The present invention relates to the concentration of phosphate minerals from their ores and more especially to an improved double flotation process.

In concentrating phosphate minerals from their ores of the size between about minus 28 and about plus 150 mesh by flotation, one method heretofore practiced extensively has been to make a pulp of the finely divided phosphate-bearing ore in a flotation machine and agitate the mixture in the presence of a suitable negative-ion reagent and frothing material while bubbling air there through. The froth collecting at the top of the machine contains a greater proportion of phosphate minerals and around 3 to 10 per cent of siliceous impurities. In this method the phosphate particles are rendered non-wettable by employing reagents which selectively coat the phosphate material. Such reagents are usually a fatty acid, an inert oil, such as fuel oil, and caustic soda or a mixture of soap and an inert oil.

Another method of concentrating phosphate minerals is of a reverse type, which employs a positive-ion reagent, together with suitable frothing material, to selectively render the siliceous gangue non-wettable and hence floatable. The float is removed as tailing or waste, while the greater proportion of the phosphate concentrate remains in the non-floated material.

This process has been found, however, because of the large amounts of reagents required to make it workable.

A third method of separating phosphate from the siliceous gangue results from combining the two steps outlined above. According to this method a dual process is employed, whereby the phosphates are first roughly concentrated by flotation with a negative-ion reagent to produce a product containing a substantial amount of silica, and the rougher phosphatic concentrate, after a suitable intermediate treatment, subjected to the action of a cationic reagent in the presence of proper cooperating agents to float from the rougher phosphatic concentrate the siliceous impurities contained therein. The intermediate treatment between the two concentrating operations of the double flotation process consists in agitating the rougher phosphatic concentrate, obtained from the first flotation step, with a mineral acid, such as sulfuric acid, and then removing the dead reagents. The acid decends or removes the charge of the phosphates so that they can no longer float, and most of the dead negative-ion reagents, such as soap and fuel oil, rise to the surface and may be removed.

According to the double flotation method heretofore practiced, the phosphatic concentrate, after the intermediate treatment with the mineral acid, is further conditioned for the cationic reagent treatment. Heretofore it has been the practice to vigorously agitate the rougher phosphatic concentrate with the mineral acid, then thoroughly wash, scrub, as by raking, and de slime the concentrate before the treatment thereof with the positive-ion reagent, such as the higher amines or their salts. The underlying reason for such a thorough cleaning operation has been thought to be productive of better results, since by thoroughly cleaning the silica particles by agitating vigorously with mineral acid, then thoroughly washing to remove all scum and dead reagents, it was thought that the silica would thus be in a condition better to receive the effects of the cationic reagent, thus making it possible not only to increase the amounts of floated silica, but also to decrease the amounts of reagents required to float the maximum of silica. In the art of froth-floatation it is generally considered to be good practice to rid the material to be subjected to flotation of all alimes, scums, and other impurities, the presence of which reduces the amounts of floated material and increases the amounts of reagents required to float the mineral. By "silica" is meant the siliceous impurities, or gangue, usually found accompanying phosphate minerals as they exist in the natural state.

I have now discovered that the use of a mineral acid when employed in a proper manner has the additional function of activating the silica contained in the rougher concentrate so as to make it more receptive to the effects of the reagents used in the second concentrating operation, but pursuant to the procedure heretofore practiced the activation of the silica by the mineral acid is destroyed, and thus not all of the functions of the mineral acid are utilized. On the other hand, if the activating property imparted to the silica by the mineral acid is utilized, results far superior to any heretofore achieved in the double flotation process for the recovery of phosphate minerals are obtained. I have also found that, whereas according to prior practice the addition of the cationic reagent occurs in an acidic medium, according to my process good results are obtained on the alkaline side, and best results at a definite alkaline pH range, as hereinafter to be described.

I have discovered that the destruction heretofore of the activation of the silica by the mineral acid is caused by the vigorous agitation involved
in the mixing of the phosphatic concentrate with the mineral acid and in the subsequent vigorous washing operations, and that such treatment produces results opposite to those desired. The activation of the silica by the mineral acid is perhaps destroyed by the abrasive and rubbing action of one silica particle with another. I have also found that, whereas hitherto better results have been secured by the use of amine salts, such as octadecyl amine acetate as the cationic reagent, in my process equally good results are achieved by the use of either the free amines or the salts thereof.

To retain the activation imparted by the mineral acid to the silica and to predispose the silica to the positive-ion reagent treatment, I have found that it is essential that the treatment of the rougher phosphatic concentrate with the mineral acid and the subsequent decantation and washing be carefully controlled.

In carrying out the invention, it is important that two essential factors be kept in mind: first, a minimum of mixing and reagent removal being employed to bring about contact of the mineral acid with the silica concentrate; second, once the phosphates have been treated with the acid, the subsequent operations of washing, treating with the cationic reagent to float the silica, and floating are carried out promptly after a regulated period of conditioning time, for example, 10 to 20 seconds, since the silica is deactivated on standing in water. Also, if, in the second concentrating operation, floating is not begun soon after mixing the floating agents with the concentrate, the phosphates absorb the silica flotation reagents or the silica is deactivated by remaining in contact with the phosphate.

In order to effect cleaning and yet dispense with the vigorous washing and scrubbing of the concentrate after the mineral acid treatment, I have devised a special process, hereafter to be fully described.

In treating with a mineral acid the phosphatic concentrate obtained from the first concentrating operation, agitation of a force sufficient merely to mix the acid with the concentrate is carried out. If the agitation is too vigorous, the activation of the silica is greatly impaired. Also, in the decantation step and in the washing and scrubbing operations the concentrate is maintained in as quiescent a state as possible, while the scum and dead reagents are removed.

Retention of the charge imparted to the silica by the mineral acid produces such a change in the silica as to bring about certain modifications in the second concentrating operation, which cause superior results. For example, while according to the prior art, flotation of the silica occurs in an acid medium, according to my process good results are achieved on the alkaline side, a pH of about 7.5 to 8 usually producing the best results. Moreover, according to the prior method the use of amine salts as cationic reagents gives better results while, in accordance with my process, one may use the free amines and amine salts interchangeably as cationic reagents. Because of these modifications in the second concentrating operation, it is possible to effect a more complete separation of the silica impurities from the rougher phosphatic concentrate, whereby a silica float free of phosphates and a final phosphatic concentrate containing less silica are obtained.

A preferred embodiment of the invention is illustrated by the following drawings.

Figure 1 is a diagrammatic side elevation, partly in section, showing the equipment used in the mixing of anionic reagents and phosphatic feed, the first flotation step, the washing operation, and the second flotation step.

Figure 2 is a plan view of the mechanism shown in Figure 1.

Figure 3 is a detailed side elevation of the washing equipment.

Figure 4 is a sectional end elevation of the washing equipment, taken on line 4-4 of Figure 3.

Figure 5 is a plan view of a perforated plate forming a part of the washing equipment.

Referring to the drawings, phosphatic feed is introduced into the first of a series of mixers 10 by means of chute 5. The negative-ion reagents, such as a fatty acid, an inert oil, and caustic are introduced therein by means of inlets 11, 12, and 13, respectively. The anionic flotation reagents are introduced separately, each reagent through its inlet 11, 12, or 13.

After stirring of the ore with the reagents, the resultant mixture is diluted with water introduced by line 17 at the overflow 18, and a pulp is formed, which is introduced into the first of a series of flotation cells 20. The flotation cells may be of any conventional type, and in the drawings the flotation cells are of a type wherein the pulp is frothed by means of air introduced into the cells at the bottom thereof by means of inlets 21, which connect with air line 22. Bubbling air through the pulp contained in cells 20 causes a frothing of the phosphatic material. The froth rises to the top of the cells and is mechanically discharged into launder 24, while the tailings, or waste material, are impelled over baffles 25 by means of impellers (not shown) and are withdrawn through outlet 26.

The rougher phosphatic concentrate collects at point 27 of launder 24 (see Figure 2) preparatory to its removal from the launder through line 28 by means of pump 29. Oil which is removed from the launder and mixed with the concentrate is carried away through line 25 and the mixture of acid and rougher phosphatic concentrate, as a slurry, is propelled by pump 29 through line 30 into upper vessel 32, which is preferably a V-box. Line 30 is provided with four outlets 33, so as to effect a uniform distribution of the slurry over the length of V-box 32. Sufficient mixing action is afforded by pump 29 and in line 30 to effect the necessary contact of the acid with the material to deaden the charge imparted to the phosphatic material by the negative-ion reagents, and to activate the silica contained therein. The mixing action in the pump and in line 30, although sufficient to bring about contact between acid and phosphatic material, is insufficient to deactivate the charge on the silica imparted thereby to the concentrate.

After a suitable amount of phosphatic slurry is accumulated in V-box 32, sufficient water is introduced into V-box 32 by means of line 34 to overflow the dead anionic reagents and remaining mineral acid, but insufficient to overflow any solid matter. The spent negative-ion reagents and the colloid acids run to launder 37 and removed to waste through outlet 38. The washing operation in V-box 32 removes roughly 75 per cent of the dead reagents and excess mineral acid.
The partially washed phosphatic material then passes through outlets 40, located at the bottom of V-box 32, which outlets are provided with suitable means 41, such as pinchcocks or valves, for closing the orifices of outlets 40 and thus controlling the amount of material entering the washing tubs 45. These washing tubs, as the upper vessel 32, are preferably V-shaped. The shape of the washing boxes, or vessels, gives direction to the phosphatic material and makes possible a funneling of the material from one place to another with a minimum of agitation. The phosphatic material enters the washing tubs 45, it is met with a countercurrent of clean water introduced through inlets 47 (Figure 4), the water coming up through the perforated plates 48, which are placed in the bottom of the washing boxes 45. Plates 48 are provided with a large central opening 49 surrounded by a number of smaller openings. The velocity of water entering the wash boxes is sufficient to overflow remaining dead reagents, but insufficient to prevent the phosphatic material from settling and passing through the openings 49 of the perforated plates 48 and through outlets 50 into launder 51.

The phosphatic material flows into overflow 53, where the positive-ion reagents for the flotation of silica are collectively introduced by means of line 54, after which the material is frothed there-in cells 55 which are of the same type as those employed in the first concentrating operation, namely, cells 20. Air is introduced into the cells by inlets 56 which connect with air line 57. Silica in the form of a froth results from the bubbling of air through the cells and is gathered in launder 60 and removed through line 61, while the depressed phosphatic material is collected at 62.

As hereinbefore mentioned, the mineral acid treatment of the rougher phosphatic concentrate not only serves to deslime the effects of the reagents employed to float the phosphates from phosphatic feed, but also activates the silica which remains in the rougher phosphatic concentrate after the first concentrating operation, and which it is desired to remove therefrom by a later flotation step employing reagents of a charge opposite to that possessed by the reagents used to float the phosphates. These positive-ion reagents float the silica and depress the phosphates. The power of the positive-ion reagents to float the silica is enhanced by the preservation of the activation imparted to the silica by the mineral acid. This activation of the silica by the mineral acid is readily destroyed, and the means employed in mixing acid with the rougher phosphatic concentrate and in subsequently washing the resultant mixture are such as to effect mixing and washing with a minimum of agitation, since too much agitation destroys the activation of the silica. According to the invention herein described, the washing means are effective in washing the rougher phosphatic concentrate and also in preserving the activation of the silica. For best results, it is important that the washing of the material in the V-box and in the washing tubs be carried out as promptly as possible, since the silica tends to become deactivated upon prolonged standing with the water in the V-box and wash tubs.

In order to illustrate how silica may be activated by means of a mineral acid and subsequently deactivated by scrubbing, the following examples are given, in which the silica was in the form of minus 35 mesh sand that had been washed clean of slimes and other impurities, and the mineral acid was sulfuric.

**Example I**

300 grams of wet sand were treated with 0.5 g. of 95 per cent sulfuric acid. The mixture of acid and sand in a pulp of about 50 per cent solids was conditioned in a glass jar in which the sand was not allowed to come in contact with any metal. The acid water was then decanted, and the sand washed once with clean water. The treated sand was then introduced into a laboratory flotation cell with 0.5 g. of sodium hydroxide, 0.04 g. of amine reagent, and 0.04 g. of B-23 frother (a product marketed by DuPont consisting of 40-45 per cent of 2-4 dimethylpentanol-1, 40-45 per cent 2-4 dimethylhexanol, and 6-10 per cent of unidentified ketones). In this test 200 g. of silica were floated.

**Example II**

300 grams of wet sand were treated with 0.5 g. of 95 per cent sulfuric acid. The mixture of acid and sand in a pulp of about 50 per cent solids was conditioned in a glass jar in which the sand was not allowed to come in contact with any metal. The acid water was then decanted, and the sand washed once with clean water. The treated sand was then introduced into the laboratory M. S. cell with 0.5 g. sodium hydroxide and 0.4 g. of amine reagent and 0.04 g. of B-23 frother. In this test only 142 g. of silica were floated, as compared with Example I in which no scrubbing or agitation of the silica occurred as was the case here.

**Example III**

300 grams of wet sand were introduced into a laboratory M. S. cell with 0.05 g. of sodium hydroxide, 0.04 g. of an amine reagent containing 70 per cent primary amines and 30 per cent nitrogen obtained from double distilled cottonseed fatty acids, and 0.04 g. of B-23 frother. In this test, wherein the acid treatment of sand was omitted, only 32 g. of silica were floated.

In addition to observing special conditions in the washing step, I have found that, in order to achieve best results, flotation of the silica in the second concentrating operation is carried out at an alkaline pH. Although a pH range of 7-8 produces satisfactory results, still better results are obtained at a pH of between 7.4 and 8. Adjustment of the pH is effected by means of any suitable base, such as the hydroxides of the alkalai metals and of the alkaline earth metals. Sodium hydroxide is generally to be preferred for it is readily available and consequently cheap. The proper pH range serves to depress the phosphates, and I have found that this effect may be enhanced by the addition of starch to the sodium hydroxide solution.

Although sulfuric acid is the preferred mineral acid for the preconditioning of the concentrate prior to the treatment thereof in the second concentrating operation, other mineral acids, such as hydrochloric acid and nitric acid, may be employed. Other acid reacting substances, for example, acid reacting inorganic salts, such as sodium acid sulfate, potassium acid sulfate, etc., may be employed. While the effective amounts of the latter substances are large, it is not intended to exclude them from the scope of the invention and are embraced by the term "mineral acid" used in the claims.
As negative-ion reagents for the flotation of phosphates in the first concentrating operation may be mentioned fatty acids of both animal and vegetable origin and their soaps, fatty acids obtained from wood by-products, the resin acids and their soaps, esters of inorganic acids with high molecular weight aliphatic amines and their salts, the resin amines and their salts, esters formed between the high molecular weight fatty acids and amino alcohols, etc.

Examples of positive-ion reagents for the flotation of silica in the second concentrating operation are the high molecular weight aliphatic amines and their salts, the resin amines and their salts, esters formed between the high molecular weight fatty acids and amino alcohols, etc.

In general, however, preference is for the high molecular weight free aliphatic amines, such as n-monohexadecyl, n-monoctadecyl, and n-monoctadecemyl amines.

Obviously, the amounts of flotation reagents in either concentrating step may be varied within wide limits. Good results may be achieved in floating the phosphates by using 0.3 to 1.0 pounds of 20 per cent sodium hydroxide, 0.05 to 0.2 pounds of fatty acids, 1 to 4 pounds of fuel oil, all for each ton of feed.

In the second concentrating operation, approximately 0.04 pounds of distillate or kerosene, 0.14 to 0.16 pounds of positive-ion reagent, approximately 0.04 pounds of frother, pine oil or the higher alcohols such as B-23, plus 0.05 to 0.2 of 20 per cent sodium hydroxide, are sufficient amounts of silica flotation reagents for each ton of original feed. The amount of sodium hydroxide indicated above is usually sufficient to bring the pH of the pulp up to 7.4 to 8.0.

It is, of course, understood by those skilled in the art that substances other than those mentioned above may be employed as effectively. Also, it is to be understood that some of the substances mentioned may not only be substituted by others, but may be omitted altogether.

Example IV

In order to further illustrate the practical operation of the invention, comparative test runs will be described on two sample portions of the same phosphatic feed which had been screened over a 28 mesh screen. The fraction passing through the screen was washed and subjected to the first flotation step to float a rougher phosphatic concentrate therefrom. Before flotation, a pulp of about 25 per cent solids was made of the phosphatic feed. In both samples the same amounts of negative-ion reagents were employed for each ton of feed, namely, 0.3 pounds sodium hydroxide, 0.4 pounds fatty acid, 1.33 pounds fuel oil. Both samples of rougher phosphatic concentrate were then mixed with 3.0 pounds of 95 per cent sulfuric acid per ton of rougher concentrates.

In sample No. 1 the mineral acid and phosphatic material were thoroughly agitated, the dead reagents decanted, and the phosphates thoroughly washed with water and scrubbed by raking. Sample No. 2 was subjected to the mineral acid treatment and subsequent washing in accordance with the principles of this invention; that is, the rougher phosphatic concentrate was mixed with the acid and washed with water with a minimum of agitation. After the mineral acid and subsequent washing operations, both samples of phosphates were treated with positive-ion reagents to float the silica therefrom. Sample No. 2, treated in accordance with this invention, was mixed with 0.4 pounds sodium hydroxide, 0.32 pounds of an amine reagent comprising a mixture of the amines n-monohexadecyl, n-monoctadecyl, and n-monoctadecemyl, and the pH of the resultant mixture being 7.5. The mixture was frothed and the silica floated. The amount of silica in the finished concentrate was 1.61 per cent. The rougher phosphatic concentrate of sample No. 1, which had been thoroughly cleaned and scrubbed following the mineral acid treatment, was formed into a pulp of about 25 per cent solids and frothed in the presence of about 0.32 pounds of octadecylamine acetate, the pH of the solution being 6.8. The amount of silica remaining in the finished concentrate in this case was 4.48 per cent.

In another comparative test wherein two samples were treated similarly, as above described, the amount of silica remaining in the finished concentrate treated in accordance with prior art methods was 7.86 per cent, whereas the silica content in the finished concentrate obtained by following the principles of the invention was 2.02 per cent.

While the invention has been described as directed to the concentration of phosphate minerals from their ores, it is not to be intended as being limited to the purification of phosphates only. Other ores, such as those containing lead, zinc, iron, or copper minerals, or even coal, which are subjected to a froth-flotation process to remove the siliceous impurities therefrom, fall within the scope of this invention. That is, the invention may be applied to any case in the art of froth-flotation wherein the siliceous impurities are to be floated efficiently, which effect may be achieved by activating the silica and maintaining it in an active state, as hereinabove described.

Obviously, many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imparted as are indicated in the appended claims.

1. Claim:

1. In the process of treating mineral-bearing material by flotation whereby the siliceous impurities incorporated therewith are floated, the steps of mixing mineral acid with said mineral-bearing material to activate the siliceous impurities, flowing said mixture to a frothing zone contacting said mixture with water diffused into said zone whereby substantially all of the acid is removed, withdrawing said mineral-bearing material from said zone, and adding silica flotation reagents thereto before any appreciable agitation has destroyed the acid activation of the silica.

2. In the process of treating mineral-bearing material by flotation whereby the siliceous impurities incorporated therewith are floated, the steps of mixing mineral acid with said mineral-bearing material to activate the siliceous impurities, flowing the mixture so formed to a frothing zone, washing said material with water diffused into said zone to remove substantially all of said acid therefrom, withdrawing said washed, acid-treated, mineral-bearing material from said zone, and adding positive-ion reagents to said material before any appreciable agitation has destroyed the acid activation of the silica, and floating the siliceous impurities at a pH between about 7.4 and 8.

3. The process of concentrating phosphate minerals from their ores, which comprises making a pulp of the ore of a size suitable for flotation, subjecting said pulp to a concentrating operation in the presence of a negative-ion reagent to separate a rougher phosphatic concentrate admixed with a lesser proportion of silica, mixing
said phosphatic concentrate with mineral acid to destroy the effects of the negative-ion reagents and to activate the silica, flowing the mixture of concentrate and acid to a quiescent zone, washing the acid-treated concentrate with water diffused into said zone to remove the spent reagents and substantially all of the acid from said concentrate, and then subjecting the pulp of the phosphatic concentrate before any appreciable agitation has destroyed the acid activation of the silica to a second concentrating operation in the presence of a positive-ion reagent to separate therefrom a greater proportion of silica, thereby producing a relatively pure phosphatic concentrate.

4. The process of concentrating phosphatic minerals from their ores, which comprises making a pulp of the ore of a size suitable for flotation, subjecting said pulp to a concentrating operation in the presence of a negative-ion reagent to separate a rougher phosphatic concentrate admixed with a lesser proportion of silica, mixing said phosphatic concentrate with mineral acid to destroy the effects of the negative-ion reagents and to activate the silica, washing said concentrate with water diffused into a quiescent zone to remove the spent reagents and substantially all of the acid from said concentrate, removing said washed, acid-treated concentrate from said zone, and then subjecting the pulp of the phosphatic concentrate before any appreciable agitation has destroyed the acid activation of the silica to a second concentrating operation in the presence of a positive-ion reagent at a pH of about between 7.4 and 8 to separate therefrom a greater proportion of silica, thereby producing a relatively pure phosphatic concentrate.

5. In the process of treating mineral-bearing material by flotation whereby the siliceous impurities incorporated therewith are floated, the steps of mixing mineral acid with said mineral-bearing material to activate the siliceous impurities, flowing the mixture thus formed to a quiescent settling zone, withdrawing the settled concentrate from the bottom of said zone, introducing said concentrate into a quiescent washing zone, diffusing water into said zone to float substantially all of the acid from said concentrate, removing the settled, washed concentrate from the bottom of said zone, and adding positive-ion reagents to the settled, washed concentrate before any appreciable agitation has destroyed the acid activation of the silica.

WILLIAM ARTHUR HODGES.

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