Patented Jan. 18, 1938 2,105,807

UNITED STATES PATENT OFFICE

2,105,807

DIFFERENTIAL CONCENTRATION OF NON-METALLIC MINERALS

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No Drawing. Application February 15, 1933, Serial No. 656,887

5 Claims. (Cl. 209—167)

The present invention relates in general to a concentration of non-metallic minerals from their ores, and more particularly to a process of differential concentration applicable to ores of the class consisting of phosphate-calcite-silica ores, fluorspar-calcite-silica ores, and fluorspar-barite-silica ores.

In accordance with the invention, a pulp of the ore to undergo treatment is agitated in the presence of a fraction of one per cent of a free fatty acid and a fraction of one per cent of a substantially insoluble and unsaponifiable oil, without added agents capable of substantially affecting its pH value, the desired concentrate being subsequently separated by froth flotation or other manner known in the art. By this procedure omitting the use of alkali or other pH-affecting substance, it has been found possible to differentially concentrate one non-metallic mineral with respect to both another non-metallic mineral and siliceous gangue. Either phosphate or fluorspar can thus be separated from both calcite and silica; and fluorspar can be separated from both barite and calcite. It has also been found possible to separate calcite from silica by the process of the present invention.

In order that the best results may be obtained by the process of the present invention, it has been found advisable to limit rather narrowly the size of the ore particles subjected to the concentrating operation, as well as to largely deslime the ore pulp prior to its admixture with the reagents.

In preparing the ore for treatment by the process of the present invention, it is ordinarily first subjected to a preliminary grinding operation and is 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.

The procedures herein described in detail are flotation procedures, but in many cases parallel results may be obtained by effecting the concentrating operation on a shaking table, the concentrate coming off at the side of the table as if it were the lighter material and the tailing at the end as if it were the heavier material.

Other features and advantages will appear in connection with the examples described below.

Ground crude fluorspar ore from Hillside Fluorspar Mines, Rosiclare, Illinois, with a gangue principally of calcium carbonate, but containing some silica, was screened through 35-mesh, the oversize being ground to pass 35-mesh and added to the undersize. The resulting mixture was agitated in a relatively large amount of water to facilitate removal of the slimes, the agitation being conducted in a subaeration-flotation laboratory testing machine, and the slimes removed by decantation. The deslimed pulp was thickened to contain 72% solids, and then there was added during further agitation 0.28 pound of a solution of fish-oil fatty acids in an equal weight of fuel oil, enough more fuel oil to make a total of one pound of fuel oil, and 0.14 pound of a frothing agent consisting of three parts of crude rosin residue dissolved in one part of kerosene oil, all per ton of dry material present. The pulp showed a pH value of 7.4.

After three minutes agitation the thick pulp was then diluted and agitated in the machine for the production of a froth over a period of three minutes, a rougher float concentrate being separated. The tailing was discarded and the rougher concentrate cleaned four times by reagitation without added agents. The tailing from each cleaning was assayed separately, but constituted a middling which, in commercial operations, could be returned to the flotation cells for additional recovery of values therefrom.

The results are shown in the following table:

	Percent wt.	Percent CaF_2	Percent SiO_2	Percent $CaCO_3$	CaF_2 recovered
Feed	100.0	52.76	9.11	37.37	-------
Finished conc.	32.3	98.38	0.18	0.88	60.4
4th midd.	2.4	94.48	0.16	5.05	4.3
3rd midd.	3.5	87.54	0.00	12.24	5.7
1st and 2d midd.	16.4	51.60	0.51	47.48	16.
Tails.	35.	10.02	23.42	65.57	6.8
Slimes	10.4	34.64	7.45	55.29	6.8

Other fatty acids, such as oleic acid, have also been found useful as reagents.

Fluorspar carrying more than 2% of silica yields so much fluosilicic acid as to be useless for the production of hydrofluoric acid. As a result of this and other reasons, fluorspar containing upwards of 98% of calcium fluoride commands at least double the price of the spar carrying only 96% of calcium fluoride. It has hitherto proved impossible to produce a 98% fluorspar from the relatively impure material generally mined. According to the present invention, by a suitable choice of reagents it has proved possible to obtain a satisfactory so-called acid spar, as shown by the example given above.

A phosphate ore from North Africa, known as Constantine rock, with a gangue largely of calcium carbonate, was raised from uncommercial grade to commercial grade by flotation with fuel oil and a soap-forming fatty acid. The ore was ground to pass a 35-mesh sieve, and deslimed by agitation with water and decanting the slimes. The wet deslimed material, in a pulp containing 72% of solids, was mixed with one pound of fuel

oil, one pound of crude oleic acid (red oil) and 0.14 pound of the kerosene-rosin solution above identified, all per ton of dry material present. The thick pulp was diluted and agitated in the flotation machine, and a rougher froth concentrate was separated. Upon removal of the tailing, the rougher concentrate was put back into the machine and reagitated without added agents for two minutes, and thereafter a finished or cleaned concentrate was separated. The results are shown in the following table, in which the tailing from the cleaning operation is designated as a middling.

	Percent Wt.	B. P. L.	$CaCO_3$	Ins.	B. P. L. recovery	$CaCO_3$ recovery
Feed	100.	55.58	25.3	6.25		
Conc	57.8	69.70	14.3	0.99	72.6	32.9
Midd	12.6	58.55	26.7	1.42	13.3	13.6
Tail	5.9	17.55	65.2	15.53	1.9	15.4
Slime	23.7	28.92	40.6	19.28	12.2	38.1

It was found that better results were sometimes obtained when solid fatty acids of fish oil, dissolved in part of the fuel oil, were substituted for the oleic acid.

By slightly varying conditions, it was found possible to float limestone away from silica. A mixture consisting of one part Ocala limestone, largely calcite, and about three parts of the tailings from a mill of the Phosphate Recovery Corporation treating Florida pebble phosphate, was screened through 24-mesh, and the oversize ground to the same mesh and added to the undersize. The resulting material was deslimed by agitation with water and decantation, and thickened to contain 70% solids. The thick pulp was agitated for three minutes with 2 pounds of fuel oil and 0.53 pound of crude oleic acid, both per ton of dry material present, the pH value of the pulp being 7.8. No bubble-forming agent or other added flotation agent was found necessary. The oiled pulp was diluted and frothed in the flotation machine for one minute, during which a calcium carbonate float was separated. The results are shown in the following table:

	Percent wt.	Assay $CaCO_3$	Ins.	$CaCO_3$ recovery
Feed	100	23.04		
Conc	22	90.64	4.16	86.5
Tail	78	4		13.5

The tailings were evidently mostly silica, which was the principal ingredient of the phosphate tailings put into the original mixture.

Another lot of the same Constantine ore was ground to pass 65-mesh, and deslimed by agitation with water and decantation. The deslimed coarse material in a dilute pulp was agitated with 1.20 pounds of sodium oleate and 0.1 pound of pine oil, both per ton of solids, and a carbonate float concentrate was first removed. The sodium oleate was of course a soap, produced from fatty acid and alkali. The tailing remaining was thickened and in this state agitated with 1 pound of fuel oil, 0.5 pound of crude oleic acid, and 0.14 pound of the kerosene-rosin solution above identified, all per ton of original solids in the deslimed pulp, whereupon it was diluted and a phosphate float concentrate removed.

The detailed results and assays are shown in the following table:

	Percent wt.	B. P. L.	Ins.	CO_2	B. P. L. recovery	CO_2 recovery
Feed	100.	54.85	6.41	11.57		
$CaCO_3$ conc	5.8	16.57	1.21	35.35	1.8	18.2
B. P. L. conc	62.5	89.40	1.09	6.16	79.1	33.3
Tail	5.3	35.55	15.14	17.76	3.4	8.1
Slime	26.4	32.55	18.40	17.69	15.7	40.4
Flotation feeds for $CaCO_3$	73.6	63.83	2.11	9.38	84.3	89.6
For phos	67.8	65.70	2.18	7.08	82.5	41.4

A lot of phosphate ore from Consolidated Mining and Smelting Co., of Trail, B. C., had to be ground to pass 200-mesh to free the silica gangue. The ore was then treated to remove part of a calcium carbonate gangue, whereupon a phosphate concentrate was separated. To effect these results the ground ore was deslimed by agitation with water and decantation. The deslimed material in the state of a thick pulp was agitated with 2.5 pounds of fuel oil, 0.84 pound of crude oleic acid, and 0.28 pound of Tarol No. 2 (a mixture of 75% steam distilled pine oil and 25% rosin oil by volume), all per ton of deslimed solids. The material thus conditioned was diluted and frothed to separate a small weight concentrate, richer in the carbonate and poorer in the phosphate. The remaining pulp was thickened and agitated with 0.2 pound of caustic soda, 4 pounds of fuel oil, 0.64 pound of crude oleic acid, and 0.14 pound of the frothing agent above referred to as Tarol No. 2, all per ton of solids, whereupon it was diluted, and a phosphate float concentrate separated.

The detailed results and assays are shown in the following table:

	Percent wt.	B. P. L.	Ins.	CO_2	B. P. L. recovery	CO_2 recovery
Feed	100.	51.75	17.20	7.42		
CO_3 conc	2.9	56.64		8.76	3.2	3.4
Phos. conc	26.9	69.50	6.10	4.94	36.1	17.9
Tail	5.1	38.41		5.05	3.8	3.5
Slime	65.1	45.24		8.57	56.9	75.2
Flotation feeds, for CO_3	34.9	63.90		5.28	43.1	24.8
For phos	32.	64.56		4.96	30.9	21.4

The foregoing procedure raised the B. P. L. content to a grade of commercial utility.

By a somewhat modified procedure fluorspar has been separated from barite. A table feed fluorspar ore carrying calcium carbonate, from Hillside Fluorspar Mines, Rosiclare, Ill., was mixed with an equal weight of deslimed barite ore from Paga Mining Co., Cartersville, Ga., and the mixture ground to pass 35-mesh. The ground material was deslimed by agitation for a three-minute period with water and decantation until all the slimes seemed to have been removed. The results of the desliming operation are shown in the following table:

	Percent wt.	Assays				Percent recovery	
		CaF_2	SiO_2	$CaCO_3$	$BaSO_4$	CaF_2	$BaSO_4$
Feed	100.	26.36	29.69	19.31	22.43	100.	100.
Deslimed material	86.8	28.18	29.79	18.79	21.46	92.8	83.1
Slime	12.2	14.40	28.98	22.74	28.8	7.2	16.9

The pulp of deslimed material was thickened

to 72% solids and agitated with 0.5 pound of fuel oil, 0.19 pound of fish-oil fatty acids, and 0.14 pound of the kerosene-rosin solution above identified, all per ton of flotation feed, whereupon it was diluted and a fluorspar float concentrate separated. The fluorspar rougher concentrate thus obtained was refloated four times, in each instance without the addition of further agents, to yield a finished concentrate of over 98% purity, four cleaner tailings constituting middlings being obtained which, in commercial practice, would be retreated to yield further recoveries. The fluorspar finished concentrate contained over 86% of the fluorspar in the original material. The rougher tailing resulting from the first float was rethickened, agitated with 0.32 pound of caustic soda, 2 pounds of fuel oil, 0.45 pound of fish-oil fatty acid, and 0.14 pound of the kerosene-rosin solution above identified, all per ton of solids present, whereupon it was diluted and agitated to yield a barite rougher concentrate, a final tailing being also obtained. The barite rougher concentrate was refloated twice without added agents to yield a finished concentrate, as well as two cleaner tailings constituting middlings. The results are shown in the following table:

Product	Percent wt.	Assays				Percent of recovery	
		CaF_2	SiO_2	$CaCO_3$	$BaSO_4$	CaF_2	$BaSO_4$
Feed	100.0	28.18	29.79	18.79	21.46	100.0	100.0
CaF_2 Conc.	26.6	98.28	0.08	1.26	0.10	92.8	0.1
Midd. #4	0.4	66.37	0.42	27.37	4.54	1.0	0.1
Midd. #3	1.0	50.19	0.35	33.63	15.43	1.8	0.7
Midd. #2	2.9	21.19	1.05	41.67	34.42	2.2	4.7
Midd. #1	8.9	4.58	4.76	41.65	46.96	1.5	19.5
$BaSO_4$ Conc.	34.6	0.30	14.65	37.34	46.00	0.3	74.2
Midd. #2	3.4	0.50	91.90	0.92	3.10	0.1	0.5
Midd. #1	5.6	0.26	93.64	0.95	0.94	0.0	0.2
Tail	16.6	0.45	95.72	0.52	0.03	0.3	0.0

The barite concentrate thus obtained may be further treated to raise its grade. It will be noted that 86.1% of the original fluorspar was recovered in the form of a concentrate carrying 98.28% of fluorspar and conforming to the most exacting commercial demands.

Having thus described certain embodiments of the invention, what is claimed is:

1. A process of differential concentration which comprises agitating a pulp, nearly free from slimes, of suitably divided particles of an ore of the class consisting of phosphate-calcite-silica ores, fluorspar-calcite-silica ores, and fluorspar-barite-silica ores, in the presence of a fraction of one per cent of a free fatty acid and a fraction of one per cent of a substantially insoluble and unsaponifiable oil, without added alkali or other agent capable of substantially affecting its pH value; and separating in the case of a phosphate-calcite-silica ore a concentrate relatively rich in phosphate and relatively poor in calcite-silica, in the case of a fluorspar-calcite-silica ore a concentrate relatively rich in fluorspar and relatively poor in calcite-silica, and in the case of a fluorspar-barite-silica ore a concentrate relatively rich in fluorspar and relatively poor in barite-silica.

2. A process of differential concentration which comprises agitating a pulp, nearly free from slimes, of suitably divided particles of an ore of the class consisting of phosphate-calcite-silica ores, fluorspar-calcite-silica ores, and fluorspar-barite-silica ores, in the presence of a fraction of one per cent of a free fatty acid and a fracion of one per cent of a substantially insoluble and unsaponifiable oil, without added alkali or other agent capable of substantially affecting its pH value; and separating by froth flotation in the case of a phosphate-calcite-silica ore a concentrate relatively rich in phosphate and relatively poor in calcite-silica, in the case of a fluorspar-calcite-silica ore a concentrate relatively rich in fluorspar and relatively poor in calcite-silica, and in the case of a fluorspar-barite-silica ore a concentrate relatively rich in fluorspar and relatively poor in barite-silica.

3. A process of differential concentration which comprises agitating a pulp, nearly free from slimes, of suitably divided particles of an ore of the class consisting of phosphate-calcite-silica ores, fluorspar-calcite-silica ores, and fluorspar-barite-silica ores, in the presence of a fraction of one per cent of a free fatty acid and a fraction of one per cent of a substantially insoluble and unsaponifiable oil, without added alkali or other agent capable of substantially affecting its pH value, the fatty acid being carried in at least a part of the oil; and separating in the case of a phosphate-calcite-silica ore a concentrate relatively rich in phosphate and relatively poor in calcite-silica, in the case of a fluorspar-calcite-silica ore a concentrate relatively rich in fluorspar and relatively poor in calcite-silica, and in the case of a fluorspar-barite-silica ore a concentrate relatively rich in fluorspar and relatively poor in barite-silica.

4. A process of differential concentration comprising agitating a pulp, nearly free from slimes, of suitably divided particles of a phosphate-calcite-silica ore in the presence of a fraction of one per cent of a fatty acid soap and a fraction of one per cent of a substantially insoluble and unsaponifiable oil; separating a float concentrate relatively rich in calcite and relatively poor in phosphate-silica; dewatering the remaining pulp; agitating the dewatered pulp in the presence of a fraction of one per cent of a free fatty acid and a fraction of one per cent of a substantially insoluble and unsaponifiable oil, without added alkali or other agent capable of substantially affecting its pH value; and separating a float concentrate relatively rich in phosphate and relatively poor in calcite-silica.

5. A process of differential concentration comprising agitating a pulp, nearly free from slimes, of suitably divided particles of a phosphate-calcite-silica ore in the presence of a fraction of one per cent of a free fatty acid and a fraction of one per cent of a substantially insoluble and unsaponifiable oil, without added alkali or other agent capable of substantially affecting its pH value; separating a small-weight float concentrate richer in calcite and poorer in phosphate; dewatering the remaining pulp; agitating the dewatered pulp in the presence of a fraction of one per cent of a fatty acid soap and a fraction of one per cent of a substantially insoluble and unsaponifiable oil; and separating a float concentrate relatively rich in phosphate and relatively poor in calcite-silica.

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