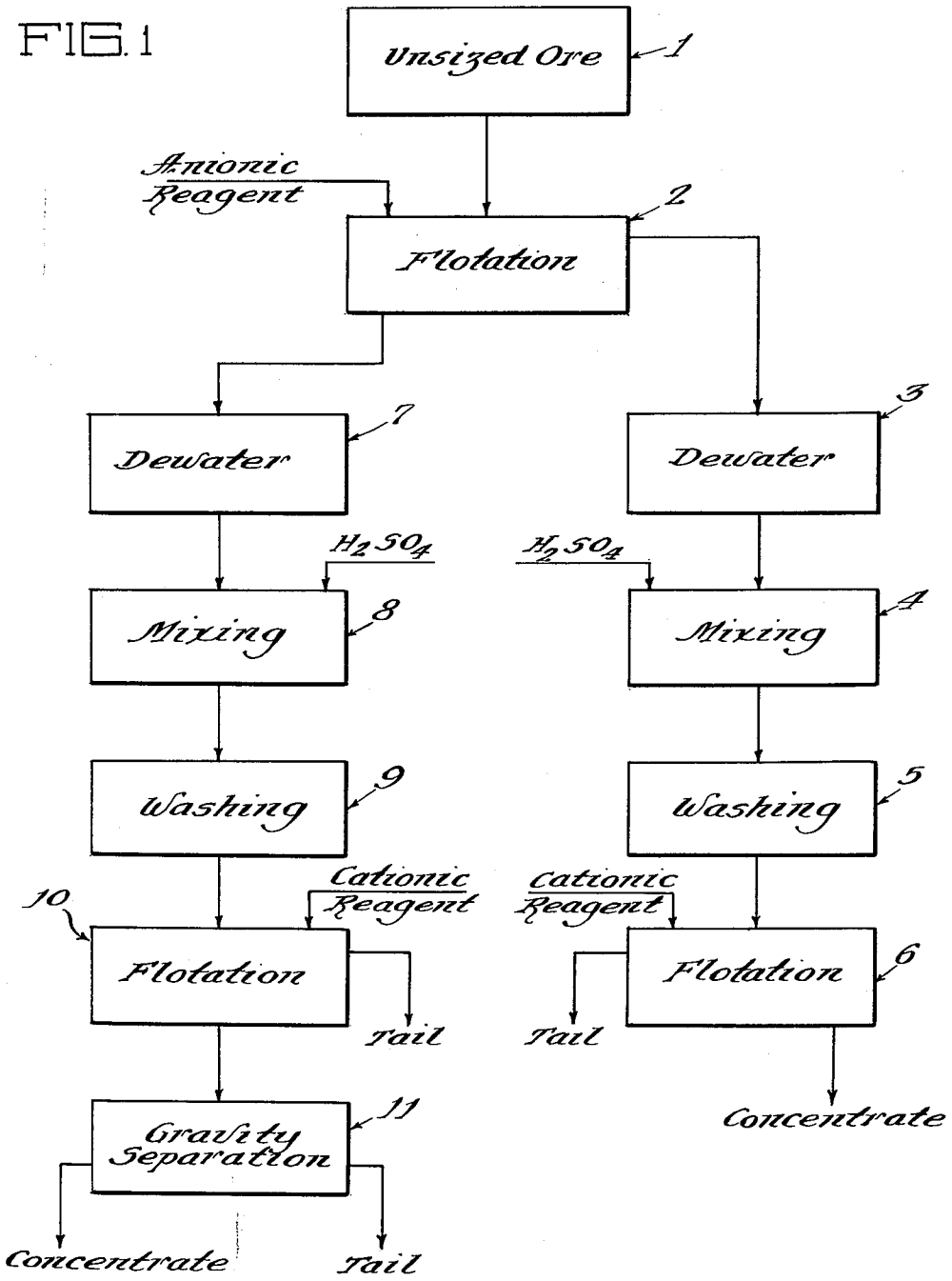
July 30, 1963 H. W. ADAM 3,099,620

WET BENEFICIATING OF PHOSPHATE ORES

Filed Aug. 31, 1960 2 Sheets-Sheet 1

FIG. 1



Inventor:
Howard W. Adam

By:

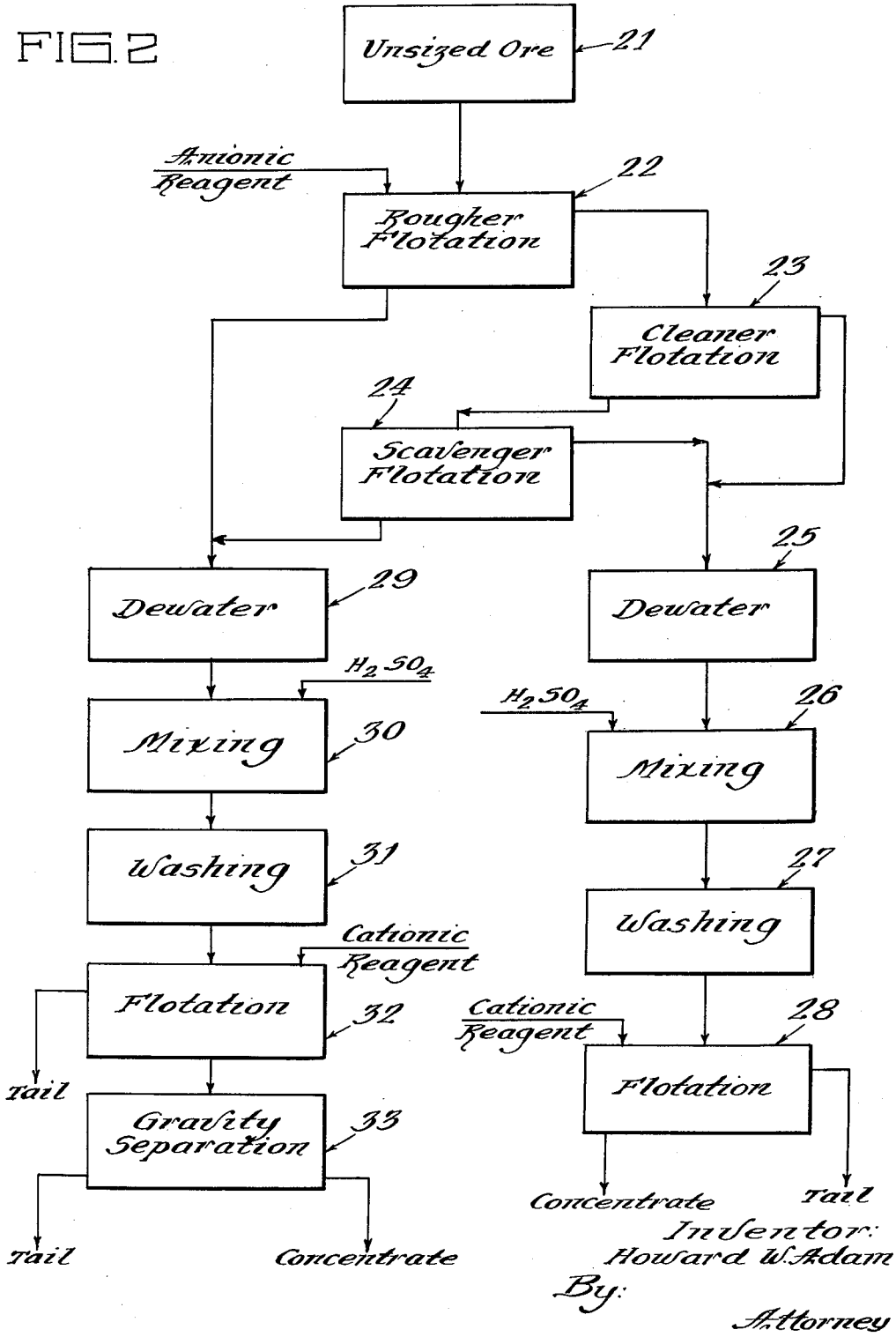
Attorney

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WET BENEFICIATING OF PHOSPHATE ORES

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FIG. 2



Inventor:
Howard W. Adam
By:
Attorney

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3,099,620

WET BENEFICIATING OF PHOSPHATE ORES

Howard W. Adam, Gouverneur, N.Y., assignor to International Minerals & Chemical Corporation, a corporation of New York

Filed Aug. 31, 1960, Ser. No. 53,133
14 Claims. (Cl. 209—12)

This invention relates to the beneficiation of phosphate ores. More particularly, the invention relates to a process for the wet concentration of unsized phosphate minerals pursuant to which a substantial portion of the phosphate values of the ore are recovered.

Wet beneficiation of phosphate ores has long been a common expedient widely practiced in the industry. Ore ground to substantial liberation of its mineral values for example, to —14 mesh conventionally is sized by means of classifiers, screens, trommels, hydroseparators and the like to provide a —14 +35 fraction and —35 +150 or 200 mesh fraction. The coarser fraction, generally considered to be too coarse for froth flotation, is beneficiated by means of spirals, shaking tables and the like. The finer —35 mesh fraction is subjected to froth flotation.

Early practice in the concentration of phosphate ores comprising apatite or fluorapatite and a siliceous gangue entailed reagentizing the liberated finely divided ore with an anionic reagent effective selectively to coat at least a portion of the surfaces of the phosphatic particles present, followed by concentration of the reagentized ore by froth flotation to provide a phosphate concentrate as a froth product and a silica tail as a depressed or sink product. At acceptable levels of recovery, particularly from relatively low-grade ores, the grade of the concentrates was objectionably low.

An alternative procedure known to the early art embraced reagentizing the liberated phosphate ore with a cationic reagent effective selectively to coat at least a portion of the surfaces of the silica particles, followed by froth flotation to produce a silica tail as a froth product and a phosphate concentrate depressed or sink product. Such a procedure likewise failed to afford a concentrate of satisfactory grade and recovery.

The Florida phosphate industry, in particular, accordingly resorted to a combined process pursuant to which (1) the liberated phosphate ores are subjected to a first state of wet beneficiation in the presence of an anionic reagent to produce a rougher concentrate comprised of reagent-bearing phosphatic minerals and a substantial amount of silica, (2) the rougher concentrate is treated with a mineral acid to remove the reagent coating, and (3) the essentially reagent-free rougher concentrate is subjected to a second stage wet concentration in the presence of a cationic reagent effective to coat selectively the silica particles to produce a final phosphate concentrate and reagent-bearing silica tail. The combined process is described in detail in Crago Patent 2,293,640. Modifications of the Crago process which treat finely divided ore and embrace the same general sequence of steps are described in a plurality of subsequently issued patents including: Duke 2,461,813; Duke 2,661,842; Houston 2,706,558; Hunter 2,750,036; and Duke 2,753,997. Reference is made to the disclosures of each of the aforementioned patents for a more detailed teaching in respect to the concentration of phosphatic minerals with anionic and cationic reagents, and methods known to the art for the removal of such reagents from the concentrates produced. Significantly, each of the above patents sizes the phosphate feed to obtain a —35 mesh feed which is subjected to the flotation process. Further, each of the above patents describes a process wherein only the froth concentrate from the anionic flotation is subjected to further processing.

Further modifications of the Crago process are exemplified by Duke Patent 2,676,705. In this instance phosphate ore is sized to obtain a coarser fraction and a finer fraction, each of said fractions being subjected to an anionic flotation. Again, however, the underflow from the anionic flotation is discarded as siliceous waste.

Processes, such as the above, must rely on an accurate sizing of the liberated ore to achieve efficient separation. In practice, however, it is extremely difficult to achieve an accurate sizing of the ore. As a threshold matter, much of the ground ore is characterized by a size of about 35 mesh. Moreover, variations in the shape and specific gravity of the particles and their tendency to blind screens further contribute to an inaccurate sizing and ultimately to a lower recovery of the phosphate values of the ore.

Typical screen sizings of a liberated phosphate ore are as follows:

Mesh size	Coarse fraction, percent	Fine fraction, percent
+35	60–40	5–15
—35	40–60	95–85

It will be apparent that such processing, requiring extensive sizing equipment, does not provide an efficient sizing of the ore.

It is a primary object of this invention to provide a method for the wet beneficiation of phosphate ores pursuant to which high recoveries of phosphate values are realized.

It is another object of this invention to provide a method for the wet beneficiation of unsized phosphate ores pursuant to which a high proportion of the phosphate values are recovered.

It is a further object of this invention to provide a method for the wet beneficiation of phosphate ores which does not require that the entire ground ore be subjected to a preliminary sizing.

In accordance with this invention there is provided a method of beneficiating unsized phosphate ore which comprises:

(1) Subjecting unsized liberated phosphate ore to froth flotation in the presence of an anionic flotation reagent to provide a phosphate-rich overflow concentrate and an underflow stream;

(2) Subjecting the underflow from (1) to froth flotation in the presence of a cationic flotation reagent to provide a phosphate-containing underflow concentrate and an overflow discard tail; and

(3) Subjecting the underflow concentrate from (2) to gravity separation to provide a phosphate-rich gravity concentrate product.

In a preferred embodiment of the invention, the phosphate-rich concentrate from the anionic flotation is subjected to further froth flotation in the presence of a cationic reagent to provide a phosphate-rich underflow concentrate product and an overflow silica tail.

The process of this invention provides a significant recovery of phosphate materials and may reduce the amount of ore to be processed by gravity separation as compared to standard prior art processes wherein phosphate ores are sized to obtain a coarse fraction which is subjected to gravity separation and a fine fraction which is subjected to flotation. Moreover, the process of this invention eliminates the necessity of sizing the entire ground ore.

Whereas conventional commercial processes recover

from 85 to 90% of the phosphate values from a phosphate ore originally containing 35 to 40% phosphate values, this invention permits recoveries of 90% to 95% of the phosphate values present. Accordingly, as compared to such process, this invention provides a simplified process which increases phosphate recovery.

This invention is generically applicable, without limitation, to phosphate ores amenable to wet concentration. Specific ores contemplated include Florida pebble phosphate, the various Tennessee phosphates, hard rock phosphates indigenous to the Western United States, and the various foreign phosphate ores such as Moroccan phosphates.

The phosphate ore to be treated in accordance with the process of this invention is preliminarily ground employing standard grinding apparatus known to the art to a mesh size generally of about —10, preferably about —12 mesh and deslimed to provide a mesh range of about —10 or 12 to about +150 or 200 mesh. Grinding the ore to this stated mesh size generally is sufficient to liberate the phosphate values of the ore and to permit the ore effectively to be processed by this invention.

The ground ore then is reagentized employing any of the standard anionic or negative ion flotation agents known to the art. The particular anionic reagent utilized in the preliminary froth flotation of the phosphate ores does not constitute an essential feature of this invention which is operable with and contemplates all such reagents. Representative conventional anionic reagents comprise fatty acids or fatty acid soaps, particularly mixed fatty acids or soaps thereof; fatty acids derived from natural sources such as tall oil soaps and floating soap; fatty acids or soaps of acids derived from animal and vegetable fats; esters of inorganic acids with high molecular weight alcohols; and the like. Conventionally, such anionic reagents are applied in solution or in a dispersion in a carrier medium such as a hydrocarbon oil, normally kerosene or fuel oil. One widely used specific reagent combination comprises about one to about three parts tall oil, from about two to about four parts kerosene, and from about two to about four parts "Bunker C" fuel oil.

The reagentized ore is subjected to froth flotation again employing any of the standard flotation equipment known to the art. The flotation is effective to remove in the overflow a substantial amount of the phosphate values of the ore together with some of the finer silica particles. The underflow will contain a substantial portion of silica and also will contain phosphate values, particularly in the form of coarser phosphate particles.

In accordance with the preferred embodiment of this invention, the anionic overflow concentrate is subjected to a further flotation in the presence of a cationic flotation reagent.

The anionic reagents advantageously are removed from the phosphate-rich overflow concentrate employing such standard prior art means as scrubbing with water or, more desirably, with a mineral acid such as sulfuric acid, hydrochloric acid and the like. In conformance with recognized procedures, the anionic concentration slurry may be partially dewatered in order to permit a more efficient removal of the reagent. Following the removal of the anionic reagent, the phosphate-rich concentrate is reagentized with a cationic reagent. While removal of the anionic reagent may improve the efficiency of subsequent processing, it is not critical to the operability of the process. Significant phosphate recovery can be achieved without removing the anionic reagent.

Again, this invention generically embraces the cationic or positive ion flotation reagents known to the art. Such reagents include, inter alia, the higher aliphatic amines and their salts with water-soluble acids; the ester of amino alcohols with high molecular weight fatty acids and their salts with water-soluble acids; the higher alkyl-O-substituted isoureas and their salts with water-soluble acids; the higher aliphatic quaternary ammonium bases and their salts with water-soluble acids; the higher alkyl pyridinium water-soluble acids; the higher alkyl quinolinium salts of water-soluble acids and the like.

The phosphate-rich overflow from the first flotation, now reagentized with a cationic reagent, is subjected to a second froth flotation. The flotation removes predominantly the finer silica particles which were collected in the overflow concentrate of the anionic flotation and the overflow silica tail, substantially free of phosphate values, may be discarded, or if desired, processed further for other purposes.

The underflow stream from the anionic froth flotation also desirably is de-reagentized and then reagentized with a cationic reagent and subjected to froth flotation. The flotation provides a phosphate-containing underflow which contains both phosphate and silica and particularly coarse phosphate particles and coarse silica. The overflow silica tail is substantially free of phosphate.

The phosphate-containing underflow finally is subjected to gravity separation to provide a second phosphate-rich concentrate product. The gravity separation may be carried out employing any of the means known to the art including, without limitation, spirals, tables, belts and the like. Spirals, for example, Humphrey spirals, are found to be particularly appropriate for the gravity separation of phosphate-rich concentrates. In conformance with recognized practice, the ore may be reagentized before being subjected to the gravity separation.

While each flotation above described has been referred to as if conducted in a single flotation unit, it will be apparent that a battery of units in parallel or in series may be employed for each flotation stage. Thus, for example, the preliminary anionic flotation can be accomplished in a battery of rougher anionic flotation cells to produce a phosphate-rich rougher overflow which in turn is processed further in anionic cleaner flotation cells to produce a phosphate-rich overflow concentrate. Such expedient is particularly appropriate in the event that the phosphate concentrate is not to be subjected to further upgrading by cationic flotation. Similarly, the cationic flotation stages referred to above may consist of a battery of rougher cells employed in conjunction with a secondary battery of cleaner cells.

The control of flotation air rates, the solids content of the slurry in the flotation unit and similar process conditions are within the skill of the routineer. Tests indicate that the anionic reagent can most appropriately be employed in amounts of at least about .2 pound per ton, and the anionic underflow most appropriately may be conditioned with at least about 0.8 pound per ton of a cationic reagent. These reagents may be employed in amounts up to 10 pounds per ton or more, if desired. The use of large quantities of reagent, of course, tends to effect adversely the economics of the process.

The method of this invention is demonstrated by the flowsheets in the attached drawings.

FIGURE 1 represents a diagrammatic flowsheet of the method of this invention.

FIGURE 2 represents one preferred flowsheet for the method of this invention.

Referring to FIGURE 1, the deslimed, unsized ore (—14 +150) from feed bin 1 is mixed with a flotation agent composition such as tall oil and delivered to flotation unit 2. Froth flotation provides an overflow phosphate-rich fraction which is de-watered at de-watering station 3 to provide a high-solids slurry, e.g. 75% solids. The de-watered concentrate then is conveyed to mixing station 4 where sulfuric acid is added to remove the anionic flotation reagents. The concentrate then is washed to neutrality at washing station 5 and conveyed to flotation unit 6 wherein it is floated with a cationic flotation agent such as a long-chain aliphatic amine. Flotation unit 6 yields an underflow phosphate product and an overflow silica tail. The underflow from the

flotation unit 2 is de-watered at station 7, mixed with a mineral acid such as sulfuric acid at station 8 to remove the anionic reagent and washed at station 9 to neutrality. Since the underflow stream from flotation unit 2 contains predominantly unreagentized material, stations 7, 8 and 9 may be eliminated if desired. The underflow from flotation unit 2 is fed to flotation unit 10 wherein it is subjected to froth flotation in the presence of a cationic reagent, such as a long-chain aliphatic amine. Flotation unit 10 provides an overflow silica tail and an underflow product containing the coarser phosphate and silica values of the ore. This stream is subjected to gravity separation, such as spiraling, at station 11 to provide a final phosphate concentrate and a silica tail. From the earlier description of the process it will be apparent that this invention also contemplates a process wherein a first phosphate product is removed as the overflow from flotation unit 2 and reagent removal stations 3, 4, 5 and flotation unit 6 are not employed.

FIGURE 2 represents one preferred embodiment of the process of this invention. The unsized de-slimed phosphate ore from the feed bin 21 is reagentized with an anionic reagent such as tall oil and subjected to a rougher flotation operation in flotation unit 22. The phosphate-rich overflow from unit 22 is subjected to a cleaner flotation at flotation unit 23 to provide a phosphate-rich overflow and a silica-containing underflow. The silica-containing underflow is subjected to a scavenger flotation in flotation unit 24 again to provide a phosphate-rich overflow and a silica-containing underflow. The overflows from flotation units 23 and 24 are combined and de-watered, scrubbed with a mineral acid and washed at stations 25, 26 and 27. The concentrate then is subjected to flotation in the presence of a cationic reagent at flotation unit 28 to provide an overflow silica tail and an underflow final phosphate concentrate. The underflow from rougher flotation unit 22 is combined with the underflow from scavenger flotation unit 24 and the combined underflows are subjected to de-watering, scrubbing with a mineral acid and washing at stations 29, 30 and 31. The combined underflows then are subjected to flotation in the presence of a cationic flotation reagent such as a long-chain aliphatic amine at flotation unit 32. Flotation unit 32 provides an overflow silica tail and underflow stream containing the coarser particles of phosphate and silica. The underflow is subjected to gravity separation, as for example in spirals, at station 33 to provide a second phosphate concentrate and a silica tail.

The following examples are included in order more fully to describe the process of this invention. These examples are included for illustrative purposes only and in no way are intended to limit the scope of this invention.

EXAMPLE I

Approximately 700 t./h. (tons per hour) of phosphate or (37.5% BPL), ground and washed to about −16 +150, is conditioned with 1.5 lb./ton of anionic reagent (1:1:2—tall oil:kerosene:Bunker C fuel oil) and subjected to a rougher flotation to yield an overflow of 372 t./h. (55% BPL) and an underflow of 328 t./h. (8% BPL).

The overflow is subjected to a cleaner flotation to yield a cleaner overflow of 293 t./h. (63% BPL) and a cleaner underflow of 79 t./h. (25% BPL).

The combined underflows from the anionic rougher and cleaner floats is conditioned with 1 lb./ton of a mixture of long-chain amines with added kerosene and subjected to flotation to yield an underflow of 84 t./h. (45% BPL) and an overflow of 323 t./h. (2.5% BPL).

Finally, the 84 t./h. cationic underflow is subjected to gravity separation in a spiral section to provide a concentrate of 47 t./h. (74.4% BPL) and a tail of 37 t./h. (9% BPL).

The total BPL recovery of the above process is 94.3%. A standard process utilizing gravity separation for +35 mesh ore and an analogous method to the above to process −35 mesh ore recovers only about 88% of the BPL of the ore.

EXAMPLE II

In order to determine the characteristics of the anionic float and of the cationic float of the anionic underflow, without dereagentizing phosphate ore ground and washed to −16 +150 mesh size and analyzing 37.5% BPL was subjected to anionic rougher flotation and the overflow was subjected to a cleaner flotation. The combined underflow from the rougher and cleaner floats then was subjected to a cationic flotation.

The ore was fed to the process at a rate of 0.15 ton per hour. Five cells were employed for the rougher float, 3 cells for the cleaner float, and 4 cells for the cationic float. For the anionic float, the ore was reagentized with 1.47 pounds/ton of tall oil in an emulsion (1:1:2—tall oil:kerosene:Bunker "C" fuel oil), and 0.45 lb./ton of NaOH. For the cationic float, ore was reagentized with 1.02 lbs./ton of mixed long-chain amines.

The analyses of the process streams are set forth in Table 1 below.

Table 1

Stream	BPL		
	Weight percent	Assay, percent	Distribution, percent
Anionic cleaner float	39.1	68.4	71.4
Cationic underflow	21.4	45.9	26.3
Cationic float	39.5	2.2	2.3
Composite	100.0	37.5	100.0

Each of the streams was also screened at 35 mesh. The screen analysis of the streams is reflected by Table 2.

Table 2

Stream	+35 mesh		−35 mesh	
	Weight percent	BPL percent	Weight percent	BPL percent
Anionic cleaner float	18.1	78.7	81.9	67.5
Cationic underflow	51.0	54.6	49.0	39.3
Cationic float	7.7	1.9	92.3	2.2
Composite	21	55.0	79.0	34.3

The data of Table 2 demonstrate that the +35 mesh fraction constituted about 51% of the cationic underflow as contrasted to only 21% of the feed. The data also demonstrate that predominately finer material was removed by both the anionic and the cationic float.

While the method has been described as a continuous process, it will be apparent that it also can be practiced as a batch process. Since this and other modifications will be apparent to one skilled in the art, it is intended that this invention be limited only by the scope of the appended claims.

I claim:

1. The method of beneficiating unsized phosphate ore which comprises:

(1) subjecting an unsized liberated deslimed phosphate ore fraction containing particles of a mesh size of from about 10 mesh to about 200 mesh to froth flotation in the presence of an anionic flotation reagent to provide a phosphate-rich overflow concentrate and an underflow stream;

(2) subjecting the underflow from (1) to froth flotation in the presence of a cationic flotation reagent to provide a phosphate-containing underflow concentrate and an overflow discard tail; and

(3) subjecting the underflow concentrate from (2) to gravity separation to provide a phosphate-rich gravity concentrate product.

2. The method of claim 1 wherein the anionic reagent is selected from the group consisting of fatty acids and fatty acid soaps.

3. The method of claim 1 wherein the cationic reagent is an aliphatic amine.

4. The method of beneficiating unsized phosphate ore which comprises:

(1) subjecting an unsized liberated deslimed phosphate ore fraction containing particles of a mesh size of from about 10 mesh to about 200 mesh to froth flotation in the presence of an anionic flotation reagent to provide a phosphate-rich overflow concentrate and an underflow stream;

(2) subjecting the phosphate rich overflow from (1) to froth flotation in the presence of a cationic flotation reagent to provide a phosphate-rich underflow concentrate and an overflow silica tail;

(3) subjecting the underflow from (1) to froth flotation in the presence of a cationic flotation reaagent to provide a phosphate-containing underflow concentrate and an overflow discard tail; and

(4) subjecting the underflow concentrate from (3) to gravity separation to provide a phosphate-rich gravity concentrate product.

5. The method of claim 4 wherein the anionic reagent is selected from the group consisting of fatty acids and fatty acid soaps.

6. The method of claim 4 wherein the cationic reagent is an aliphatic amine.

7. The method of beneficiating an unsized phosphate ore which comprises:

(1) subjecting an unsized liberated deslimed phosphate ore fraction containing particles of a mesh size of from about 10 mesh to about 200 mesh to froth flotation in the presence of an anionic flotation reagent to provide a phosphate-rich overflow concentrate and an underflow stream;

(2) subjecting the phosphate-rich overflow from (1) to a cleaner froth flotation to provide a phosphate-rich cleaner overflow and an underflow;

(3) subjecting the phosphate-rich overflow from (2) to froth flotation in the presence of a cationic flotation reagent to provide a phosphate-rich underflow and an overflow silica tail;

(4) subjecting the underflows from (1) and (2) to froth flotation in the presence of a cationic flotation reagent to provide a phosphate-rich underflow and an overflow silica tail; and

(5) subjecting the underflow from (4) to gravity separation to provide a phosphate-rich concentrate and a silica tail.

8. The method of claim 7 wherein the anionic reagent is selected from the group consisting of fatty acids and fatty acid soaps and the cationic reagent is an aliphatic amine.

9. The method of beneficiating unsized phosphate ore which comprises:

(1) subjecting an unsized liberated deslimed phosphate ore fraction containing particles of a mesh size of from about 10 mesh to about 200 mesh to froth flotation in the presence of an anionic flotation reagent to provide a phosphate-rich overflow concentrate and an underflow stream;

(2) subjecting the phosphate-rich overflow from (1) to a cleaner froth flotation to provide a phosphate-rich cleaner overflow and an underflow;

(3) subjecting the underflow from (2) to a scavenger froth flotation to provide a phosphate-rich scavenger overflow and an underflow;

(4) subjecting the phosphate-rich overflows from (2) and (3) to froth flotation in the presence of a cationic flotation reagent to provide a phosphate-rich underflow and an overflow silica tail;

(5) subjecting the underflows from (1) and (3) to froth flotation in the presence of a cationic flotation reagent to provide a phosphate-rich underflow and an overflow silica tail; and

(6) subjecting the underflow from (5) to gravity separation to provide a phosphate-rich concentrate and a silica tail.

10. The method of claim 9 wherein the anionic reagent is selected from the group consisting of fatty acids and fatty acid soaps and the cationic reagent is an aliphatic amine.

11. The method of claim 1 wherein said unsized liberated deslimed phosphate ore fraction contains particles of a mesh size of from about 12 mesh to about 150 mesh.

12. The method of claim 4 wherein said unsized liberated deslimed phosphate ore fraction contains particles of a mesh size of from about 12 mesh to about 150 mesh.

13. The method of claim 7 wherein said unsized liberated deslimed phosphate ore fraction contains particles of a mesh size of from about 12 mesh to about 150 mesh.

14. The method of claim 9 wherein said unsized liberated deslimed phosphate ore fraction contains particles of a mesh size of about 12 mesh to about 150 mesh.

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