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Jones et al.

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[54] **FLOTATION-BENEFICIATION OF PHOSPHATE ORES**

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 149,859, June 3, 1971, abandoned.

[52] **U.S. Cl.** **209/166,** 209/10

[51] **Int. Cl.** **B03d 1/02**

[58] **Field of Search** 209/5, 166, 10; 252/61; 210/54

[56] **References Cited**

UNITED STATES PATENTS

2,740,522	4/1956	Aimone	209/166
3,138,550	6/1964	Woolery	209/166 X
3,321,649	5/1967	DeBenedictis	209/166 X
3,575,868	4/1971	Galvin	210/54 X
3,635,857	1/1972	Restaino	210/54 X
3,669,915	6/1972	Jones	209/5 X

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[57] **ABSTRACT**

An improved method of separating minerals from phosphate ores is described. The addition of silica depressants to flotation slurries substantially increases the efficiency of mineral separation and thereby reduces the number of flotation steps required to obtain a good yield of ore having the desired mineral concentration.

5 Claims, No Drawings

FLOTATION-BENEFICIATION OF PHOSPHATE ORES

This is a continuation-in-part application of Ser. No. 149,859 now abandoned filed June 3, 1971.

BACKGROUND OF THE INVENTION

This invention relates to an improvement in the flotationbeneficiation of phosphate ores containing a substantial quantity of siliceous materials.

Crude ores are first comminuted, then subjected to various physical methods of concentration to separate valuable minerals from the waste materials (i.e., gangue) which usually consist of clay, silicas, and other minerals having little or no value.

Much of the gangue can be removed by water washing, screening, and gravity separations, but in most beneficiation processes of siliceous ores, the final and most important step is flotation.

Phosphate ore deposits, particularly those in Florida, are subsurface pockets of phosphate ore (matrix) which consist mainly of about one-third each of sand, clay, and calcium fluorapatite. The phosphate contained in the matrix ranges in size from ¾-inch "pebbles" down to minus 150 mesh particles and generally is in the form of discrete grains with rather small amounts of included quartz sand. The free silica is normally mainly minus 20 mesh. The type and consistency of the clay varies and is mixed but generally is distributed throughout the matrix.

The nature of the phosphate pebble and the size of the silica lends the matrix to an effective beneficiation process which consists of the following main steps after mining of the ore:

1. Washing--to remove clay.
2. Screening--to remove +16 mesh pebble (generally relatively high-grade material).
3. Flotation--to recover −16 to +150 mesh phosphate from silica and clay.

Pebble rock removed by screening varies in grade from ore body to ore body but generally ranges from 65–75 percent BPL (bone phosphate of lime or tricalcium phosphate). Constituting about 10 percent of the matrix, pebble phosphate is marketable without further processing.

The balance of the material remaining from the matrix is chiefly fluorapatite and sand of varying and similar particle sizes which precludes separation by physical means. An elegant and now widely used method of separating the two involves twostage flotation. In the first flotation stage, flotation reagents such as tall oil fatty acids (anionic collectors or frothers), and No. 5 fuel oil (activator or extender to aid in froth control) are used to float phosphate from the sand tailings (nonfloat). Anionic flotation of phosphates is not specific, especially under conditions providing high BPL recovery required by process economics, and the float concentrate normally contains 10–15 percent silica. The second flotation stage further reduces the amount of silica by treating the float concentrate from the first stage with a mineral acid to remove the flotation reagents, and refloating the concentrate in the presence of an amine collector. The final float concentrate from this two-step flotation usually contains over 75 percent BPL, less than 5 percent acid insolubles (silica), and a BPL recovery of from about 90 to 95 percent.

Dual flotation in the manner described is obviously more expensive than single-stage flotation because of additional equipment, reagents, etc. It is the method of choice, however, since single-stage flotation cannot provide marketable grade phosphate concomitant with satisfactory BPL recovery. Preventing complete separation with good BPL recovery is the lack of specificity of the anionic collector for phosphate particles. Search for a more specific collector or for a selective depressant for silica (e.g., U.S. Pat. Nos. 2,740,522 and 3,321,649) antedates development of the two-stage flotation with only limited success as evidenced by the continuing use of the twostage process in phosphate production.

It is the object of this invention to provide an improvement in the efficiency of the flotation process and thereby reduce the number of flotation steps.

In accordance with the above-stated object, we have discovered in a method of flotation-beneficiation of phosphate ores which normally includes the steps of:

a. floating the ore in the presence of flotation reagents;
b. collecting the first float;
c. removing the flotation reagents from the first float;
d. floating the first float in the presence of an amine collector; and
e. collecting the second float;

an improvement by which flotation is accomplished in a single stage, comprising the steps of:

a. froth floating phosphate ore in the presence of flotation reagents and from 0.025 to 0.2 pound/ton of ore of a graft polymer comprised of a starch substrate onto which is grafted a member selected from the group consisting of a polymerized quaternary ammonium derivative of aminoalkyl methacrylate and mixtures of a polymerized quaternary ammonium derivative of aminoalkyl methacrylate with polyacrylamide; and
b. collecting, filtering, and drying the resulting float.

The potential importance of this discovery cannot be estimated precisely. However, a rough estimate can be determined assuming annual Florida pebble phosphate production volume of about 10 million tons. Approximately 7 million tons of this is produced by flotation processes which consume an estimated 35 million pounds of flotation reagents annually. Use of starch graft copolymer as described herein would replace approximately 15 million pounds of flotation reagent (specifically, sulfuric acid and amine collector) with a graft polymer consumption of 0.35–0.70 million pounds. This it should be noted pertains only to domestic phosphate production in Florida.

DETAILED DESCRIPTION OF THE INVENTION

In a comprehensive review J. C. Arthur, Jr. describes the state of the art of graft polymerization onto polysaccharide backbones (Advances in Macromolecular Chemistry, Vol. 2, Academic Press, London and New York, 1970). Celluloses, starches, modified starches, and starch derivatives are included in the list of polysaccharides used as substrates onto which many vinyl-type monomers have been grafted. In most methods of producing graft polymers, the reaction is initiated by forming free radical sites on the substrate. This is accomplished with initiators such as ceric ion, ferrous ion-hydrogen peroxide, and irradiation.

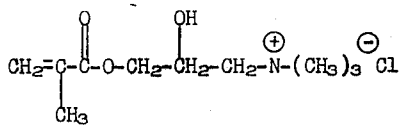
Graft polymers of starch and quaternary ammonium derivatives of aminoalkyl methacrylate have been shown to flocculate silica suspended in water, but set-

tling times of at least one-half hour were required to remove from 45 to 85 percent of the silica from a 1 percent aqueous dispersion (U.S. Pat. No. 3,669,915). We were surprised, therefore, when the instant compositions, used in the highly agitated conditions found in a flotation cell, provided float concentrates having BPL concentrations and recoveries sufficient to completely eliminate the necessity for the amine flotation step.

In preparing the instant compositions gamma irradiation is the preferred polymerization initiator and starch the preferred substrate. This combination is simple and usually results in clean, easy-to-recover products. Chemical initiators (e.g., Ce^{+4}, Fe^{+2}-H_2O_2) and other irradiation initiators (e.g., electron, ultraviolet) are equivalent to gamma irradiation in the method, and any starch such as that from corn, rice, sorghum, etc. is an equivalent substrate to the wheat starch described in the examples.

In the preferred embodiments (Example 1, infra), wheat starch is irradiated with a total dosage of 5.0 megarad of gamma radiation with a cobalt 60 source. It has been previously determined that a dose of 5.0 megarad of gamma radiation gave the maximum concentration of trapped free radicals [Reyes et al., J. Polym. Sci. 23: 401-408 (1968)]. The irradiated starch, under a nitrogen atmosphere, is then brought in contact with a solution of monomer and allowed to react for times sufficient to obtain maximum grafting. Reaction temperatures of between 25°–30° C. are preferred because higher temperatures cause the starch to swell and produce graft polymers that are difficult to recover.

The quaternary ammonium derivative of aminoalkyl methacrylate monomer which was selected as a representative example has the structure shown below:



This monomer, 2-hydroxy-3-methacryloyloxypropyltrimethylammonium chloride, is to be known herein as I. The acrylamide comonomer is to be known as III. The starch graft polymers will be designated as "st-g-poly(I)" and "st-g-poly(I-co-III)" according to the method described by Battaerd and Tregear, *Graft Polymers*, Interscience Publishers, New York, New York, pages 14–16.

To estimate the effectiveness of the starch graft polymers as silica depressants, a series of flotation runs were made with sand and a fatty acid amine collector (a good flotation aid for sand), Example 2, infra. The results show that flotation of the sand is significantly depressed by the addition, at 0.25 pound/ton (of sand), of a graft polymer containing less than 2 percent poly(I) and less than 5 percent poly(III). This particular product (reaction No. 4, Table 1) contained chlorine and nitrogen at levels too low for accurate determination of polymer content.

Flotation studies on Florida phosphate ore were carried out in a Denver Laboratory flotation cell. Examples 3 through 6 indicate procedures valuable for determining the optimum conditions of parameters such as addition levels for flotation reagents (e.g., collectors, activators, extenders, or depressants), order of addition, and effects of additives on each other. The preferred conditions for the particular flotation system and phosphate ore discussed herein are elaborated in Example 7. The addition level for the graft polymers is from 0.025 to about 0.2 pound/ton. However, the preferred addition level is from 0.025 to 0.05 pound/ton. The preferred polymer content is from about 2.5 to 15 percent by weight of poly(I) in st-g-poly(I) and from about 2 to 11 percent by weight poly(I) and 5 to 20 percent by weight poly(III) in st-g-poly(I-co-III).

EXAMPLE 1

Powdered wheat starch (100 g.; 9.8 percent moisture; 0.56 equivalent) was irradiated under a nitrogen atmosphere in a cobalt 60 source for 330 minutes at a dose rate of 0.91 megarad/hour (total dosage 5.0 megarad) transferred to a reaction flask containing a nitrogen-prepurged aqueous solution of monomer (for reactions of I, 475 ml. H_2O used; reaction with I and III, 550 ml. H_2O used). The reaction was allowed to proceed for 2 hours at 25°–30° C. under a nitrogen atmosphere. The product was isolated by filtration after dilution of the reaction mixture with two volumes of isopropanol, washed successively with isopropanol and acetone, and dried 16 hours in vacuo at 40° C. The products were analyzed for nitrogen, chlorine, and moisture. These values were used to calculate graft content and graft composition, Table 1.

Table 1

Reaction No.	Vinyl monomer, g		Product yield, g.	Nitrogen content, %	% Monomer in product	
	I	III			I	III
1	9.10	...	102	0.147	2.5	...
2	18.20	...	104	0.41	6.9	...
3	36.4	...	112	0.89	14.9	...
4	1.82	5.0	101	0.31	...[1]	...[1]
5	18.2	50.0	125	4.55	10.8	19.8 19.8

[1] Nitrogen and chlorine values too low for accurate estimation.

EXAMPLE 2

Screening studies of products as silica depressants were conducted as follows: A suspension of 30–60 mesh sand (washed but unfired) in water was conditioned (mixed) successively with depressant and collector (each for 4 minutes) and floated by subaeration with a stream of compressed air for 2 minutes. The overflow was collected, filtered to recover floated sand, dried, and weighed, Table 2. Proportions used were 40 g. sand, 360 ml. tap water, 5.0 ml. depressant (0.10 percent solution), and 2.0 ml. of a fatty amine collector (Alamine 26 acetate; 1.0 percent aqueous solution).

Table 2

Additive	Additive level, lb./ton	Amount floated, g.	% Sand depressed
1[1]	0.25	4.04	89.9
2[1]	0.25	0.18	99.5
4[1]	0.25	12.7	68.1
5[1]	0.25	0.50	98.8
Wheat starch	0.25	28.7	27.7
Cationic starch	0.25	1.03	97.4
Cationic polyacrylamide	0.25	0.49	98.8
Blank	...	39.7	...

[1] Run no. from Table 1.

EXAMPLE 3

Flotation studies with phosphate ore were conducted in a Denver Laboratory flotation cell using 1.0-kg. samples (dry weight) of deslimed, flotation grade (16–55 mesh) ore (35.7 percent BPL and 56.5 percent acid insolubles) preconditioned at 70 percent solids with flotation reagents in a drill-press conditioning cell. Flotation reagents--1.14 pounds/ton of ore of tall oil fatty acid (collector) and No. 5 fuel oil (activator)--were added as a 1:1 mixture after addition of caustic to pH of 9. Depressants were added as 0.10 percent dispersions with and before addition of flotation reagents. Overflow and tailing fractions were recovered by filtration, dried, and weighed. Portions of each were analyzed for phosphorous pentoxide and hydrochloric acid insolubles and results reported as BPL and acid insolubles content, Table 3.

EXAMPLE 4

Flotation studies were run as described in Example 3, except no graft polymer was added and the collector (tall oil fatty acids) was added as a 1:1 mixture with No. 5 fuel oil at various addition levels. For analyses, see Table 4.

EXAMPLE 5

Flotation studies were run as described in Example 3, except that the graft polymer from Run No. 5, Table 1, was added prior to the collector in various levels. The collector and activator were added at a 1.14-pound/ton level in each run. For analyses, see Table 5.

Table 3

Run No.	Flotation conditions	Flotation product	Yield, %	Analyses, % BPL	Analyses, % Insols	% BPL recovery
1	Blank	Float	51.2	71.5	11.8	92.2
		Tails	48.8	6.3	90.5	...
2	Graft polymer[1] added with flotation reagents	Float	50.0	72.2	10.5	89.9
		Tails	50.0	8.1	88.2	...
3	Graft polymer[1] added before flotation reagents	Float	41.4	75.7	7.2	78.1
		Tails	58.6	15.1	80.5	...

[1] Graft polymer from Run No. 5, Table 1.

Table 4

Run No.	Additive level, lb./ton Collector	Flotation product	Yield, %	Analyses, % BPL	Analyses, % Insols	% BPL recovery
4	0.91	Float	52.9	69.6	12.6	93.6
		Tails	47.1	5.3	91.5	...
5	1.14	Float	54.1	68.8	14.3	94.1
		Tails	45.9	5.1	91.7	...
6	1.37	Float	58.1	64.6	18.4	95.6
		Tails	41.9	4.0	93.0	...
7	1.82	Float	60.6	63.6	20.5	97.0
		Tails	39.4	3.0	94.8	...

Table 5

Run No.	Additive level, lb./ton SGP	Flotation product	Yield, %	Analyses, % BPL	Analyses, % Insols	% BPL recovery
8	0.025	Float	36.0	73.6	9.5	67.7
		Tails	64.0	19.7	63.0	...
9	0.050	Float	38.5	74.4	8.8	73.0
		Tails	61.5	17.2	66.4	...
10	0.100	Float	43.4	72.8	10.1	79.4
		Tails	56.6	14.5	60.0	...
11	0.200	Float	53.0	70.4	12.9	94.3
		Tails	47.0	4.8	90.2	...
5	...	Float	54.1	68.8	14.3	94.1
		Tails	45.9	5.1	91.7	...

EXAMPLE 6

Flotation studies were run as described in Example 3, except 0.05 pound/ton of graft polymer (Run No. 5, Table 1) was added prior to the addition of various amounts of collector (tall oil fatty acids; 1:1 mixture with No. 5 fuel oil). For analyses, see Table 6.

EXAMPLE 7

Flotation studies were run as described in Example 3. Three different starch graft polymers were compared as silica depressants to two cationic starches and a wheat starch. Each was added prior to the addition of flotation reagents (1:1 mixture of tall oil fatty acids and No. 5 fuel oil each at the 1.14-pound/ton level), Table 7.

Table 6

Run No.	Additive level, lb./ton Collector	Flotation product	Yield, %	Analyses, % BPL	Analyses, % Insols	% BPL recovery
5	1.14	Float	54.1	68.8	14.3	94.1
		Tails	45.9	5.1	91.7	...
12	0.91	Float	38.9	74.6	8.0	74.3
		Tails	61.1	16.4	67.2	...
13	1.14	Float	38.5	74.4	8.8	73.0
		Tails	61.5	17.2	66.4	...
14	1.37	Float	41.1	72.2	10.9	75.6
		Tails	58.9	16.3	67.4	...
15	1.82	Float	44.2	69.7	13.1	77.9
		Tails	55.8	15.7	68.5	...

Table 7

Run No.	Additive Description	Additive Amount, lb./ton	Flotation product	Yield, %	Analyses, % BPL	Analyses, % Insols	% BPL recovery
16	2[1]		Float	45.5	72.6	10.0	84.6
			Tails	54.5	11.0	84.2	...
17	3[1]	0.05	Float	37.6	75.9	7.0	73.2
			Tails	62.4	16.7	77.0	...
9	5[1]	0.05	Float	38.5	74.4	8.8	73.0
			Tails	61.5	17.0	66.4	...
18	Wheat starch	0.10	Float	54.1	65.0	15.9	96.8
			Tails	45.9	2.7	95.3	...
19	Cationic starch	0.10	Float	53.3	66.0	18.1	90.5
			Tails	46.7	8.0	87.3	...
20	Cationic starch	0.25	Float	50.0	67.0	11.4	91.5
			Tails	50.0	6.2	90.1	...

[1]Run no. from Table 1.

We claim:

1. In a method of flotation-beneficiation of phosphate ores which normally includes the steps of:

a. floating the ore in the presence of tall oil fatty acids and No. 5 fuel oil;

b. collecting the first float;

c. removing the tall oil fatty acids and No. 5 fuel oil from the first float;

d. floating the first float in the presence of an amine collector; and

e. collecting the second float;

an improvement by which flotation is accomplished in a single stage, comprising the steps of:

a. froth floating phosphate ore in the presence of tall oil fatty acids and No. 5 fuel oil and from 0.025 to 0.2 pound/ton of ore of a graft polymer comprised of a starch substrate onto which is grafted a member selected from the group consisting of a polymerized quaternary ammonium derivative of aminotrialkyl methacrylate and mixtures of a polymerized quaternary ammonium derivative of aminotrialkyl methacrylate with polyacrylamide; and

b. collecting, filtering, and drying the resulting float.

2. The method described in claim **1** in which the graft polymer contains from about 2.5 to 15 percent by weight of a polymerized quaternary ammonium derivative of aminotrialkyl methacrylate consisting of 2-hydroxy-3-methacryloyloxypropyltrimethylammonium chloride.

3. The method described in claim **1** in which the graft polymer contains from about 2 to 11 percent by weight of a polymerized quaternary ammonium derivative of aminotrialkyl methacrylate consisting of 2-hydroxy-3-methacryloyloxypropyltrimethylammonium chloride and from about 5 to 20 percent by weight polyacrylamide.

4. The method described in claim **2** in which the ore is floated in the presence of 0.05 pound/ton of ore of the starch graft polymer.

5. The method described in claim **3** in which the ore is floated in the presence of 0.05 pound/ton of ore of the starch graft polymer.

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