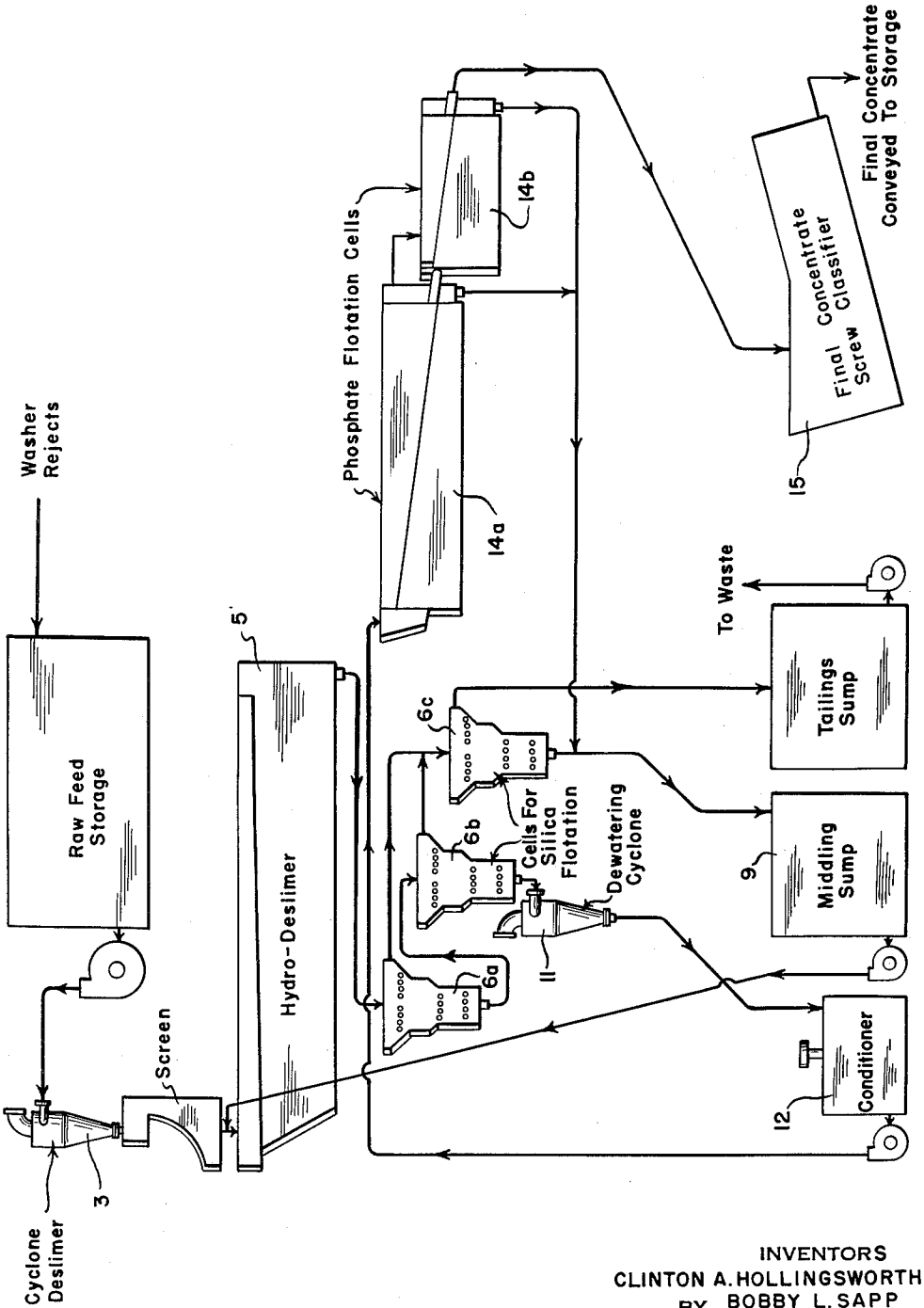
Dec. 19, 1961 C. A. HOLLINGSWORTH ET AL 3,013,664

BENEFICIATION OF PHOSPHATE ROCK

Filed Aug. 6, 1959



INVENTORS
CLINTON A. HOLLINGSWORTH
BY BOBBY L. SAPP
Pennie, Edmonds, Morton, Barrows & Taylor
ATTORNEYS

United States Patent Office 3,013,664 Patented Dec. 19, 1961

3,013,664

BENEFICIATION OF PHOSPHATE ROCK

Clinton A. Hollingsworth, Lakeland, and Bobby L. Sapp, Plant City, Fla., assignors to Smith-Douglass Company, Incorporated, Norfolk, Va., a corporation of Virginia

Filed Aug. 6, 1959, Ser. No. 832,077
5 Claims. (Cl. 209—166)

This invention relates to the beneficiation of phosphate rock and similar phosphatic materials, and in particular to an improved method of flotation of the phosphate rock to obtain a high grade phosphate concentrate.

Phosphate rock and other similar phosphatic minerals commonly are found in large natural deposits admixed with such gangue materials as sand, clay, organic matter and the like. The phosphatic constituents of these naturally occurring materials is a valuable article of commerce, and a great deal of effort has been devoted to the problem of beneficiating or concentrating these phosphatic constituents by removal of the gangue material therefrom.

In the usual process for beneficiating such phosphate-containing material (hereinafter referred to collectively as phosphate rock), the mixture of phosphatic minerals and gangue obtained from the phosphate deposit or mine is first washed to remove trash therefrom and to separate and recover the larger lumps of phosphate minerals (usually referred to as pebble rock). The remaining material (hereinafter referred to as the washer reject material) consists of a mixture of phosphate rock particles, sand, clay and similar gangue materials substantially all of which is less than about 10 mesh (Tyler Standard), and preferably is less than 14 mesh, in size. The phosphate rock constituent of the washer reject material is then concentrated and recovered for subsequent use, commonly by a combination of froth and table flotation techniques.

The need for employing a combination of froth and table flotation techniques to effect concentration of the phosphate constitutents of the washer reject material stems from the fact that it has not been feasible heretofore to float by froth flotation any significant amount of the coarse (plus 35 mesh) washer reject material, and particularly coarse silica having a particle size of more than about 35 mesh. Consequently, it has heretofore been the practice to size the washer rejects to obtain a coarse fraction having a particle size of between about minus 14 mesh and plus 35 mesh and a fine fraction having a particle size between about minus 35 mesh and plus 150 mesh. The phosphate values of the coarse fraction, not heretofore susceptible to concentration by froth flotation, are now commonly concentrated and recovered by means of table or belt flotation techniques. On the other hand, the phosphate values of the fine fraction of the washer rejects are susceptible to concentration and recovery by froth flotation techniques well known in the art, and these techniques are commonly employed for this purpose. As a result, the process currently employed in commercial practice for the beneficiation of the washer reject material requires the installation and maintenance of an elaborate and expensive flotation plant equipped to carry out both table and froth flotation operations. Moreover, the amount of phosphate values recovered by the combination of flotation operations is, at best, limited to about 83 to 88% by weight of the phosphate content of the initial washer reject material.

It has long been recognized that it would be more efficient and economical to effect concentration and recovery of the phosphate rock constituent of the washer reject material by subjecting all of this material to a single type of flotation operation, preferably froth flotation, rather than to a combination of such operations,

such as the aforementioned combination froth and table flotation.

Specifically, the most successful process heretofore employed for the froth flotation of phosphate rock, and the one currently almost universally employed by the phosphate industry for this purpose, comprises forming an aqueous pulp of the sized, deslimed phosphate-containing material, and subjecting the aqueous pulp to flotation with an anionic flotation reagent (such as a fatty acid) to collect and float from the aqueous pulp a rougher concentrate containing a high proportion of phosphate values mixed with some of the siliceous gangue. The rougher phosphate concentrate is then deoiled to remove the anionic reagent, is again deslimed to remove the accumulation of very fine particles or slimes unavoidably produced during the first flotation step and subsequent deoiling operation, and is then subjected to flotation with a cationic flotation reagent (such as one of the known amine reagents) to collect and float therefrom most of the aforementioned siliceous gangue contained in the rougher concentrate which is discarded as tails. The underflow from the second flotation step comprises a high grade, commercially valuable phosphate concentrate. Alternatively, it has also heretofore been proposed that the aforementioned sequence of anionic and cationic flotation steps be reversed, but the inherent limitations and inefficiencies of the froth flotation operation remain essentially unchanged. That is to say, all prior froth flotation techniques have been limited in their application to the concentration of the phosphate rock constituent of the washer reject material having a particle size of less than about 35 mesh, and the overall phosphate recovery is only about 83–88% by weight of the phosphate content of the initial washer reject material.

As a result of an intensive investigation of various flotation techniques, both in the laboratory and pilot plant, we have now discovered a new froth flotation process by which the phosphate constituent of the washer reject material can be efficiently and economically recovered without the necessity for sizing the washer rejects to split it into a fine fraction suitable for concentration by known froth flotation techniques and a coarse fraction that heretofore had to be concentrated by table or belt flotation techniques. Moreover, we have found that our new froth flotation process results in an unexpected and surprisingly great increase in the percentage recovery of the phosphate values of the initial washer reject material.

Our new process is based on our important discovery that the coarse particles of the washer reject material (i.e. particles between about minus 14 mesh and plus 35 mesh), and particularly the coarse silica particles, can be treated in such a way as to become "activated" so that these particles can be floated by conventional flotation reagents. Specifically, we have discovered that the coarse particles of the washer rejects become activated when these particles are recirculated through a two-step flotation operation comprising a bulk silica float followed by a phosphate float. Moreover, because the selectivity and efficiency of most known cationic reagents as collectors of siliceous material are adversely affected by the presence of slimes in the aqueous pulp, we have found that the aforementioned necessary sequence of floation steps is at the present time practicable only when the first or bulk silica flotation step is carried out in a hydraulic-pneumatic flotation cell such as that described in Patent 2,758,714 to Clinton A. Hollingsworth, the use of this type of cell avoiding the formation of slimes during the bulk silica float that heretofore prevented efficient and economic separation and recovery of a silica float free from excessive amounts of phosphate minerals. The continuous recirculation of the underflow of tails from the second or phosphate flotation step not only results in the flotation of

activated coarse silica particles but, in addition, permits recovery of the course and other difficult to float phosphatic material, and contrary to normal expectations there is no appreciable build-up of silica or other gangue materials or of difficult to float phosphate minerals due to the continuous recirculation of the underflow from the second flotation step of our new flotation process.

Accordingly, our new process for beneficiating phosphate rock having a particle size of between about minus 14 mesh and plus 150 mesh (i.e. the washer reject material) comprises subjecting an aqueous pulp of rock to flotation with a cationic flotation reagent to float from the aqueous pulp substantially all of the fine silica and recirculated activated coarse silica present in the pulp, the silica floated being discarded as tailings. The underflow from the bulk silica float, referred to as the rougher phosphate concentrate, contains substantially all of the phosphate values of the rock, unactivated coarse silica, and other gangue material such as clay. The rougher concentrate is conditioned with an anionic flotation reagent and is then subjected to froth flotation to collect and float a phosphate concentrate which is recovered as the desired product of the process. The underflow from the second flotation step which contains coarse silica and difficult to float phosphate particles is recycled to the start of the bulk silica flotation operation, the coarse silica activated as a result of being recycled through the flotation operations being floated and recovered in the first flotation step and the recirculated difficult to float phosphate values being floated and recovered in the second step of the flotation operation. As a result of our process phosphate recoveries in excess of 95%, and commonly of about 98%, by weight of the initial phosphate content of the pulp are obtained.

Our new process will be more fully described in connection with the accompanying schematic drawing of an actual plant equipped to carry out our process on a commercial scale.

The raw feed, which comprises an aqueous pulp of plant heads or washer reject material having a particle size of between about minus 14 and plus 150 mesh (Tyler Standard screen), is first deslimed by passing it through a desliming cyclone 3, is again screened to scalp out trash and oversized particles, and is again deslimed in a hydrodeslimer 5 to remove any slimes which pass through the desliming cyclone or which were produced as the result of the screening operation. As hereinafter more fully described, the underflow from the second or phosphate flotation step comprising coarse silica and difficult to float phosphate together with the underflow from the cleaner cells of the first or bulk silica flotation step of our process (collectively referred to as middlings) are recirculated and advantageously are mixed with the raw feed in the hydrodeslimer. The mixture of raw feed and recirculated material is introduced into the first of the bulk silica flotation cells 6 together with sufficient water to form an aqueous pulp of suitable density for flotation and a sufficient amount of a cationic flotation reagent (e.g., a conventional amine-type reagent) to effect flotation of the fine silica (between about minus 35 and plus 150 mesh) and the activated coarse silica (between about minus 14 mesh and plus 35 mesh).

The presence of slimes in the aqueous pulp during the bulk silica float have a serious adverse effect on both the selectivity and the efficiency of cationic reagents as collectors of siliceous material. Accordingly, the first or bulk silica flotation step of our new process must be carried out in froth flotation cells that minimize the formation of slimes during the flotation operation, and we have found that the type of hydraulic-pneumatic flotation cell described in U.S. Patent 2,758,714 to Clinton A. Hollingsworth is most satisfactory for this purpose. As will be seen from the schematic drawing, a series of three of such hydraulic-pneumatic cells 6 are advantageously employed to carry out the bulk silica float. As previously mentioned, the mixture of raw feed and recirculated material is introduced into the first cell 6*a* of the series of cells, the overflow or float from this cell comprising fine silica and activated coarse silica and the underflow or first rougher concentrate comprising the phosphatic material, unactivated coarse silica, clay pellets, and other unfloated material. The underflow from the first cell is introduced into the second or rougher concentrate cleaner cell 6*b* of the series of cells, the overflow or float from this cell comprising fine silica and activated coarse silica that was not floated in the first cell 6*a* and the underflow comprising the final rougher phosphate concentrate that is to be subjected to anionic flotation in the second step of our process. The overflow from the first and second cells is introduced into the third or tailing cleaner cell 6*c* of the series of cells, the overflow from this cell being discarded as tailings and the underflow being delivered to the middling sump 9 for recycling through the first flotation step of our process.

The rougher phosphate concentrate from the second silica float cell 6*b* comprises essentially the unfloated phosphatic material, unactivated coarse silica and clay pellets. This concentrate is dewatered, advantageously in a dewatering cyclone 11, and the dewatered rougher concentrate is delivered to a conditioner 12. The rougher concentrate is conditioned for the second step of our flotation operation by admixing it with one of the well-known anionic flotation reagents (e.g., fatty acids and their soaps) used for this purpose in the phosphate industry. The conditioned rougher concentrate is then introduced into the first of a series of phosphate flotation cells 14.

The flotation of phosphate minerals is not greatly affected by the presence of slimes in the phosphate flotation cell. As a consequence, any of the froth flotation cells heretofore employed in the phosphate industry for the flotation of phosphate rock can be employed in the second step of our new process. However, we presently prefer to employ the type of hydraulic-pneumatic cells described in Patents 2,758,714 or 2,753,045 to Clinton A. Hollingsworth.

The second step of our flotation operation is advantageously carried out in a series of at least two of the aforementioned hydraulic-pneumatic flotation cells. The conditioned rougher phosphate concentrate is introduced into the first cell 14*a* of the series of cells, the overflow or float from this cell comprising the phosphate concentrate and the underflow or tails from this cell comprising unactivated coarse silica and difficult to float phosphate particles. The overflow from the first of the series of phosphate float cells is introduced into the second or phosphate concentrate cleaner cell 14*b*, the overflow or float from this cell being the final phosphate concentrate and the underflow or tails from this cell comprising any silica or other gangue material which carried over from the first or the phosphate flotation cells.

The underflow from the two phosphate flotation cells 14 contains difficult to float phosphate and unactivated coarse silica together with other unfloatable materials such as clay pellets and the like. This material is delivered to the middling sump 9 where it is admixed with the underflow from the third cell 6*c* of the silica flotation cells 6 from whence it is delivered to the hydro-deslimer 5 for recirculation through the flotation operation. The overflow from the phosphate concentrate cleaner cell 14*b* is delivered to a screw classifier 15 which dewaters the concentrate.

The recycling of the underflow from the second or phosphate float step of our process leads to a completely unexpected and different result than that which ordinarily is achieved by recirculation of flotation tailings. That is to say, recycling of the tailings from the second step of our flotation process would ordinarily be expected to result in the mere scavenging of normally floatable fine silica and phosphate particles which somehow escaped

flotation in the course of the preceding flotation cycle. As a consequence, it would ordinarly be expected that the coarse silica and other difficult to float particles would build up in the system with resulting dilution and downgrading of the raw feed material so that eventually the tailings would have to be discarded without recycling. However, we found that the recycled coarse silica and other difficult to float particles did not build up in the system, and upon further investigation we discovered that these particles somehow became "activated" as a result of being repeatedly subjected alternately to cationic and anionic flotation, the activated particles being floated by the corresponding flotation reagent and thereby being removed from the system.

The activation of the coarse silica and other difficult to float particles is a surface phenomenon the mechanism of which is not fully understood. However, the activation of these particles is nonetheless a fact as evidenced by the appearance of coarse silica in the overflow from the coarse silica flotation cells **6** and the appearance of difficult to float phosphate particles in the overflow from the phosphate flotation cells **14** after the tailings from the second step of our process have been recycled one or more times. The surprising activation and flotation of the coarse silica and difficult to float phosphate particles makes it possible to obtain substantially greater recoveries than those achieved by the most efficient flotation processes heretofore employed in the phosphate industry. We have consistenly obtained phosphate recoveries of at least about 95%, and commonly as high as about 98%, of the phosphate content of the initial washer reject material, These phosphate recoveries obtained by the practice of our invention are to be contrasted with the recovery of between about 89 and 92% of the phosphatic material initially present obtained by the practice of our process but without recycling of the tailings from the second step of the process, and with phosphate recoveries of between about 83 and 88% of the phosphatic material originally present which are obtained by the practice of the most efficient flotation processes heretofore employed by the phosphate industry.

The clay pellets which are sometimes present in the initial raw feed material are not floated. However, these clay pellets eventually break up and disintegrate after being subjected to repeated flotation and conditioning operations, whereupon the dispersed particles of clay are removed from the system in the form of slimes.

The following examples are illustrative but not limitative to the practice of our invention:

EXAMPLE I

The flotation procedure employed in the present example was the same in its essential steps as that shown in the schematic drawing of our process hereinbefore described. The raw feed comprised washed, screened and deslimed plant heads or washer reject material having a particle size of between minus 14 mesh and plugs 150 mesh and containing 35.8% by weight of calcium phosphate (referred to as the bone phosphate of lime or B.P.L. content of the material). The feed material together with sufficient water to form an aqueous pulp containing about 20% by weight of solids and with about one pound of an amine-type cationic flotation reagent per ton of feed material on a dry basis were introduced into the froth flotation cell in which the first or bulk silica flotation step of the process was carried out. The overflow or float from the first step flotation cell contained fine silica and recirculated activated coarse silica, and this float material was discarded as tailings. These tailings were analyze and found to contain 1.32% by weight B.P.L. The underflow from the first step flotation cell comprising the rougher phosphate concentrate was dewatered, conditioned with an ionic flotation reagent in a vessel equipped with an impeller-type mixer, and the conditioned rougher concentrate was introduced into the froth flotation cell in which the second or phosphate flotation step of the process was carried out. The overflow or float from the second step flotation cell was cleaned by again subjecting this float material to anionic flotation to float and recover the final phosphate concentrate. The underflow from both of the anionic flotation operations was recirculated back to the beginning of the two step process where this material was subjected successively to cationic and anionic flotation operations along with the raw feed material. The final phosphate concentrate was analyzed and found to contain 76.91% by weight B.P.L. and 2.78% by weight of insoluble matter. The overall B.P.L. recovery was 98.0% of the phosphate content of the initial feed material. These results are summarized in the following table.

Table 1

Feed, Percent B.P.L.	Concentrate		Tails, Percent B.P.L.	Percent B.P.L. Recovery
	Percent B.P.L.	Percent Insol.		
35.80	76.91	2.78	1.32	98.0

EXAMPLE II

The flotation procedure employed in this example was the same as that employed in Example I. The feed material comprised washed, screened and deslimed plant heads having a particle size of between minus 20 mesh and plus 150 mesh, and this material contained 30.89% by weight B.P.L. The overflow from the first flotation step which was discarded as tailings contained 1.28% by weight B.P.L., and the overflow from the second flotation step of the process which comprised the final phosphate concentrate contained 75.37% by weight B.P.L., and 2.21% by weight of insoluble matter. The overall phosphate recovery was 97.6% of the initial B.P.L. content of the feed material. These results are summarized in the following table.

Table 2

Feed, Percent B.P.L.	Concentrate		Tails, Percent B.P.L.	Percent B.P.L. Recovery
	Percent B.P.L.	Percent Insol.		
30.89	75.37	2.21	1.28	97.6

EXAMPLE III

The flotation procedure employed was essentially the same as that employed in Examples I and II with the exception that the underflow from the second step of the flotation operation was not recycled through the flotation operation but instead was discarded as tails. The feed material comprised washed, screened and deslimed plant heads having a particle size of minus 14 mesh and contained 34.08% by weight B.P.L. The overflow from the first flotation step and the underflow from the second flotation step of the process were discarded as tailings and these tails contained 4.12% by weight B.P.L. The overflow or float from the second flotation step comprised the final phosphate concentrate and contained 75.19% by weight of bone phosphate of lime and 2.90% by weight of insoluble matter. The overall phosphate recovery comprised 92.9% of the B.P.L. content of the initial feed material. These results are summarized in the following table.

Table 3

Feed, Percent B.P.L.	Concentrate		Tails, Percent B.P.L.	Percent B.P.L. Recovery
	Percent B.P.L.	Percent Insol.		
34.08	75.19	2.90	4.12	92.9

The foregoing results obtained by the practice of our new process are to be compared with the average results obtained during a twelve month period from the operation of a commercial flotation plant for the beneficiation of phosphate rock. The aforesaid commercial plant employs the conventional sizing operations to split the feed material with coarse and fine fractions, these fractions being beneficiated by the usual combination of table and froth flotation operations, respectively. In this commercial process, the feed material is first subjected to anionic flotation to float a rougher phosphate concentrate which concentrate is then deoiled, deslimed, and subjected to cationic flotation to float and remove the silica content of the rougher concentrate, the underflow from the second flotation step being the final phosphate concentrate. The underflow from the first flotation step and the overflow from the second flotation step are discarded as tailings. The results obtained by the practice of our invention and those obtained by the conventional commercial plant are compared in the following table:

Table 4

	Feed, Percent B.P.L.	Concentrate		Tails, Percent B.P.L.	Percent B.P.L. Recovery
		Percent B.P.L.	Percent Insol.		
Example I	35.80	76.91	2.78	1.32	98.0
Example II	30.89	75.37	2.21	1.28	97.6
Example III	34.08	75.19	2.90	4.12	92.9
Commercial Plant 7/56-6/57	30.21	76.67	3.02	7.27	83.9

From the foregoing description of our new froth flotation process it will be seen that we have made an important contribution to the art of beneficiating phosphatic materials.

We claim:

1. The method of beneficiating phosphate rock having a particle size of less than about 14 mesh which comprises subjecting an aqueous pulp of the rock to a first froth flotation operation with a cationic flotation reagent to float from the aqueous pulp substantially all of the silica having a particle size of about minus 35 mesh, conditioning the rougher phosphate concentrate underflow from the cationic flotation operation with an anionic flotation reagent, subjecting the conditioned rougher concentrate to a second froth flotation operation to float a final phosphate concentrate which is recovered as the desired phosphate product, and recirculating the unfloated tailings from the phosphate flotation operation successively through the first and second flotation steps of the process, said recirculated tailings from the phosphate flotation step containing activated silica having a particle size of between about minus 14 mesh and plus 35 mesh and difficult to float phosphate particles, said activated silica particles and difficult to float phosphate particles being floated during the succeeding silica flotation steps and phosphate flotation steps of the process.

2. The method of beneficiating phosphate rock having a particle size of less than about 14 mesh which comprises subjecting an aqueous pulp of the rock to a first froth flotation operation with a cationic flotation reagent to float from the aqueous pulp substantially all of the silica having a particle size of about minus 35 mesh,

said cationic flotation operation being carried out in a flotation cell that minimizes the formation of slimes, conditioning the rougher phosphate concentrate underflow from the cationic flotation operation with an anionic flotation reagent, subjecting the conditioned rougher concentrate to a second froth flotation operation to float a final phosphate concentrate which is recovered as the desired phosphate product, and subjecting the unfloated tailings from the phosphate flotation operation successively to cationic and to anionic froth flotation operations, said tailings from the phosphate flotation operation containing activated coarse silica having a particle size of between about minus 14 mesh and plus 35 mesh and difficult to float phosphate particles, said activated coarse silica particles and difficult to float phosphate particles being floated during the succeeding cationic silica flotation and anionic phosphate flotation operations of the process.

3. The method of beneficiating phosphate rock having a particle size of between about minus 14 mesh and plus 150 mesh which comprises subjecting a deslimed aqueous pulp of the rock to a first froth flotation operation with a cationic flotation reagent to float from the aqueous pulp substantially all of the silica having a particle size of about minus 35 mesh, said cationic flotation operation being carried out in a flotation cell that minimizes the formation of slimes, conditioning the rougher phosphate concentrate underflow from the cationic flotation operation with an anionic flotation reagent, subjecting the conditioned rougher concentrate to a second froth flotation operation to float a final phosphate concentrate which is recovered as the desired phopshate product, and recirculating the unfloated tailings from the phosphate flotation operation successively through the first and second flotation steps of the process, said recirculated tailings from the phosphate flotation step containing activated silica having a particle size of between about minus 14 mesh and plus 35 mesh and difficult to float phosphate particles, said activated silica particles and difficult to float phosphate particles being floated during the succeeding silica flotation steps and phosphate flotation steps of the process.

4. The method of beneficiating phosphate rock having a particle size of between minus 14 mesh and plus 150 mesh which comprises subjecting a deslimed aqueous pulp of the rock to a first froth flotation operation with a cationic flotation reagent to float from the aqueous pulp substantially all of the silica, said cationic flotation operation being carried out in a non-slime forming hydraulic-pneumatic flotation cell, conditioning the rougher phosphate concentrate underflow from the cationic flotation operation with an anionic flotation reagent, and subjecting the conditioned rougher concentrate to a second froth flotation operation to float a final phosphate concentrate which is recovered as the desired phosphate product.

5. The method of beneficiating phosphate rock having a particle size of between about minus 14 mesh and plus 150 mesh which comprises subjecting an aqueous pulp of the rock to a first cationic froth flotation operation with a cationic flotation reagent to float from the aqueous pulp substantially all of the silica having a particle size of about minus 35 mesh, said cationic flotation operation being carried out in a flotation cell that minimizes the formation of slimes, subjecting the silica-containing overflow from the first cationic flotation operation again to cationic froth flotation to float a final silica fraction which is discarded as tailings, the underflow middlings from the latter cationic flotation operation being recycled to the start of the process, conditioning the rougher phosphate concentrate underflow from the first cationic flotation operation with an anionic flotation reagent, subjecting the conditioned rougher concentrate to a first anionic froth flotation operation to float an uncleaned final phosphate concentrate which is again subjected to anionic froth flotation to float a cleaned final phosphate

concentrate which is recovered as the desired phosphate product, and recirculating the unfloated tailings from both of the phosphate flotation operations successively through the cationic and anionic flotation steps of the process, said recirculated tailings from the phosphate flotation step containing activated silica having a particle size of between about minus 14 mesh and plus 35 mesh and difficult to float phosphate particles, said activated silica particles and difficult to float phosphate particles

being floated during the succeeding cationic silica flotation steps and anionic phosphate flotation steps of the process.

References Cited in the file of this patent

UNITED STATES PATENTS

2,553,905	Evans	May 22, 1951
2,614,692	Lawver	Oct. 21, 1952
2,753,997	Duke et al.	July 10, 1956