United States Patent Office 2,811,254 Patented Oct. 29, 1957

2,811,254

METHOD FOR THE BENEFICIATION OF PHOSPHATE ORES

Phillip E. McGarry, Palmerton, Pa., assignor to International Minerals & Chemical Corporation, a corporation of New York

No Drawing. Application January 6, 1955, Serial No. 480,290

6 Claims. (Cl. 209—166)

This invention relates to a process for beneficiation of phosphate ores. More particularly it relates to a process for separating phosphate material from gangue constituents of phosphate ore such as Florida pebble phosphate ore bodies. Still more particularly it relates to a method for the recovery of phosphate values normally lost in the tailings of the flotation process.

In the processing of minerals such as pebble phosphate ore bodies, generally speaking, the material is mined from the natural deposit and transferred to washers and then to flotation plants in which latter stages the material is treated in aqueous slurry form. This slurry contains sizable amounts of silica, so-called colloidal phosphates, and clays normally delineated as slimes, as well as other gangue materials. In the flotation operation the phosphate is recovered in as pure a form as possible and is substantially free of slimes. In a flotation process the phosphate particles must be of such a size that they may be economically treated.

As an initial step in obtaining a flotation slurry, the ore material is subjected to a preliminary washing operation wherein a sizable quantity of the coarse phosphatic values are removed by a screen operation which produces a pebble product containing all of the +1 mm. values. The −1 mm. values containing the phosphatic particles, silica particles, and the slimes as a slurry must be further processed to give maximum recovery of the granular material and substantially complete removal of the slime material which if allowed to remain would adversely effect the subsequent concentration process, i. e., silica removal.

A rough separation of the slime material may be accomplished in a number of ways. As practiced commercially in the phosphate fields of Florida, recourse is taken to a hydroseparation or hydrocone process. The overflow from this hydro-separator or classification system is withdrawn and sent to a settling or slime pond. This overflow is made up chiefly of suspended clay and extremely fine particles of phosphate, i. e., particles of a sufficient degree of fineness that they could not be economically recovered at any subsequent step of the process. This separation is commonly made, in the phosphate field, at approximately 150 or 200 mesh. The coarser fraction, essentially −1 mm. and +150 mesh, is separately withdrawn. Following removal of this fraction, it is sized further; usually by hydraulic classification or screening at about 35 mesh to about 48 mesh. The coarser fraction (i. e. −1 mm. +35 mesh) is then treated for removal of the phosphate values on agglomerate tables, spirals, belts, underwater screens or by froth flotation. The finer fraction (i. e. −35 +150 mesh) is then subjected to froth flotation operations.

In the froth flotation operation reagents are employed to float selectively a desired constituent of the ore. If the desired constituent is phosphate, then such reagents as fuel oil, kerosene along with long chain fatty acids and caustic soda, fatty acid soaps and the like are used. In general, the concentrates from rougher flotation steps are subjected to scrubbing with chemical agents to remove

flotation reagents and then to secondary flotation operations which float the minor constituents of the concentrates. In the case of phosphate flotation, the reagents utilized in the secondary flotation are amines derived from long chain fatty acids or salts thereof such as the acetate salt. This secondary flotation operation floats the minor constituent of the concentrate, which at this stage of phosphate flotation procedure is silica. Amines and their salts, while effective as flotation reagents for silica, are nevertheless not highly selective, i. e., are not effective depressants for phosphates. As a consequence, considerable quantities of phosphate material are floated together with the silica, and this phosphate material is lost in the silica tail which is sent to waste.

It is a primary object of this invention to overcome the shortcomings and disadvantages of the processes heretofore in use.

It is still another object of this invention to provide a method wherein the selectivity of the amine flotation is improved, thus effecting a greater recovery of phosphate.

It is still another object of this invention to provide a method wherein the amounts of amine flotation reagent are reduced with subsequent reduction in processing costs.

These and other objects of the invention will be obvious to those skilled in the art from a study of the method hereinafter outlined in detail.

Now it has been discovered that the effectiveness of amine flotation in removing silica from anionic flotation concentrates is improved, if the anionic flotation concentrate is aged prior to removal of the anionic flotation reagent.

More in detail, the method as applied to the processing of Florida pebble phosphate ores comprises, generally speaking, conditioning comminuted ore of a minimum particle size in the range between about 14 mesh and about 35 mesh with anionic reagents for flotation, effecting froth flotation to float the phosphate from the silica and minor amounts of gangue material, againg the reagentized concentrate for a minimum of about 12 hours, scrubbing the aged concentrate with mineral acid to remove anionic reagents, conditioning the scrubbed, aged concentrate with amines or salts of amines, and floating silica away from the phosphate.

Florida pebble phosphate ore processing begins with the transfer of matrix as mined from the natural deposits in slurry form. This slurry contains sizable amounts of silica, clay and miscellaneous gangue material as well as phosphate particles in various forms and particle sizes. Particles having a diameter of approximately +1 mm. are removed from the slurry by washing and screening operation and marketed as pebble. The −1 mm. material is subjected to hydroseparation or other wet classification operation. The overflow product from the hydroseparator constitutes the so-called slimes of the system and is made up chiefly of dissolved and suspended clay and so-called colloidal phosphate, i. e., phosphate of a particle size of the same order of magnitude as the suspended clays.

Underflow solids from the hydroseparation step are subjected to beneficiation processes such as froth flotation to free the phosphate of silica and minor amounts of gangue material in order to produce a phosphate concentrate, preferably of about 74% to about 78% bone phosphate of lime content if the character of the rock is such as to permit production of such a grade.

In the froth flotation operation reagents are employed depending upon the constituent which is to be floated. In a typical phosphate operation the first stage flotation utilizes carboxyl-containing negative ion agents such as are found in the mixture of fuel oil, kerosene, and long chain fatty acids as well as caustic soda. This mixture characterized by the fatty acids generally denominated

anionic agent flotation froths up and floats away a predominantly phosphate material as concentrate.

Phosphate concentrate produced by flotation in the presence of anionic reagents is sent to storage, i. e., to bins or tanks where the concentrate slurry or dewatered concentrate solids are held for a period of between about 12 and about 48 hours. Less than 12 hours aging shows a marked reduction in the effectiveness of an aging period. More than 48 hours shows substantially no gain in process effectiveness. The preferred aging period is between about 18 hours to about 30 hours.

After aging the reagentized concentrate the anionic agent or agents are removed by scrubbing the solids with about a 20% sulfuric acid solution. The language "scrubbing" as used in wet mineral processing means agitating the solids in slurry form generally in a solids content of about 45% to about 75% solids. Scrubbing is usually accomplished with between about 2 lbs. and about 6 lbs. of sulfuric acid (60° Bé.) per ton of solids. After scrubbing the phosphate concentrate, the acid solution is removed in dewatering and washing steps. Concentrate solids are then slurried in water and conditioned with amines or salts of amines derived from long chain fatty acids such as primary monoamines derived from hydrogenated tallow, fatty acids or from soya fatty acids, N-dodecylamine, N-hexadecylamine, etc.; diamines or salts of diamines such as laury fatty diamine or soya fatty diamine acetate, i. e. Armour Chemical Division Duomeen 12 and Duomac S, respectively, and the like.

Under current operating procedures, the amine tail product is sent to waste with from about 10% to about 45% bone phosphate of lime content. In a plant processing 500 tons per hour of underflow solids from the hydroseparator this percentage of B. P. L. material constitutes an appreciable loss.

The amount of negative and positive ion agents which are employed in the flotation steps which are an integrated part of the instant novel process may vary according to the phosphatic or silicious content of the ore. The amount of negative ion agent which is employed to produce a flotation concentrate may vary over a fairly wide range, but between about 0.4 pound and about 2 pounds of negative ion agent per ton of solids in the flotation pulp has been found to be particularly advantageous. When conducting a flotation operation in the presence of positive ion agent, for example, long chain aliphatic amines or their water soluble acid addition salts, the amount of such reagent may vary over fairly wide limits but between about 0.2 pound and about 1 pound of such reagent per ton of ore based upon the solids content of the reagentized pulp is conveniently employed. The amount of frothing and other agents, such as pine oil, kerosene, fuel oil, etc., which is optionally but generally present during flotation may also vary over fairly wide limits, between about 0.1 pound and about 1 pound per ton of solids in a flotation pulp. The type of reagent employed will be particularly effective within certain pH ranges, for example, the negative ion agents are generally effective in the alkaline pH range. Negative ion reagents selected from the group comprising fatty acids, resin acids, tall oil, naphthalene acids, soaps of these reagents, etc. are particularly effective when conducting a flotation operation at a pH in the range between about 7 and about 9. The invention is not limited to such reagents, but any reagent which has an affinity for phosphate values may be employed similarly. Reagents other than long chain aliphatic amines or their water soluble acid addition salts are effective at pH's in the range between about 3 and about 6. It will be obvious to those skilled in the art of flotation that the selectivity of any particular reagent or mixtures of several reagents is not usually sufficient to achieve a complete recovery of the desired component in any one flotation operation. It is, therefore, within the scope of the invention to recycle various pulp streams from any particular flotation operation whether this will be a rougher or a cleaner flotation.

The invention will be better understood from the following description and examples.

Example I

A phosphate rock such as the type found in the phosphate pebble fields of central Florida is subjected to a washing operation in order to remove slimes and organic matter. The washed rock in an aqueous pulp is subjected to screening or hydraulic sizing operation whereby the larger particles of rock are segregated from material which is −35 mesh particle size. The material remaining after the pebble has been removed, which consists of phosphate, clay, silica and the like, is further treated by hydroseparation to overflow the fine particles normally discarded from the system as slimes and to recover underflow particles which are then conditioned in an aqueous pulp containing about 60% solids with about one pound per ton of ore solids, the reagent comprising about 75% tall oil and about 25% kerosene. About 3 pounds of fuel oil is added to the mixture and sufficient caustic soda is added to give the mixture a pH in the range of between about 8.5 to about 9.0. The resultant pulp is then subjected to a flotation operation at a solids content of about 30% by weight in a Denver laboratory machine and a float recovered containing approximately 60% tricalcium phosphate, the balance being silica and silicious gangue. A portion of this phosphatic concentrate from the plant phosphate ore cleaner section was divided into two portions. Portion A was conditioned with varying proportions of amine reagent. Portion B was held for 48 hours, then divided into several portions and conditioned with various amounts of the same amines for flotation. This phosphatic concentrate was scrubbed in each instance just prior to amine flotation for 3 minutes at 65% solids with about 4 pounds of sulfuric acid (60° Bé.) per ton of concentrate solids in order to remove the anionic reagents therefrom. The acid treated product was washed until it was substantially neutral and then conditioned in an aqueous pulp with a mixture of long chain aliphatic amines, the latter comprising a mixture of about 73% mono-octadecylamine and about 24% mono-hexadecylamine, known in the trade as "Armac T," and 5% of a water solution of sodium hydroxide added so as to bring the tailing water to a pH of between about 7.6 and about 7.8.

Kerosene was added to the mixture so as to give a weight ratio of kerosene to amine of approximately 3 to 1. This conditioned concentrate was then subjected to a flotation operation at a solids content of about 30% in a Denver laboratory flotation machine. The float product from this operation is a predominantly silica material.

Phosphate concentrate removed from the Denver flotation machine was analyzed for acid insoluble material by boiling a sample of concentrate with a large excess of hydrochloric acid for 15 minutes, filtering the undissolved material, and determining the insol on a dry weight basis.

Results were as follows:

	Amine, Lbs./Ton, For Conc. Insol Grade of—		
	2%	3%	4%
Fresh Fatty Acid Conc.	0.52	0.42	0.37
Same Fatty Acid Conc. (48 Hrs.)	0.28	0.21	0.15
Amine Saving, Lbs./T. of Amine Feed	0.24	0.21	0.22

Example II

Samples of fatty acid concentrate produced in a phosphate flotation plant having a rougher separation flotation and a cleaner and recleaner operation were held for 1, 24, 48 and 72 hours. Portions held for each period of time were scrubbed in slurry form at approximately 65%

solids concentration with 4 pounds of sulfuric acid per ton of dry solids just prior to conditioning in slurry form by adding to each washed portion varying amounts of 5% solution of the above amines mentioned in Example I known commercially as "Armac T." Each conditioned portion was introduced into the Denver subaeration flotation machine and a concentrate recovered under identical operating conditions. Samples of each concentrate were analyzed as described in Example I to determine the proportion of insoluble material present in the concentrate after amine flotation.

Results were as follows:

Age of Fatty Acid Concentrate in Hours	Amine, Lbs./Ton, For Conc. Insol Grade of—		
	2%	3%	4%
1		0.30	0.22
24			0.19
48		0.20	0.16
72	0.30	0.17	0.14
Amine Saving, Lbs./Ton, After:			
24			0.03
48		0.10	0.06
72		0.13	0.08
Amine Saving, Percent, After:			
24			13.6
48		33.3	27.2
72		43.4	36.4

It will be noted that while a 2% by weight insoluble material grade concentrate could not be made on fresh feed, it could be made on concentrate aged for 72 hours with the same quantity of amine reagent per ton of solids as was required for the production of a 3% insoluble material grade product from fresh feed. Further, the aging of feed, it will be observed, lowers the reagent consumption required to obtain the same grade of product as is produced by the conventional operation shown in Example I.

Having thus described my invention, what I claim is:

1. In a process for the flotation of phosphate ore wherein phosphate ore in a liberated state is subjected to flotation with carboxyl-containing negative ion flotation agent and the flotation product is subjected to a second flotation operation employing nitrogenous positive ion flotation agent, the improvement comprising aging the phosphate flotation product from the negative ion flotation while still reagentized for at least about 12 hours, removing negative ion flotation agent after aging, and subjecting the aged concentrate to flotation employing nitrogenous positive ion flotation agent to recover a phosphate concentrate.

2. The method of improving the grade of phosphate from Florida pebble phosphate ore which comprises first subjecting ore in the liberated state to a flotation operation employing carboxyl-containing negative ion flotation agent, recovering a phosphate concentrate, aging the reagentized concentrate for a period in the range of between about 12 and about 48 hours while still reagentized, scrubbing the reagentized concentrate to remove negative ion flotation agent, conditioning the scrubbed concentrate with nitrogenous positive ion flotation agent, and subjecting the conditioned concentrate to a froth flotation operation to recover a beneficiated fraction of phosphate ore.

3. The method of improving the grade of phosphate from Florida pebble phosphate ore which comprises wet classifying the ore to remove the low density fraction slimes therefrom, subjecting the slime-free ore to a flotation operation at a pH in the range between about 7 and about 9 for the concentration of phosphate values with carboxyl-containing negative ion agent, aging the phosphate concentrate while still reagentized with anionic reagent for a period of between about 12 and about 48 hours, scrubbing the concentrate to remove negative ion agent, and subjecting the phosphatic concentrate to a silica flotation operation with a long chain aliphatic amine acid addition salt to recover a phosphate concentrate.

4. The method of improving the grade of phosphate from Florida pebble phosphate ore which comprises washing and sizing the ore to remove the +1 mm. size phosphate pebble, wet classifying the −1 mm. material to remove the −200 mesh standard screen size so-called slime material, subjecting the +200 mesh standard screen size fraction from the classification in a finely divided step to a flotation operation at a pH of at least higher than 7 for the concentration of phosphate values with carboxyl-containing negative ion agent, aging the phosphatic float while still reagentized for a period between about 12 hours and about 48 hours, subjecting the phosphatic float to a silica flotation operation with a long chain aliphatic amine-acid addition salt to recover a concentrate rich in phosphate material.

5. The method of improving the grade of phosphate from Florida pebble phosphate ore which comprises wet classifying the ore to remove the low density fraction slimes therefrom, subjecting the slime-free ore to a flotation operation at a pH in the range between about 7 and about 9 for the concentration of phosphate values with carboxyl-containing negative ion agent, aging the phosphate concentrate while still reagentized with anionic reagent for a period of between about 12 hours and about 48 hours, scrubbing the concentrate with between about 2 pounds to about 6 pounds of sulfuric acid calculated as 60° Bé. acid per ton of solids to remove negative ion agent, and subjecting the phosphate concentrate to a silica flotation operation with a long chain aliphatic amine acid addition salt to recover a phosphate concentrate.

6. The method of improving the grade of phosphate from Florida pebble phosphate ore which comprises wet classifying the ore to remove the low density fraction slimes therefrom, subjecting the slime-free ore to a flotation operation at a pH in the range between about 7 and about 9 for the concentration of phosphate values with carboxyl-containing negative ion agent, aging the phosphate concentrate while still reagentized with anionic reagent for a period of between about 12 hours and about 48 hours, scrubbing the concentrate with between about 2 pounds to about 6 pounds of sulfuric acid calculated as 60° Bé. acid per ton of solids to remove negative ion agent, and subjecting the phosphatic concentrate to a silica flotation operation with a mixture of amines consisting predominantly of mono-octadecylamine and mono-hexadecylamine to recover a phosphate concentrate.

References Cited in the file of this patent

UNITED STATES PATENTS

2,409,665 Cole et al. ---------- Oct. 22, 1946