indicated in the following table:

Product	Weight percent	$Ca_3(PO_4)_2$ percent assay	Insoluble percent	$Ca_3(PO_4)_2$ percent recovery	Ratio of concentration
Feed	100.0	28.50		100.0	
Concentrate	33.7	72.65	5.73	86.0	2.96
Middling	3.9	45.65		6.7	
Tailing	62.4	3.39		7.3	

pH of pulp after mixing with reagents . . . 3.8.

Example 2

The same feed was taken and the same procedures were followed as in Example 1, but in this instance caustic soda in the amount of 1 pound per ton was also employed and the proportion of lead nitrate was reduced to 1 pound per ton, the proportions of fuel oil, caproic acid, and kerosene-rosin solution remaining the same. The lead nitrate and caustic soda were mixed together prior to addition to the pulp, the caustic soda employed being a commercial brand of sodium hydroxide. Notwithstanding the reduced quantity of lead nitrate, a concentrate of substantially the same grade as before was obtained, as shown by the following table:

Product	Weight percent	$Ca_3(PO_4)_2$ percent assay	Insoluble percent	$Ca_3(PO_4)_2$ percent recovery	Ratio of concentration
Feed	100.0	28.20		100.0	
Concentrate	33.0	73.25	5.60	85.8	3.03
Middling	5.1	47.16		8.5	
Tailing	61.9	2.55		5.7	

pH of pulp after mixing with reagents . . . 4.4.

As a basis of comparison with the examples which have been described, the following test was carried out.

Comparative test 1

A sample of the same feed was similarly formed into a thick pulp with water, and to this pulp were added 2 pounds of caustic soda, 2 pounds of fuel oil, 10 pounds of caproic acid, and 0.14 pound of Hercules Powder Company's Tarol #2 (a mixture of three parts of steam distilled pine oil and 1 part of rosin oil), all per ton of dry material. Soon after agitation of the pulp with these reagents was started, it was apparent that their nature was not such that successful flotation could be effected. The period of agitation was thus lengthened to as much as ten minutes, and during this extended agitation further additions of caustic soda at the rate of 2 pounds per ton and further additions of caproic acid at the rate of 10 pounds per ton were repeatedly made, until a total of 40 pounds of caustic soda and a total of 100 pounds of caproic acid were present in the pulp. Upon dilution and agitation in the flotation machine, no flotation whatever could be effected with the material thus treated.

In the above comparative test it is to be noted that only 2 pounds of fuel oil were used as compared to 6 pounds in Examples 1 and 2. This is due to the fact that in the comparative test no reaction could be obtained between the reagents and the pulp with which they were admixed. The pulp did not take up even as much as 2 pounds of fuel oil, so it was considered useless to increase the amount.

Example 3

A pulp of the same feed and of the same consistency as before was agitated with 1.50 pounds of lead nitrate, 6 pounds of fuel oil, 14.74 pounds of heptylic acid, and 0.14 pound of the same kerosene-rosin solution as described in Example 1, all per ton of dry material. The procedures were otherwise the same as in Example 1, the following results being obtained:

Product	Weight percent	$Ca_3(PO_4)_2$ percent assay	Insoluble percent	$Ca_3(PO_4)_2$ percent recovery	Ratio of concentration
Feed	100.0	28.53		100.0	
Concentrate	34.2	73.15	6.61	87.7	2.92
Middling	5.4	19.69		3.7	
Tailing	60.4	4.06		8.6	

pH of pulp after mixing with reagents . . . less than 6.

Example 4

The procedures of Example 3 were repeated on another sample of the same phosphate feed, but instead of the 1.50 pounds per ton of lead nitrate a mixture of 1 pound per ton of lead nitrate and 1 pound per ton of caustic soda was added to the pulp. The same proportions of the other reagents were employed, the results being as follows:

Product	Weight percent	$Ca_3(PO_4)_2$ percent assay	Insoluble percent	$Ca_3(PO_4)_2$ percent recovery	Ratio of concentration
Feed	100.0	28.69		100.0	
Concentrate	32.0	77.17	6.53	86.1	3.13
Middling	9.5	31.05		10.3	
Tailing	58.5	1.79		3.6	

pH of pulp after mixing with reagents . . . less than 6.0.

Comparative test 2

A sample of the same feed as before was treated with 36 pounds (total) per ton of caustic soda, 2 pounds per ton of fuel oil, 100 pounds (total)

per ton of heptylic acid, and 0.14 pound per ton of the same frothing agent as used in comparative test 1 (Tarol #2), the procedures being otherwise the same as in that test. No concentrate whatever was obtained, the reasons for employing only 2 pounds of fuel oil being the same as expressed in connection with comparative test 1.

In another test treatment with 55 pounds per ton of heptylic acid without any other reagents resulted in floating a concentrate containing 73.62% of calcium phosphate, but representing a recovery of only 11.5%.

Example 5

In the same manner as indicated in Example 1, flotation was effected on a pulp of the same feed as before but employing as reagents and proportions thereof: 1 pound per ton of lead nitrate, 6 pounds per ton of fuel oil, 6.07 pounds of caprylic acid, and 0.14 pound of the kerosene-rosin solution, the following results being obtained:

Product	Weight percent	$Ca_3(PO_4)_2$ percent assay	Insoluble percent	$Ca_3(PO_4)_2$ percent recovery	Ratio of concentration
Feed	100.0	28.39		100.0	
Concentrate	25.7	77.77	7.34	70.4	5.89
Middling	22.5	28.84		22.9	
Tailing	51.8	3.68		6.7	

pH of pulp after mixing with reagents . . . less than 6.0.

Example 6

With the same reagents as in Example 5, but with the proportions of lead nitrate and caprylic acid respectively reduced to 0.65 pound per ton and 6 pounds per ton, and with the lead nitrate added in admixture with 1 pound per ton of caustic soda, the following results were obtained, the same feed as before being employed:—

Product	Weight percent	$Ca_3(PO_4)_2$ percent assay	Insoluble percent	$Ca_3(PO_4)_2$ percent recovery	Ratio of concentration
Feed	100.0	28.02		100.0	
Concentrate	27.3	79.08	4.82	77.1	3.66
Middling	12.7	39.24		17.8	
Tailing	60.0	2.41		5.1	

pH of pulp after mixing with reagents . . . less than 6.0.

Example 7

For the purpose of this example caprylic acid was used in conjunction with copper sulphate admixed with caustic soda, fuel oil being also employed together with the same kerosene-rosin solution as previously described. Flotation was effected on a pulp of the same feed as before, the reagents being present in the pulp in the following proportions: copper sulphate 1 pound, caustic soda 1 pound, fuel oil 6 pounds, caprylic acid 6 pounds, and kerosene-rosin solution 0.14 pound, all per ton of dry material. The results were as follows:—

Product	Weight percent	$Ca_3(PO_4)_2$ percent assay	Insoluble percent	$Ca_3(PO_4)_2$ percent recovery	Ratio of concentration
Feed	100.0	28.11		100.0	
Concentrate	22.2	77.47	7.26	61.2	4.49
Middling	28.0	24.62		24.5	
Tailing	49.8	8.08		14.3	

pH of pulp after mixing with reagents . . . less than 6.0.

Example 8

The same procedures as outlined in detail in Example 1 were again carried out on a sample of the same phosphate feed, but employing the following reagents and proportions thereof: zinc sulphate 1 pound, caustic soda 1 pound, fuel oil 6 pounds, caprylic acid 6 pounds, and kerosene-rosin solution 0.14 pound, all per ton of dry mineral, the zinc sulphate and caustic soda being added as a mixture to the pulp. The results were as follows:

Product	Weight percent	$Ca_3(PO_4)_2$ percent assay	Insoluble percent	$Ca_3(PO_4)_2$ percent recovery	Ratio of concentration
Feed	100.0	28.03		100.0	
Concentrate	21.3	79.68	4.60	60.5	4.70
Middling	11.9	56.77		24.1	
Tailing	66.8	6.43		15.4	

pH of pulp after mixing with reagents . . . less than 6.0.

Example 9

The same phosphate feed was employed, with aluminum chloride as the activating salt. The reagents were used in the following proportions: aluminum chloride 1 pound, caustic soda 0.8 pound, fuel oil 6 pounds, caprylic acid 6 pounds, and kerosene-rosin solution 0.14 pound, all per ton of dry material, the aluminum chloride and caustic soda being added as a mixture to the pulp. The results were as follows:—

Product	Weight percent	$Ca_3(PO_4)_2$ percent assay	Insoluble percent	$Ca_3(PO_4)_2$ percent recovery	Ratio of concentration
Feed	100.0	28.68		100.0	
Concentrate	33.0	71.94	12.93	82.6	3.03
Middling	23.2	12.44		10.2	
Tailing	43.8	4.68		7.2	

pH of pulp after mixing with reagents . . . less than 6.0.

Example 10

Ferrous chloride was the salt, the feed being the same as before. The reagents were employed in the following proportions: ferrous chloride 1 pound, caustic soda 1 pound, fuel oil 6 pounds, caprylic acid 6 pounds, and kerosene-rosin solution 0.14 pound, all per ton of dry material, the ferrous chloride and caustic soda being added as a mixture to the pulp. The results were as follows:

Product	Weight percent	$Ca_3(PO_4)_2$ percent assay	Insoluble percent	$Ca_3(PO_4)_2$ percent recovery	Ratio of concentration
Feed	100.0	28.08		100.0	
Concentrate	21.4	79.47	4.93	60.5	4.67
Middling	14.0	57.39		28.7	
Tailing	64.6	4.76		10.8	

pH of pulp after mixing with reagents . . . less than 6.0.

Comparative test 3

A sample of the same feed as before was processed in the manner indicated in comparative test 1, but employing the following reagents and proportions thereof: caustic soda 24 pounds (total), fuel oil 2 pounds, caprylic acid 70 pounds

(total), and the same kerosene-rosin solution as previously described 0.14 pound, all per ton of dry material. These reagents were also found to be totally ineffective, the reasons for employing only 2 pounds of fuel oil being again the same as expressed in connection with comparative test 1.

By the use of fuel oil and caprylic acid as the only reagents in another test, a recovery of 82.1% was effected in a concentrate assaying 73.21% calcium phosphate, but this flotation required the use of 55 pounds per ton of such acid.

Example 11

As shown by the following table, a sample of the same feed as before was successfully concentrated by the procedures indicated in detail in Example 1, but employing the following reagents and proportions thereof: lead nitrate 1 pound, fuel oil 4 pounds, pelargonic acid 4.09 pounds, and the same kerosene-rosin solution 0.14 pound, all per ton of dry material:—

Product	Weight percent	$Ca_3(PO_4)_2$ percent assay	Insoluble percent	$Ca_3(PO_4)_2$ percent recovery	Ratio of concentration
Feed	100.0	28.80		100.0	
Concentrate	32.0	73.14	5.64	81.3	3.12
Middling	7.7	32.31		8.7	
Tailing	60.3	4.86		10.0	

pH of pulp after mixing with reagents . . . 5.5.

Example 12

Successful concentration was also effected on another sample of the same phosphate feed by the use of the same reagents and proportions indicated in Example 11, but with the 1 pound per ton of lead nitrate replaced by a mixture of 0.5 pound per ton of lead nitrate and 0.75 pound per ton of caustic soda, the results in this instance being as follows:

Product	Weight percent	$Ca_3(PO_4)_2$ percent assay	Insoluble percent	$Ca_3(PO_4)_2$ percent recovery	Ratio of concentration
Feed	100.0	29.00		100.0	
Concentrate	32.8	72.54	6.40	82.1	3.05
Middling	11.1	31.41		12.1	
Tailing	56.1	3.11		5.8	

pH of pulp after mixing with reagents . . . 6.7.

Comparative test 4

A sample of the same feed as before was processed in the manner indicated in comparative test 1, but employing 20 pounds (total) of caustic soda and 55 pounds (total) of pelargonic acid, both per ton of dry material. There were no other reagents employed, no concentration whatever being effected.

In another test the use of pelargonic acid alone yielded a concentrate assaying 72.08% of calcium phosphate and containing 88% of the calcium phosphate originally present in the sample employed, but 55 pounds per ton of such acid were necessary to effect the concentration.

Example 13

Again following procedures similar to those indicated in Example 1, another sample of the same phosphate feed was concentrated with the aid of the following reagents and proportions thereof: a mixture of 0.65 pound per ton of lead nitrate and 1 pound per ton of caustic soda, 5 pounds per ton of fuel oil, 3 pounds per ton of capric acid, and 0.14 pound of the kerosene-rosin solution. The results were as follows:

Product	Weight percent	$Ca_3(PO_4)_2$ percent assay	Insoluble percent	$Ca_3(PO_4)_2$ percent recovery	Ratio of concentration
Feed	100.0	28.55		100.0	
Concentrate	30.4	77.06	6.67	82.0	3.29
Middling	7.5	25.99		6.8	
Tailing	62.1	5.16		11.2	

pH of pulp after mixing with reagents . . . less than 6.0.

Comparative test 5

A sample of the same feed as before was processed with the following reagents and proportions thereof: caustic soda 0.4 pound, fuel oil 2 pounds, capric acid 6 pounds, and kerosene-rosin solution 0.14 pound, all per ton of dry material. While a concentrate assaying 72.29% in calcium phosphate and containing 70.5% of the calcium phosphate present before concentration was obtained, yet these results were obtained with a quantity of capric acid twice that employed to obtain superior results in Example 13. Here again it was considered useless to increase the amount of fuel oil over 2 pounds, as the pulp treated with the reagents indicated did not even take up this amount.

Example 14

Deslimed phosphate feed to the Pembroke plant of the Phosphate Recovery Corporation in Florida, also of a particle size to pass through a screen of 28 meshes to the lineal inch, was made up with water to a pulp of the same consistency as before which pulp was agitated with 0.65 pound of lead nitrate, 1 pound of caustic soda, 2 pounds of fuel oil, 2 pounds of lauric acid, and 0.14 pound of the same kerosene-rosin solution, as previously described, all per ton of dry material, the lead nitrate and the caustic soda being added as a mixture to the pulp. The procedures were otherwise the same as outlined in detail in Example 1, the following results being obtained:

Product	Weight percent	$Ca_3(PO_4)_2$ percent assay	Insoluble percent	$Ca_3(PO_4)_2$ percent recovery	Ratio of concentration
Feed	100.0	41.09		100.0	
Concentrate	45.2	79.17	3.67	87.1	2.21
Middling	3.9	51.97		4.9	
Tailing	50.9	6.44		8.0	

pH of pulp after mixing with reagents . . . 8.6.

Comparative test 6

A sample of the same feed as in Example 14 was processed in the same manner as in that example, except that the use of lead nitrate was omitted, the same proportions of caustic soda, fuel oil, lauric acid, and kerosene-rosin solution being employed. Whereas a concentrate assaying 79.67% in calcium phosphate was obtained, the amount of calcium phosphate recovered in said concentrate was only 72.6% as compared to the 87.1% recovered in Example 14.

Example 15

A synthetic mixture of marble and silica sand was prepared in the proportion of about 20% marble and 80% sand. This mixture was sized on a screen having 28 meshes to the lineal inch, and the undersize material was formed with water

into a pulp of 70% solids. To this pulp were added, during agitation in the mixer, 1 pound per ton of lead nitrate, 4 pounds per ton of fuel oil, 3.67 pounds per ton of caprylic acid, and 0.14 pound per ton of the kerosene-rosin solution previously described, the total period of agitation being three minutes. After this mixing operation, the pulp was diluted and agitated in the flotation machine for approximately one minute, during which a rougher concentrate was separated. The tailing was removed, whereupon the rougher concentrate was refloated without further addition of reagents, yielding a final concentrate. The tailing of this cleaning was assayed separately and was found to constitute a middling, which in commercial operation would be returned to the flotation cells for additional recovery of values. The results are indicated in the following table:

Product	Weight percent	$CaCO_3$ percent assay	$CaCO_3$ percent recovery	Ratio of concentration
Feed	100.0	21.36	100.0	
Concentrate	20.2	97.68	92.3	4.95
Middling	2.1	66.42	6.5	
Tailing	77.7	0.32	1.2	

pH of pulp after mixing with reagents . . . 6.0.

Example 16

A similar mixture of marble and silica sand was treated with the aid of 1 pound per ton of ferric chloride, 4 pounds per ton of fuel oil, 3.67 pounds per ton of caprylic acid, and 0.14 pound per ton of the same kerosene-rosin solution, the procedures followed being otherwise identical to those outlined in Example 15. The following results were obtained:

Product	Weight percent	$CaCO_3$ percent assay	$CaCO_3$ percent recovery	Ratio of concentration
Feed	100.0	20.90	100.0	
Concentrate	20.4	95.43	93.0	4.89
Middling	2.8	45.58	6.1	
Tailing	76.8	0.10	0.9	

pH of pulp after mixing with reagents . . . 6.0.

Example 17

Again repeating the procedures of Example 15, but treating the marble containing pulp with 0.5 pound per ton of copper sulphate, 4 pounds of fuel oil, 2.76 pounds of caprylic acid, and 0.14 pound of the kerosene-rosin solution, the following results were obtained:

Product	Weight percent	$CaCO_3$ percent assay	$CaCO_3$ percent recovery	Ratio of concentration
Feed	100.0	20.66	100.0	
Concentrate	17.8	94.93	81.8	5.62
Middling	2.6	68.83	8.7	
Tailing	79.6	2.47	9.5	

pH of pulp after mixing with reagents . . . 6.5.

Comparative test 7

A similar mixture of marble and sand was processed in the same manner and with the same reagents and proportions as in Example 15, except that lead nitrate was not employed. The following results were obtained, it being observed that while a concentrate assaying 95.43% in calcium carbonate was obtained, only 59.3% of the calcium carbonate originally employed was recovered.

Product	Weight percent	$CaCO_3$ percent assay	$CaCO_3$ percent recovery	Ratio of concentration
Feed	100.0	20.13	100.0	
Concentrate	12.5	95.43	59.3	8.00
Middling	6.0	83.54	24.9	
Tailing	81.5	3.90	15.8	

Example 18

A crude high-grade barite matrix from Cartersville, Georgia, was taken for the purpose of this example. A sample of this ore was ground and sized on a screen of 35 meshes to the lineal inch, and the oversize material reground to pass through the same screen, the total sample being then deslimed and made up into a thick pulp with water. This pulp was agitated in the mixer with 1 pound per ton of lead nitrate, 2.50 pounds per ton of fuel oil, 1.84 pounds per ton of caprylic acid, and 0.14 pound of the kerosene-rosin solution previously described. The pulp was then diluted and agitated in the flotation machine, a rougher concentrate being separated which, upon removal of the tailing, was again floated without further addition of reagents, yielding a final concentrate. The tailing of this cleaning is indicated as a middling in the following table:—

Product	Weight	$BaSO_4$ percent assay	SiO_2 percent	CO_2 percent	$BaSO_4$ percent recovery	Ratio of concentration
Feed	100.0	92.37	5.46		100.0	
Concentrate	5.2	95.90	0.94	0.30	5.4	19.23
Middling	62.5	95.48	2.56		64.6	
Tailing	32.3	85.76	11.79		30.0	

Example 19

The identical procedures of Example 18 were repeated on another sample of the same ore, but with the proportion of caprylic acid increased to 5.52 pounds per ton. The following results were obtained:

Product	Weight percent	$BaSO_4$ percent assay	SiO_2 percent	CO_2 percent	$BaSO_4$ percent recovery	Ratio of concentration
Feed	100.0	92.22	5.73		100.0	
Concentrate	75.2	95.04	3.12	0.25	77.4	1.33
Middling	23.2	87.97	9.62		22.1	
Tailing	1.6	24.14	69.72		0.5	

Comparative test 8

With the proportion of caprylic acid the same as in Example 19, still another sample of the same ore was processed in the same manner as in Example 18, but with no addition of lead nitrate. The following results were obtained, the particularly low recovery being observed:

Product	Weight percent	$BaSO_4$ percent assay	SiO_2 percent	CO_2 percent	$BaSO_4$ percent recovery	Ratio of concentration
Feed	100.0	91.90	5.73		100.0	
Concentrate	9.5	90.24	1.94	0.22	9.3	10.53
Middling	43.2	95.50	2.42		44.8	
Tailing	47.3	89.14	9.52		45.9	

Comparing the latter table with that of Example 18, it will be noted that one-third as much caprylic acid when used with lead nitrate gives 16% more barium sulphate recovery in a rougher con-

centrate of substantially the same grade than when lead nitrate is omitted.

Example 20

A synthetic mixture of approximately equal quantities of fluorspar and quartz, and of a particle size to pass through a screen of 28 meshes to the lineal inch, was made up with water to a pulp of 70% solids. This thick pulp was agitated in the mixer with 1 pound of lead nitrate, 2.46 pounds of fuel oil, 2.46 pounds of caprylic acid, and 0.14 pound of the same kerosene-rosin solution as already described. After this mixing operation, the pulp was diluted and agitated in the flotation machine, yielding a rougher concentrate. The tailing was removed, whereupon the rougher concentrate was refloated without further addition of reagents, yielding a final concentrate. The tailing of this cleaning is indicated as a middling in the following table:

Product	Weight percent	CaF_2 percent assay	SiO_2 percent	CaF_2 percent recovery	Ratio of concentration
Feed	100.0	55.99	42.73	100.0	
Concentrate	25.8	98.75	0.66	45.5	3.88
Middling	21.9	96.44	2.82	37.7	
Tailing	52.3	17.96	80.20	16.8	

pH of pulp after mixing with reagents . . . 5.2.

Comparative test 9

The identical procedures of Example 20 were repeated on a similar mixture of fluorspar and quartz, except that the use of lead nitrate was omitted, the same proportions of fuel oil, caprylic acid, and kerosene-rosin solution being employed. A concentrate and a middling were obtained each assaying about the same calcium fluoride content as in Example 20, but the total calcium fluoride recovery effected in both concentrate and middling was only 63.7% as compared to the 83.2% in Example 20.

Experiments carried out with the view to determine the effect of the order of addition of the reagents on grade of concentrate and recovery of values have shown that there is no general method of addition by which best results may be obtained in all cases. In this respect one metallic salt may behave differently from another, and in certain cases there may be several methods of addition that will insure most successful concentration. Thus, when concentrating a phosphate mineral and employing fuel oil, caprylic acid, lead nitrate, and caustic soda as reagents, three different procedures have been determined by the use of either one of which equal and highest results are obtainable. According to one of these alternatives, lead nitrate is first added to the pulp, and thereafter are added, in the order in which they appear, caustic soda, fuel oil, and caprylic acid. Another of these alternatives consists in first adding fuel oil to the pulp and thereafter, in the order in which they appear, caprylic acid, lead nitrate, and caustic soda. The third alternative consists in first adding lead nitrate and caustic soda as a mixture to the pulp and thereafter, in the order in which they appear, fuel oil, and caprylic acid. Employing copper sulphate instead of lead nitrate, only one method of addition has been found to be then capable of giving highest results, and it does not conform to any of the three when lead nitrate is employed, this method consisting in first adding fuel oil to the pulp and thereafter, in the order in which they appear, caprylic acid, caustic soda, and copper sulphate. Employing aluminum chloride as the metallic salt, again only one method of addition has been found to be capable of giving highest results, but in this instance it conforms to the first-mentioned of the three procedures possible when lead nitrate is employed, therefore consisting in first adding aluminum chloride to the pulp and thereafter, in the order in which they appear, caustic soda, fuel oil, and caprylic acid.

It is thus apparent that the invention is not broadly limited to any specific method of addition of the reagents to the pulp, the method to be adopted which will insure most successful concentration in each individual case being of course capable of determination by simple experimentation. Moreover, while it is true that in certain cases highest results are obtained by following certain procedures of addition, yet it is not essential that these procedures be followed in order that satisfactory concentration may be effected.

It is also desired to have it understood that the invention is not broadly limited to any specific proportions of the reagents, the proportions suitable for most successful concentration being also capable of determination by simple experimentation in practice. None of the procedures described in detail herein should be interpreted as limiting the invention, these procedures being capable of being modified in many ways without departing from the spirit of the invention.

What is claimed is:

1. The process of concentrating non-metallic minerals from ores containing them in association with silicious matter, which comprises agitating a pulp of suitably divided particles of such a non-metallic mineral ore in the presence of a substantially insoluble and unsaponifiable oil, a fatty acid of less than thirteen carbon atoms to cooperate with said oil in effecting collection of the non-metallic mineral values, and an activating agent causing said fatty acid to have a preferential affinity for said values, said activating agent consisting of a soluble salt of a metal whose oxide does not exert an alkaline reaction when added to water, and separating a concentrate relatively rich in said values and relatively poor in silicious matter.

2. The process of concentrating non-metallic minerals from ores containing them in association with silicious matter, which comprises agitating a pulp of suitably divided particles of such a non-metallic mineral ore in the presence of a substantially insoluble and unsaponifiable oil, a fatty acid soap of less than thirteen carbon atoms to cooperate with said oil in effecting collection of the non-metallic mineral values, and an activating agent causing said fatty acid soap to have a preferential affinity for said values, said activating agent consisting of a soluble salt of a metal whose oxide does not exert an alkaline reaction when added to water, and separating a concentrate relatively rich in said values and relatively poor in silicious matter.

3. The process of concentrating non-metallic minerals from ores containing them in association with silicious matter, which comprises agitating a pulp of suitably divided particles of such a non-metallic mineral ore in the presence of a substantially insoluble and unsaponifiable oil, a fatty acid of less than thirteen carbon atoms to cooperate with said oil in effecting collection of the non-metallic mineral values, and an activating agent causing said fatty acid to have a preferential affinity for said values, said activating agent consisting of a soluble salt of a metal whose

oxide does not exert an alkaline reaction when added to water, and subjecting the pulp to froth flotation so as to separate a float relatively rich in said values and relatively poor in silicious matter.

4. The process of concentrating non-metallic minerals from ores containing them in association with silicious matter, which comprises agitating a pulp of suitably divided particles of such a non-metallic mineral ore in the presence of a substantially insoluble and unsaponifiable oil, a fatty acid soap of less than thirteen carbon atoms to cooperate with said oil in effecting collection of the non-metallic mineral values, and an activating agent causing said fatty acid soap to have a preferential affinity for said values, said activating agent consisting of a soluble salt of a metal whose oxide does not exert an alkaline reaction when added to water, and subjecting the pulp to froth flotation so as to separate a float relatively rich in said values and relatively poor in silicious matter.

5. The process of concentrating non-metallic minerals from ores containing them in association with silicious matter, which comprises agitating a pulp of suitably divided particles of such a non-metallic mineral ore in the presence of a substantially insoluble and unsaponifiable oil, a fatty acid of less than thirteen carbon atoms to cooperate with said oil in effecting collection of the non-metallic mineral values, an activating agent causing said fatty acid to have a preferential affinity for said values, and an alkali, said activating agent consisting of a soluble salt of a metal whose oxide does not exert an alkaline reaction when added to water, and separating a concentrate relatively rich in said values and relatively poor in silicious matter.

6. The process of concentrating non-metallic minerals from ores containing them in association with silicious matter, which comprises agitating a pulp of suitably divided particles of such a non-metallic mineral ore in the presence of a substantially insoluble and unsaponifiable oil, a fatty acid soap of less than thirteen carbon atoms to cooperate with said oil in effecting collection of the non-metallic mineral values, an activating agent causing said fatty acid soap to have a preferential affinity for said values, and an alkali, said activating agent consisting of a soluble salt of a metal whose oxide does not exert an alkaline reaction when added to water, and separating a concentrate relatively rich in said values and relatively poor in silicious matter.

7. The process of concentrating non-metallic minerals from ores containing them in association with silicious matter, which comprises agitating a pulp of suitably divided particles of such a non-metallic mineral ore in the presence of a substantially insoluble and unsaponifiable oil, caprylic acid to cooperate with said oil in effecting collection of the non-metallic mineral values, and an activating agent causing the caprylic acid to have a preferential affinity for said values, said activating agent consisting of lead nitrate, and separating a concentrate relatively rich in said values and relatively poor in silicious matter.

8. The process of concentrating non-metallic minerals from ores containing them in association with silicious matter, which comprises agitating a pulp of suitably divided particles of such a non-metallic mineral ore in the presence of a substantially insoluble and unsaponifiable oil, caprylic acid to cooperate with said oil in effecting collection of the non-metallic mineral values, an activating agent causing the caprylic acid to have a preferential affinity for said values, and caustic soda, said activating agent consisting of lead nitrate, and separating a concentrate relatively rich in said values and relatively poor in silicious matter.

9. The process of concentrating phosphate minerals from ores containing them in association with silicious matter, which comprises agitating a pulp of suitably divided particles of such a phosphate ore in the presence of a substantially insoluble and unsaponifiable oil, a fatty acid of less than thirteen carbon atoms to cooperate with said oil in effecting collection of the phosphate values, and an activating agent causing said fatty acid to have a preferential affinity for said values, said activating agent consisting of a soluble salt of a metal whose oxide does not exert an alkaline reaction when added to water, and separating a concentrate relatively rich in said values and relatively poor in silicious matter.

10. The process of concentrating phosphate minerals from ores containing them in association with silicious matter, which comprises agitating a pulp of suitably divided particles of such a phosphate ore in the presence of a substantially insoluble and unsaponifiable oil, a fatty acid soap of less than thirteen carbon atoms to cooperate with said oil in effecting collection of the phosphate values, and an activating agent causing said fatty acid soap to have a preferential affinity for said values, said activating agent consisting of a soluble salt of a metal whose oxide does not exert an alkaline reaction when added to water, and separating a concentrate relatively rich in said values and relatively poor in silicious matter.

11. The process of concentrating calcite from ores containing it in association with silicious matter, which comprises agitating a pulp of suitably divided particles of such a calcite ore in the presence of a substantially insoluble and unsaponifiable oil, a fatty acid of less than thirteen carbon atoms to cooperate with said oil in effecting collection of the calcite values, and an activating agent causing said fatty acid to have a preferential affinity for said values, said activating agent consisting of a soluble salt of a metal whose oxide does not exert an alkaline reaction when added to water, and separating a concentrate relatively rich in said values and relatively poor in silicious matter.

12. The process of concentrating calcite from ores containing it in association with silicious matter, which comprises agitating a pulp of suitably divided particles of such a calcite ore in the presence of a substantially insoluble and unsaponifiable oil, a fatty acid soap of less than thirteen carbon atoms to cooperate with said oil in effecting collection of the calcite values, and an activating agent causing said fatty acid soap to have a preferential affinity for said values, said activating agent consisting of a soluble salt of a metal whose oxide does not exert an alkaline reaction when added to water, and separating a concentrate relatively rich in said values and relatively poor in silicious matter.

13. The process of concentrating barite from ores containing it in association with silicious matter, which comprises agitating a pulp of suitably divided particles of such a barite ore in the presence of a substantially insoluble and unsaponifiable oil, a fatty acid of less than thirteen carbon atoms to cooperate with said oil in effect-

ing collection of the barite values, and an activating agent causing said fatty acid to have a preferential affinity for said values, said activating agent consisting of a soluble salt of a metal whose oxide does not exert an alkaline reaction when added to water, and separating a concentrate relatively rich in said values and relatively poor in silicious matter.

14. The process of concentrating barite from ores containing it in association with silicious matter, which comprises agitating a pulp of suitably divided particles of such a barite ore in the presence of a substantially insoluble and unsaponifiable oil, a fatty acid soap of less than thirteen carbon atoms to cooperate with said oil in effecting collection of the barite values, and an activating agent causing said fatty acid soap to have a preferential affinity for said values, said activating agent consisting of a soluble salt of a metal whose oxide does not exert an alkaline reaction when added to water, and separating a concentrate relatively rich in said values and relatively poor in silicious matter.

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