May 1, 1962 E. NORTHCOTT 3,032,197

PHOSPHATE ORE BENEFICIATION PROCESS
ENTAILING REAGENT RECOVERY

Filed Oct. 6, 1959 2 Sheets-Sheet 1

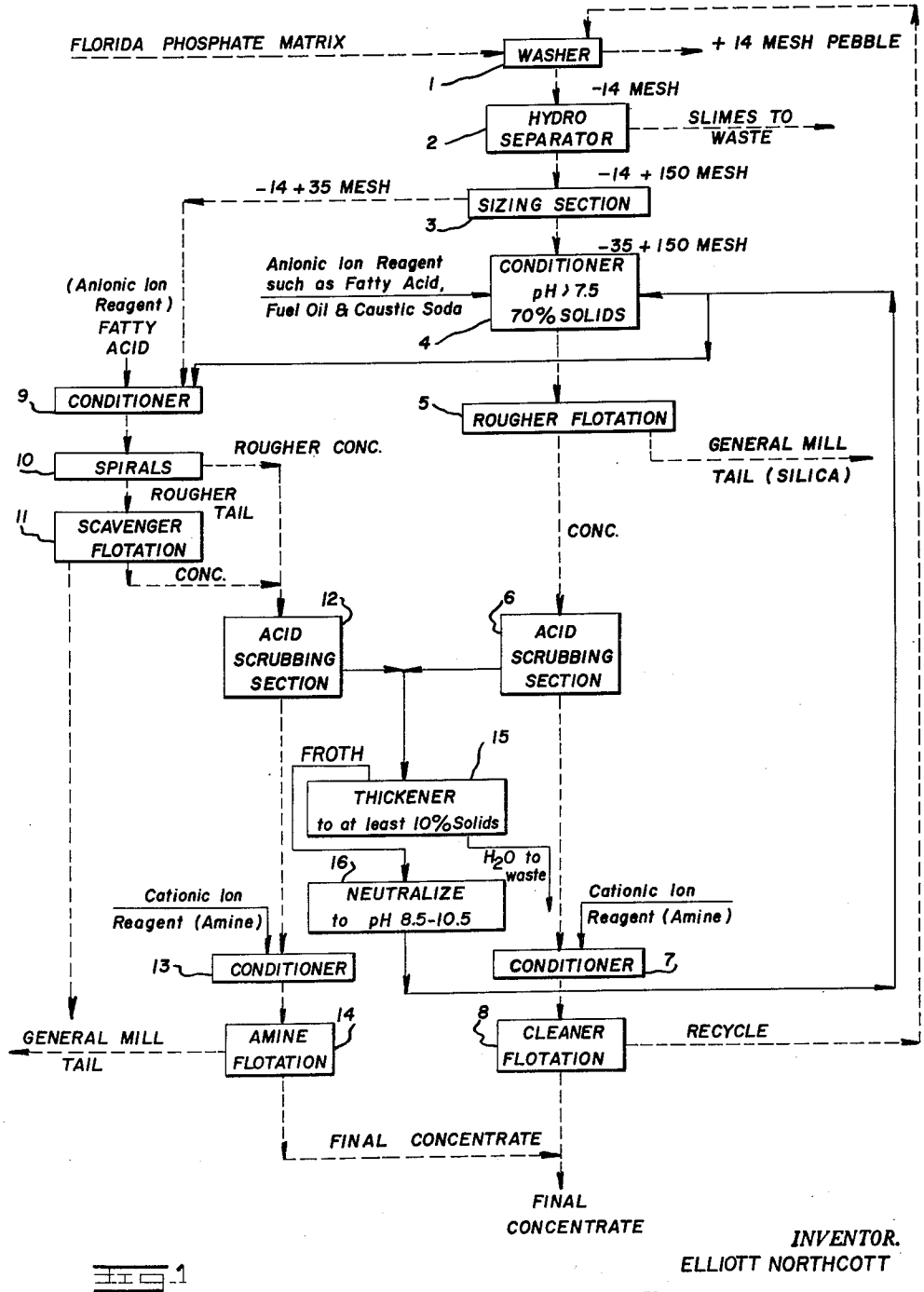


Fig. 1

INVENTOR.
ELLIOTT NORTHCOTT

BY

EVERET F. SMITH
ATTORNEY

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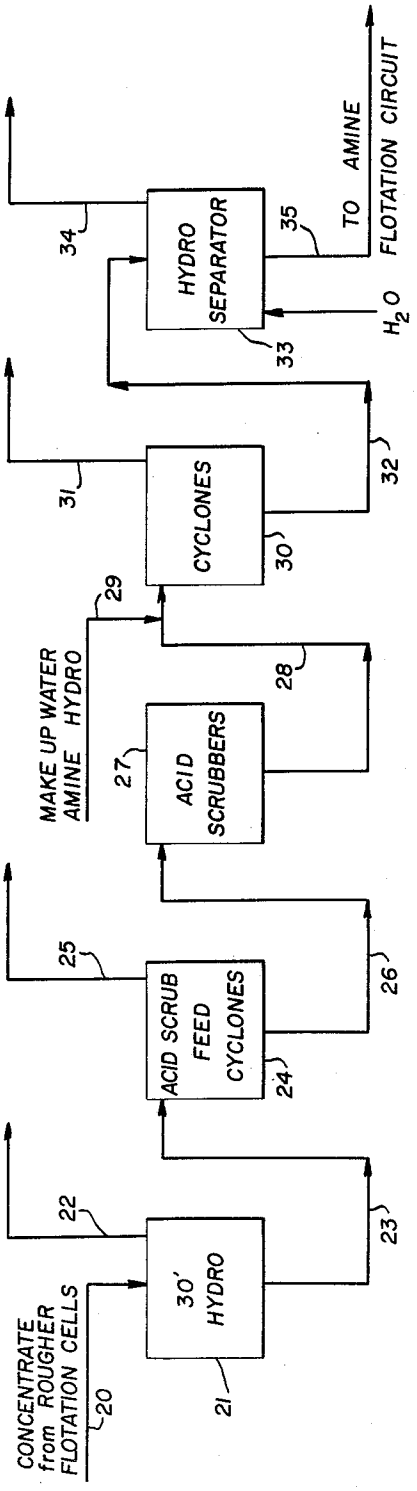


Fig. 2.

INVENTOR.
ELLIOTT NORTHCOTT

BY

EVERET F. SMITH
ATTORNEY

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PHOSPHATE ORE BENEFICIATION PROCESS ENTAILING REAGENT RECOVERY

Elliott Northcott, Lakeland, Fla., assignor to International Minerals & Chemical Corporation, a corporation of New York

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This invention relates to the beneficiation of phosphate ores. More particularly, the invention relates to a process for the wet concentration of phosphatic minerals in the presence of anionic reagents pursuant to which at least a substantial portion of such reagents are reutilized rather than discarded as in the prior art.

Early practice in the concentration of phosphate ores comprising apatite or fluorapatite and a siliceous gangue entailed reagentizing the liberated 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 No. 2,293,640. Modifications of the Crago process which emrace the same general sequence of steps are described in a plurality of subsequently issued patents including: Hodges 2,599,530; Duke et al. 2,661,842; Houston et al. 2,706,557; Hunter et al. 2,750,036; Duket et al. 2,753,997; and Chapman et al. 2,766,883. 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 reagents, and methods known to the art for the removal of such reagents from the concentrates produced. Significantly, each of such patents affirmatively teaches that the anionic reagent-containing acidic scrub liquors produced by the conventional practice of the Crago process are discarded. The consequent loss of anionic reagents represents a major expense in contemporary phosphate ore benefication operations. Prior to this invention, no satisfactory method was known for the recovery or reutilization of the anionic reagent materials used in the wet benefication of phosphate ores.

It is accordingly, a primary objective of the invention to provide a novel technique for the wet beneficiation of phosphate ores pursuant to which anionic beneficiation reagents can be reutilized.

It is a more specific objective of the invention to provide a method for the beneficiation of phosphate ores pursuant to which the ore is subjected to fet concentration in the presence of an anionic reagent which is recovered from the concentrate and utilized to condition an additional quantity of ore.

It is a more specific object of the invention to provide a method for the froth flotation or spiral concentration of siliceous apatite ore which comprises conditioning the liberated ore with an anionic reagent, at least a substantial portion of which is recovered in a form useful to condition fresh ore.

It is a particular object of the invention to provide a method for the concentration of phosphate ores, such as apatite, by the process described in Crago Patent 2,293,640, pursuant to which the liquors formed by scrubbing the anionic flotation concentrate with mineral acid are converted to a novel anionic reagent material useful to condition additional quantities of phosphatic ore.

Now, in accordance with this invention, a liberated phosphate ore is conditioned with an anionic reagent effective to coat at least a portion of the surfaces of the phosphate mineral particles present, an aqueous pulp of the conditioned ore is subjected to wet concentration to produce a concentrate containing phosphate mineral particles bearing said negative ion reagent, said concentrate is treated with an aqueous medium to remove said reagent therefrom and the resulting slurry containing said negative ion reagent is separated from said concentrate and utilized to condition an additional quantity of phosphatic ore.

The invention is best appreciated by reference to the drawings in which:

FIGURE 1 comprises a schematic flowsheet of a commercial Florida phosphate ore beneficiation plant in which a process comparable to that described in the Crago patent is utilized; and

FIGURE 2 comprises a detailed flowsheet of the acid scrubbing section 6 shown in FIGURE 1.

Conventional operations are shown in the FIGURES 1 and 2 in broken lines, whereas the improvement which constitutes the present invention is shown in solid lines.

As shown by the broken lines of FIGURE 1, in accordance with conventional procedure, liberated phosphate ore is first passed into washer 1 (Florida phosphate matrix), the overflow from which comprises a +14 mesh pebble phosphate product which is not processed by the method of the invention. The —14 mesh underflow from washer 1 is substantially deslimed in hydroseparator 2. The slime-containing overflow from the hydroseparator 2 is sent to waste. The —14+150 mesh deslimed ore comprises the underflow from the hydroseparator 2 is separated in sizing section 3, which is of conventional design, into a —14+35 mesh coarse fraction and a —35+150 mesh fine fraction.

The —35+150 mesh fine fraction is passed into a conditioning tank 4 where it is appropriately conditioned with a conventional anionic froth flotation reagent such as tall oil, in admixture with fuel oil and sodium hydroxide in an amount requisite to raise the pH to within the range of from 7.0 to about 9. The conditioned ore passes from the conditioning tank 4 into a rougher bank of flotation cells 5. The froth product concentrate from the rougher cells 5, which comprises anionic reagent coated phosphatic materials and a substantial portion of silica, is passed into the acid scrubbing section 6 (shown in greater detail in FIGURE 2) for treatment with mineral acid to remove the reagent coating. The depressed or sink product from flotation cells 5 comprises essentially silica and is discharged to general mill tails.

The acid-scrubbed, anionic reagent-free, rougher concentrate is passed into a conditioner 7 where it is appropriately conditioned with a cationic froth flotation reagent such as an amine. The cationic conditioned material is subjected to flotation in the cleaner bank of flota-

tion cells 8 to produce a froth product, comprising essentially a silica tail which may be recycled to washer 1, and a sink product consisting essentially of phosphatic material which constitutes the final concentrate.

The −14+35 mesh coarse fraction from the sizing section 3 is conditioned in conditioner 9 with anionic flotation reagents of the same type utilized in conditioner 4 and thereafter concentrated in a spiral concentration apparatus, such as a Humphrey spiral 10 to produce a spiral rougher concentrate and a spiral rougher tail. The spiral rougher tail is subjected to scavenger benefication in flotation cells 11 to produce a scavenger concentrate which is combined with the rougher spiral concentrate and passed through an acid scrubbing section 12 of the same general type as the acid scrubbing section 6 utilized in the processing of the −35+150 mesh fine fraction from the sizing section. The acid-scrubbed spiral and scavenger concentrates are combined and conditioned in conditioner 13 with a cationic reagent and subjected to a cleaner flotation in flotation cells 14 to produce a float product which is combined with the general mill tails and a sink or depressed product which is combined with the final concentrate produced in cleaner flotation cells 8.

The improvement in the conventional process which comprises the present invention and which is shown in solid lines in FIGURE 1, entails concentration in thickener 15 of at least a part of the acid scrub liquor from at least one of scrubbers 6 and 12 to a solids content preferably of at least about 10% by weight. Reagent bearing solids may be removed from the thickener 15 as an underflow as shown in FIGURE 1. The reagent bearing solids may also be removed from the thickener 15 as a froth in conventional manner not shown in FIGURE 1. The thickened acid scrub liquor is then neutralized to a pH of from about 8.5 to about 10.5 as shown at 16 to provide an anionic reagent utilized in conditioners 4 and 9 to condition additional quantities of phosphate ore. Preferably such neutralization is effected in the conditioners.

The acid scrubber sections shown at 6 and 12 of FIGURE 1 may be of any conventional or appropriate arrangement. One commercially satisfactory arrangement is shown in some detail in FIGURE 2 which will be described as corresponding to the acid scrubber section 6 of FIGURE 1.

Referring to FIGURE 2, rougher concentrate 20 from flotation cells 5 passes through hydroseparator 21 where water is removed as overflow 22. The underflow 23 is further concentrated in cycline 24 in which overflows 25 is separated from underflow 26 which flows into acid scrubber 27 where the anionic reagent materials present are removed by agitation with sulfuric acid. The acid scrubbing liquors 26 are combined with make up water 29 and passed into cyclones 30 in which a reagent containing overflow 31 is separated from the acid-scrubbed concentrate 32. Concentrate 32 is rinsed free of any residual negative ion reagent in hydroseparator 33 to which water in any desired amount may be added. A dilute, negative ion reagent-containing overflow 34 is separated in hydroseparator 33 from the substantially reagent-free concentrate 35 which then passes into the cationic reagent or amine conditioner 7, shown in FIGURE 1. A similar acid scrubbing system could of course also constittue the acid scrubber unit 12 of FIGURE 1. It is apparent that acid scrubbers 6 and 12 might comprise a single unit such that both the flotation and spiral rougher concentrates might be freed of reagent therein. The invention generally contemplates a system in which anionic reagents are removed from phosphate ore fractions after at least one stage of wet concentration.

In the specific arrangement shown in FIGURE 2, the acidic liquors separated at 31 are utilized. It will be appreciated that the liquors separated at 22, 25 and 34 also contain some anionic reagents and hence can be processed in accordance with the invention. Use of such dilute liquors complicates various physical operations such as transportation and concentration of fluids which attend the process, and is not preferred.

The acidic scrubbing liquors which are separated from the negative ion phosphate concentrates in accordance with the invention, normally contain from 0.3% to 0.5% solids by weight. In the preferred practice of the invention, the acid wash liquors are thickened or concentrated as indicated at 15 in FIGURE 1, to a substantially higher solids content of at least about 10%, preferably about 15% to about 30% by weight to facilitate utilization thereof in the conventional anionic reagent conditioners, as represented at 4 and 9 in FIGURE 1 in which a total solids content of at least about 60% preferably about 70% to about 80% by weight is maintained. Conventional thickening and concentrating apparatus such as a Dorr thickener can be effectively utilized.

Conventional organic flocculants expedite the rate of separation of the solids present in the reagent containing acid liquors without adverse effect in the subsequent stages of the process.

Such flocculants are generically embraced by the invention and include cationic starch products, guar gums, polyacrylic resin flocculants and the like. It has been discovered that certain of the flocculants such as polyacrylic resins may function to some extent as a collector effect with the result that a portion of the solids present appear in a froth which may be removed from the surface of a thickener such as shown in 15 and FIGURE 1, while an additional portion of the solids precipitate and is collected as the thickener underflow.

The data reported in Table 1 reflect the settling rate of the solids in the acidic liquors with which the invention is concerned and were determined after the addition of the indicated amount of various appropriate commercial flocculants. Each of the test samples contained 0.5% solid, demonstrated a pH of about 4.0, and was naturally moderately flocculated. Optimum settling conditions were defined as the minimum concentration of flocculant required to afford a clear supernatant liquid after a 15 minute quiescent settling period. In the absence of a flocculant, the test liquor remained cloudy for at least 30 minutes.

TABLE I

Effect of Various Flocculants on the Settling Rate of Noralyn Acid Scrubber Slimes

Flocculation Treatment, parts per million of slurry	Settling Rate prior to Compression Zone, Inches/minute	Percent Solids in Settled Material	
		After 30 min.	After 48 hrs.
No floculant	0.84	6.3	12.0
5 p.p.m. Cato starch [1]	3.0	6.3	12.2
0.5 p.p.m. Guartec [2]	3.3	8.3	12.2
1.0 p.p.m. AC–550 [3]	3.0	6.9	11.6
2.0 p.p.m. Polyox [4]	1.6	8.3	13.6
0.25 p.p.m. Separan 2610 [5]	3.3	7.8	11.5
0.20 p.p.m. AC–3171 [6]	3.3	8.0	11.7

[1] Cato starch is a cationic starch product sold by National Starch Products.
[2] Guartec is a commercial grade of guar gum sold by National Starch Products.
[3] AC–550 is a polyacrylonitrile sold by American Cyanamid.
[4] Polyox is a high molecular weight water soluble resin sold by Union Carbide, understood to be a polyacrylic material.
[5] Separan 2610 is a water soluble polyacrylic resin sold by the Dow Chemical Co.
[6] AC–3171 is a polyacrylonitrile sold by American Cyanamid Co.

It is apparent from the data appearing in Table I that low concentrations of each of the flocculants tested significantly increased the initial settling rate of the solids present. Flotation tests demonstrated that the flocculants had no adverse metallurgical effect.

A pH of at least 7; more appropriately at least about 8.5 and preferably from about 9.5 to about 10.5 is maintained in the conditioners for the anionic concentration of phosphatic ores. Generally the acidic scrub liquors are

characterized by a pH of about 4. Accordingly, pursuant to the invention, the acid liquors are neutralized to pH of at least about 7 and preferably to a pH of from about 9.5 to about 10.5 for utilization to condition fresh phosphate ore. pH adjustment is preferably effected in the conditioners.

The particular anionic reagents utilized in the concentration of the phosphatic ores does not constitute an essential feature of the invention which is operable with and contemplates the reutilization of 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, 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 dispersion in a Carver medium such as a hydrocarbon oil, normally kerosene or fuel oil. One widely used specific reagent combination comprises about one to about 3 parts tall oil, from about two to about four parts kerosene, and from about two to about four parts "Bunker C" fuel oil.

The invention is likewise 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 Morroccan phosphates.

The invention can effectively be utilized on conjunction with all wet concentration procedures including without limitation conventional flotation, skin flotation, spiral processing, tabling, belt concentration, and the like.

The process of the invention is particularly applicable, however, to the froth flotation and spiral concentration operations which are conventionally utilized in the beneficiation of Florida pebble phosphate rock. The details of phosphate ore beneficiation by flotation procedures are well understood art and are disclosed in various of the Crago, Hodges, Duke et al., Houston et al., Hunter et al. and Chapman et al. patents hereinbefore identified.

The spiral concentration of phosphate ores is a more recent expedient which has found commercial application, particularly in the Florida phosphate field. In general, such concentration procedures entail conditioning the liberated ore with reagents of the same type as contemplated for froth flotation, flowing a slurry of the conditioned ore in a spiral path at a rate of flow at least sufficient to avoid substantial agglomeration of the ore particles and collecting a concentrate from the spiral stream. Reference is made to the LeBaron Patent No. 2,783,886 for a detailed disclosure of the spiral concentration of phosphatic ores.

The spiral apparatus is formed by means of a trough constructed of any suitable material such as wood, metal or plastic. Although no specific number of turns nor any specific slope of the spiral trough is required, it has been determined that a suitable spiral pathway comprises a trough 6 feet high having five turns in the spiral. The outside diameter of the curvature of the spiral is appropriately about 24 inches, while the inside diameter of this curvature is appropriately about 6.25 inches. The slope of the spiral represents a drop of about 3 inches per foot. The trough is preferably semicircular in shape, the bottom thereof being slightly flattened.

In each turn of the spiral with the exception of the first turn, there may be one or more drawoffs or ports, positioned according to the fraction which it is desired to bleed off from each turn. For example, in the separation of silica from phosphate, the silica tends gradually to accumulate and to move in a path approaching the inner edge of the spiral. The drawoffs therefore are displaced from the center line of the flattened bottom portion of the troughs and so positioned that generally at least a portion of one component of an ore moving in the flow path will automatically fall into the drawoff.

Appropriate apparatus is disclosed, inter alia, in Humphrey Patent 2,431,610 and Hodge Patent 2,615,572.

The process of the invention is effective to recover in a form suitable for reuse a substantial portion of the negative ion reagents utilized. It is theorized that the success of the invention may be attributable to the fact that the reagent materials strongly adhere to the solids associated with the acid scrubbing liquor, yet transfer to fresh ore under the conditions which prevail in the conditioner. Moreover, undesirable solid materials which may be present in such liquors do not seem to build up in the system and appear to be eliminated with the rougher flotation siliceous tail. An analysis of a representative sample of the reagent free solid materials present in the acid scrub liquors of the commercial plant generally described in reference to FIGURE 1, appears in Table II.

TABLE II

X-Ray Analysis	Est., percent	Chemical Analysis, Wt. percent
Major Components:		
Fluorapatite	80	FE_2O_3, 1.60.
Quartz	16	Al_2O_3, 5.27.
Feldspar	2	P_2O_5, 27.75; CaO, 36.29.
Minor Components:		
Muscovite, Heavy Minerals	2	

The data appearing in Table II indicate that the solid materials present in conventional acid scrub liquors are primarily finely divided phosphate rock as distinguished from conventional phosphatic slimes which are essentially clays.

The ensuing examples reflect the best method presently known for the practice of the invention.

EXAMPLE I

Acid scrub liquors from a commercial phosphate beneficiation plant operating pursuant to the flowsheet comprising FIGURE 1 were collected on 7 different days, concentrated to about 10% solids, neutralized to a pH of about 8.5 and utilized to condition −35+150 mesh phosphate ore from the sizing section of the same plant. The 7 conditioned samples were utilized in the amounts and with the results indicated in Table III.

TABLE III

Use of Reagent Slimes Recovered From the Noralyn Amine Feed Cyclone Overflow in Flotation of Phosphate Ore

	lbs. slime per ton feed [1]	lbs. NaOH per ton feed	Grade and Recovery in Conc.		
			Wt. percent	BPL percent	BPL Rec. percent
Sample Date:					
June 2, 1958	8	0.6	45	58.8	93
June 9, 1958	20	1.0	40	58.5	90
September 19, 1958	7.6	0.6	50	48.7	96
October 10, 1958	14	0.8	45	58.9	87
October 23, 1958	8	0.7	51	57.3	94
November 5, 1958	18	1.4	36	64.5	77
November 11, 1958	20	2.0	45	51.6	85
Tall oil-fuel oil mix	2.7	0.5	55	42.6	94

[1] Flotation Feed—30% BPL.

I claim:

1. The process which comprises conditioning a liberated phosphate ore with an anionic reagent effective to coat the phosphate mineral particles present, subjecting an aqueous pulp of conditioned ore to a concentration operation to produce a concentrate containing phosphate

mineral particles bearing said reagent, treating said concentrate particles with an aqueous mineral acid to form an aqueous slurry containing said anionic reagent, separating the resulting slurry containing said anionic reagent from said concentrate particles, concentrating said separated liquid to a solids content of at least about 10% by weight, adjusting the pH of said separated liquid to at least about 7 and conditioning an additional quantity of phosphatic ore with said concentrated liquid.

2. The process of claim 1 wherein said pH adjustment is effected concurrently with said conditioning.

3. The process of claim 1 wherein said anionic reagent comprises a fatty acid.

4. The process of claim 1 wherein said anionic reagent comprises a fatty acid soap.

5. The process of claim 1 wherein said concentration operation is froth flotation.

6. The process of claim 1 wherein said concentration operation comprises spiral concentration.

7. The process of claim 1 wherein said aqueous mineral acid is sulfuric acid.

8. The process which comprises conditioning a mixture of phosphate mineral particles and silica particles with an anionic reagent effective to coat at least a portion of the surface of the phosphate particles present, subjecting an aqueous pulp of the conditioned mixture to froth flotation to provide a froth concentrate containing phosphate mineral particles bearing said reagent, treating said concentrate particles with an aqueous mineral acid to form a slurry containing said reagent, separating the resulting slurry containing said reagent from said concentrate particles, concentrating said separated liquid to a solids content of at least about ten percent by weight, adjusting the pH of said separated liquid to at least about 7, and conditioning an additional quantity of phosphatic ore therewith.

9. The process of claim 8 wherein said mixture of phosphate mineral particles and silica particles is liberated phosphate ore.

10. The process of claim 8 wherein said aqueous mineral acid is sulfuric acid.

11. The process of claim 8 wherein said anionic reagent is selected from the group consisting of the fatty acids and the fatty acid soaps.

12. The process which comprises conditioning a mixture of phosphate mineral particles and silica particles with an anionic reagent effective to coat at least a portion of the surface of the phosphate particles present forming a slurry of the conditioned mixture, gravity flowing a stream of said slurry in a spiral path at a rate of flow at least sufficient to foreclose substantial agglomeration of said particles, collecting from the spiral stream a concentrate containing phosphate mineral particles bearing said reagent, treating said concentrate particles with an aqueous mineral acid to provide a slurry containing said reagent, separating the resulting slurry containing said reagent from said concentrate particles, concentrating said separated liquid to a solids content of at least 10% by weight, adjusting the pH of said separated liquid to at least about 7 and conditioning an additional quantity of phosphate ore therewith.

13. The process of claim 12 wherein said anionic reagent comprises a material selected from the group consisting of fatty acids and fatty acid soaps.

14. The process of claim 12 wherein the said aqueous mineral acid is sulfuric acid.

15. In a process for the beneficiation of phosphatic ores wherein the liberated ore is subjected to froth flotation in the presence of an anionic reagent to produce a concentrate containing phosphate and silica particles at least some of which bear said reagent on a surface thereof, and wherein said concentrate is treated with an aqueous mineral acid to form an aqueous acid slurry containing said reagent, the improvement which comprises separating said aqueous acid slurry containing said reagent from said concentrate, concentrating said separated aqueous medium to a solids content of at least about ten percent by weight, neutralizing the concentrated medium to a pH of at least about 7, and utilizing said concentrated and neutralized medium to condition an additional quantity of phosphate ore.

16. A process which comprises conditioning a liberated phosphatic ore with an anionic reagent effective to coat the phosphate mineral particles present, subjecting an aqueous pulp of the conditioned ore to a concentration operation to produce a concentrate containing phosphate mineral particles bearing said anionic reagent, treating said concentrate with an aqueous medium to produce an aqueous slurry containing said anionic reagent, separating said anionic reagent containing slurry from said concentrate and utilizing said separated slurry to condition an additional quantity of phosphate ore.

References Cited in the file of this patent

UNITED STATES PATENTS

2,293,640	Crago	Aug. 18, 1942
2,389,727	Herkenhoff	Nov. 27, 1945
2,682,337	Hodges et al.	June 29, 1954
2,783,886	Le Baron	Mar. 5, 1957
2,936,887	Wilson	May 17, 1960
2,953,569	Last	Sept. 20, 1960