United States Patent Office

2,766,883

Patented Oct. 16, 1956

1

2,766,883

PROCESS OF DEOILING PHOSPHATE CONCENTRATE BY MEANS OF FINELY DIVIDED SOLIDS

Otto Charles Chapman, Lakeland, and Arnold Walker Dean, Nichols, Fla., assignors to Virginia-Carolina Chemical Corporation, Richmond, Va., a corporation of Virginia

No Drawing. Application December 30, 1954, Serial No. 478,917

7 Claims. (Cl. 209—166)

The present invention is concerned with the concentration of phosphate minerals from ores of the type found in the Florida pebble phosphate field and more especially with an improved double flotation process. Specifically the invention embodies an improved process for deoiling the rougher phosphate concentrate produced in the first step of the double float process.

Phosphate flotation methods were, for many years, confined to the use of anionic collecting agents with the resultant flotation of a phosphate bearing froth which contained silica to the extent of about 6%. With the advent of U. S. Patents 2,222,728 and 2,293,640, issued respectively to Francis X. Tartaron and Arthus Crago, the phosphate industry switched almost exclusively to the use of a combination of anionic and cationic reagents. In this combination the phosphate feed is first oiled with the anionic fatty acid reagent, in order to float a silica bearing phosphate froth. This is followed by a deoiling step to remove the effect of the anionic reagent and finally by a recoating with a cationic reagent and flotation to produce a low-silica, phosphate machine discharge product. This is the essence of the so-called double flotation process.

According to the double flotation method now practiced extensively in the industry, the phosphate ore of about minus 35-mesh, relatively free of slime and containing about 70% solids is conditioned with the anionic or negative-ion agent and fed to the flotation cells. The negative-ion agent collects and removes a rougher concentrate containing a high proportion of the phosphate values mixed with some silicious gangue. This first concentration step can be carried out in such a manner as to collect almost the whole amount of the phosphate present in the ore but the rougher concentrate so obtained will still contain from 10 to 20% of silica.

Examples of negative-ion agents which may be used in carrying out the first concentrating operation have been listed in U. S. 2,293,640 and comprise the higher fatty acids, such as fish oil fatty acid and oleic acid and their soaps. They include the resin acids and their soaps, wood by-product fatty acids, naphthenic acids and their salts, the higher sulfo-fatty acids and their salts formed from appropriate bases, acid esters of high-molecular-weight aliphatic alcohols with inorganic acids and their salts and high molecular weight xanthates and other similar compounds.

In present practice, the rougher phosphate concentrate is deoiled with a mineral acid, as for example according to U. S. 2,293,640. It has been the general belief that it is necessary to remove completely the anionic, fatty acid reagents before carrying out the cationic amine flotation step. Since the fatty acids are normally oils, this step has become known as a deoiling process. U. S. 2,599,530 suggests that if a small amount of mineral acid is allowed to remain on the rougher concentrate that the silica will be activated and more easily floated in the succeeding cationic concentration step.

It is a prime object of our invention to dispense entirely with the use of mineral acids for deoiling the rougher concentrate. Corrosion is a very big problem in the flotation industry and a large amount of this corrosion can be attributed to the dilute acids employed in this deoiling step. To eliminate the use of these acids and thereby to eliminate the need for handling acids in the flotation operation would materially aid in the control of corrosion. This deoiling treatment is the only step in the entire phosphate flotation process where strong mineral acids are employed. Their elimination here would thus remove them from the complete process. It is an object of our invention to deoil the rougher concentrate by a process which does not employ corrosive or hazardous materials.

It is a further object of our invention to employ for deoiling purposes material which is readily available in the phosphate industry and one which is relatively inexpensive.

An additional and equally important object is to provide a process for deoiling which will be superior to those processes now practiced and one which will leave the surface of the silica, contained admixed with phosphate in the rougher phosphate concentrate, in such a state that it is more readily floated in the succeeding cationic, amine flotation.

Before describing the actual process of our invention it is necessary to very briefly outline the succeeding cationic, amine flotation process. Any true test of the amount of deoiling must include the subsequent amine flotation with analyses of the resultant fractions.

The deoiled, rougher phosphate concentrate is returned to the flotation machine where it is formed with water into a dilute pulp of about 25% solids and, without preliminary agitation, frothed for one minute or longer in the presence of a cationic amine reagent and kerosene. The almost pure silica is floated and is removed by the scrapers. The material which remains in the machine constitutes the finished phosphate concentrate. Examples of cationic amine reagents which may be used in carrying out this second flotation step are the higher aliphatic amines and their salts with water-soluble acids, the esters of amino-alcohols with high molecular weight fatty acids and their salts with water-soluble acids, the resin amines and their salts with water-soluble acids and the higher aliphatic quaternary ammonium bases, including pyridine, quinoline and other heterocyclics capable of forming quaternary compounds, and their salts with water-soluble acids. These various examples are not, of course, equally effective or useful in this provess. The use of a cationic active amine or an amine salt generally is preferred. As will be illustrated, the actual reagent used in the tests of our invention is a mixture of two amine salts.

The above and other objects are accomplished by the practice of our invention. We have discovered that excellent deoiling is obtained by the use of a variety of finely divided solid materials among which one of the most novel, certainly the most economical, and very probably the best technically is the phosphate slimes. This is a most unusual and certainly an entirely unpredictable discovery as it has long been thought that absolute slime removal was essential to successful flotation. This is still very probably true for the actual flotation steps. However, we have found that the addition of phosphate slimes in the deoiling step is not only not harmful but results in excellent deoiling without the use of corrosive mineral acids as deoilers.

Phosphate slimes which are obtained during the beneficiation of matrix material have long presented a tremendous disposal problem to the phosphate industry. Because of their colloidal nature and extremely slow settling characteristics they are normally ponded and discarded. These are the so-called matrix slimes. The matrix fraction of the Florida phosphate deposits has for years been the mainstay of the fertilizer industry. Therefore, many hundreds of acres of matrix slimes have been ponded in Florida. Even a use for a small proportion of these slimes would be of great value in the phosphate industry. These slimes are usable as the deoiling agent in the present invention.

Recently, considerable interest has arisen in the profile of the phosphate deposits known as the leached zone. This occurs directly above the matrix zone and in normal operations has been discarded. Because of its higher uranium concentration and substantial phosphate content beneficiation of this zone is of increasing importance. We discovered that slimes formed in processes for the beneficiation of leached zone material are also operative in our invention and exhibit excellent deoiling properties. Leached zone slimes are known to contain kaolinite clay as opposed to montmorillonite clay which is present in the matrix slimes.

Phosphate slimes, both matrix and leached zone, are somewhere in the range of minus 200-mesh and contain about 2% solids when they are ponded. Some high grade slimes exist that contain up to about 5% solids and the use of such a slime in the practice of our invention is illustrated in the examples below.

We have also discovered that in addition to the phosphate slimes other finely divided material such as the oil retaining clays including fuller's earth, activated clays, diatomaceous earths, activated carbons and starch are effective deoilers for the rougher phosphate concentrate and are operative in the practice of our invention. To those skilled in the art the terms "oil-retaining clays" and "activated carbons" include a long list of similar substances, among which are included kaolin, bentonite, pyrophyllite, fuller's earth, talc and kieselguhr. These, while not disclosed as being preferred deoiling agents, fall within the scope of our invention. Other materials normally considered to be crystalline, but which can exhibit sorptive properties in extremely small particle sizes also fall within the scope of our invention; for instance, gypsum, sulfur and slate dust.

The deoiling of rougher phosphate concentrate is a step about which very little is known. The mineral acids do render the anionic reagents ineffective and also prepare the surfaces so that cationic reagents are more effective. There is no question that the oils from the fatty acid flotation step are removed because they can be seen to separate in the washing step. There is, however, a definite question as to the condition of the cleaned mineral surfaces and as to what, if any, surface coating remains. It is this remaining surface coating which is referred to as "activation" of the silica in U. S. 2,599,530. Our invention is concerned solely with the removal of the oily fatty acid reagent. Any "activation" which results is purely coincidental and our invention is not limited either by the presence or absence of such "activation". It seems quite certain that the removal of the fatty acid coatings and the subsequent amenability to flotation, although related and influencing, are nevertheless two distinct phases and conceivably can be entirely separate. When a coating is removed there might be a small amount of residual coating which could affect the subsequent flotation. It is difficult to explain how the use of such chemically inert materials as the activated clays and carbons, described above in the practice of our invention, can result in an "activation" of the resultant cleaned surfaces. However, any such "activation" which occurs through the practice of our invention falls within the scope of an incidental result brought about by operation of our process.

It has been suggested that the presence of a layer of hydrated silicic acid on the surface of the silica particles is the means by which the non-polar substance becomes amenable to flotation. The presence of water is essential and it is within the realm of possibility that the water itself is, in fact, the true means of activation. If this is a valid postulation then it might account for the good float produced after deoiling with phosphate slimes which, of course, contain a relatively large percentage of water. Our invention is not limited to, nor dependent upon, any of the theoretical points discussed above. These postulations have been reviewed only as an aid to the understanding of the complete picture of phosphate flotation processes.

Having described our invention in general terms the following specific examples are given to illustrate the use of the various clays and activated carbons.

All samples used in the illustrative examples of this invention were taken from the rougher concentrate produced in the No. 91 Flotation Plant of Virginia-Carolina Chemical Corporation, Bartow, Florida. The rougher concentrate from this plant is at least about 90% minus 35-mesh and contains about 80% solids.

To produce this rougher concentrate, phosphate debris, which contains phosphate rock and silica and runs roughly minus 14-mesh in size, is hydraulically classified in order to separate the minus 35-mesh fraction. The minus 35-mesh product is dewatered and deslimed in a rake classifier. The discharge, which runs approximately 70% solids, is fed to a conditioner where 0.6 lb./ton of caustic soda, 3 lbs./ton of Bunker C-No. 2 fuel oil (resultant specific gravity 18–20° A. P. I.), and 0.7 lb./ton of tall oil are added, with agitation. Conditioning time is two minutes. The discharge is diluted with about 4 parts of water to each part of the discharge and the mixture is fed to the flotation cells. The froth product from these cells is known as the rougher concentrate and contains a high percentage of phosphate but also some silica.

1270 gram-samples (1000 g., dry weight) of this rougher concentrate were placed in a beaker and the deoiling agent to be evaluated was added and the resultant mixture was stirred for three minutes. The thus deoiled mixture was washed by decantation until a relatively clear wash water was obtained. Normally 12 to 16 liters of water were required for this washing. The washed solid material was placed in a Fagergren laboratory flotation machine and water was added to the top of the conical part of the test-bowl. This corresponds to a dilution of approximately 2–3 parts of water to 1 part of solids. The cationic amine reagent and kerosene were added and the mixture was agitated without frothing for about 15 secs. In all tests the cationic amine reagent was a mixture composed of 50% rosin amine D acetate, a product of the Hercules Powder Co., and 50% Armac T, produced by Armour & Co. Armac T comprises the acetate salts of a mixture of 30% hexadecyl, 25% octadecyl and 45% octadecenyl amines. After the 15-second agitation the flotation machine was filled with water. Air was admitted to begin frothing and the thus formed matte-froth float was carefully removed, normally with a flexible rubber scraper.

The table is a summary of the results of deoiling rougher phosphate concentrate with clays and activated carbons. Test No. 1 has been included to illustrate the results obtained with present deoiling practices employing sulfuric acid. The percent of BPL recovery in the froth fraction is inversely proportional to the effectiveness of the deoiling. The most efficient or effective deoiling agents will give the lowest grade froth product. Phosphate which has not been deoiled will, of course, float with the silica in the cationic flotation step. A low percentage of insoluble matter in the concentrate, expressed at "percent Insol." in the table is also desirable but is not quite as accurate an evaluation of deoiling as is a low percent BPL in the froth. The percent insol. should be kept in mind as it is a measure of unfloated silica which remains in the final phosphate concentrate. Both low BPL in the froth and low insol. in the concentrate are desirable.

The deoiling agent may be added in dry form or in admixture with water and in the latter case the quantity of water added with the deoiler must be considered in determining the ratio of solids to liquids in the resulting mixture. As appears in the following table the mixtures generally contained about 75% of solids. The mixture must be sufficiently fluid to be stirrable. The upper limit of solids content is about 80%. The mixture may be more dilute than 75% solids but in that case more stirring is required.

In the following table the weight figures all refer to dry weights.

it is necessary to determine the best cationic flotation conditions for use with that agent.

The deoilers in the examples of the table are all good deoilers and all yield flotation results which are reasonable and economic from the standpoint of plant practice and percent BPL recovered.

In some instances the flotation results shown in the tests may be improved by variation of the cationic flotation conditions.

It will be appreciated from the foregoing disclosure that our invention is not concerned with the anionic and cationic flotation agents used in the two flotation steps

Table 1

Test No.	Product	Percent Wt.	Percent BPL	Percent Insol.	Percent BPL Recovered	Deoil and cationic Reagents	Lbs. per Ton of Feed	Deoiled at—Percent Solids
	Feed	100.0	60.0		100.0	H_2SO_4	6.00	
1	Froth	25.7	16.4	6.9	7.0	Kerosene	1.00	50
	Conc	74.3	75.1		93.0	Amine	0.22	
	Feed	100.0	62.2		100.0	Phosphate Matrix Slime	97.00	
2	Froth	21.4	9.3	6.4	3.2	Kerosene	1.00	75
	Conc	78.6	76.6		96.8	Amine	0.20	
	Feed	100.0	70.5		100.0	Grp. 79 Slime	100.00	
3	Froth	13.5	8.2	3.7	1.6	Kerosene	0.75	75
	Conc	86.5	80.2		98.4	Amine	0.21	
	Feed	100.0	70.3		100.0	Leached Zone Slime	100.00	
4	Froth	16.3	16.8	2.6	3.9	Kerosene	0.75	75
	Conc	83.7	80.7		96.1	Amine	0.21	
	Feed	100.0	70.3		100.0	"Attasorb"	100.00	
5	Froth	25.2	40.5	3.4	14.5	Kerosene	0.75	75
	Conc	74.8	80.3		85.5	Amine	0.21	
	Feed	100.0	69.7		100.0	"Celite"	100.00	
6	Froth	18.1	19.3	2.3	5.0	Kerosene	0.75	75
	Conc	81.9	80.8		95.0	Amine	0.21	
	Feed	100.0	70.7		100.0	"Darco S-51"	100.00	
7	Froth	12.3	5.2	4.6	0.9	Kerosene	0.75	75
	Conc	87.7	79.9		99.1	Amine	0.21	
	Feed	100.0	70.2		100.0	Fuller's Earth	50.00	
8	Froth	17.7	19.8	2.6	5.0	Kerosene	0.75	75
	Conc	82.3	81.0		95.0	Amine	0.21	
	Feed	100.0	70.6		100.0	Kaolinite	50.00	
9	Froth	21.1	29.3	2.4	8.7	Kerosene	0.75	75
	Conc	78.9	81.7		91.3	Amine	0.21	
	Feed	100.0	70.7		100.0	Argo Starch	100.00	
10	Froth	21.0	28.9	2.3	8.6	Kerosene	0.75	75
	Conc	79.0	81.8		91.4	Amine	0.21	
	Feed	100.0	70.0		100.0	Darco S-51	10.00	
11	Froth	14.5	8.7	3.0	1.8	Kerosene	0.75	75
	Conc	85.5	80.4		98.2	Amine	0.21	

NOTES TO THE TABLE

Test 3.—Group 79 Slime is a high grade slime (67.6% BPL; 4.2% insol.) prepared by grinding a phosphate rock sample and diluting with water.

Test 4.—Leached zone slime was obtained from the Clear Springs, Florida mine of Virginia-Carolina Chemical Corporation and contained kaolinite as opposed to montmorillonite in matrix slime.

Test 5.—"Attasorb" is a minus 325 mesh product of The Attapulgus Minerals and Chemicals Corporation and is a complex hydrated magnesium aluminum silicate made from attapulgite, a naturally active, highly sorptive clay. It has an average particle size of 0.4 to 0.6 micron.

Test 6.—"Celite" is a trade name of the Johns-Manville Corporation for diatomaceous earth. It has a particle size less than 9 microns and is of course minus 325 mesh.

Test 7.—"Darco S-51" is a decolorizing, activated carbon manufactured by the Darco Dept. of Atlas Powder Company from lignite and charcoal.

It can be readily seen that all of the activated clays and carbons yielded deoiled flotation products which contained less insoluble material than the sulfuric acid check. With one exception, Attasorb, they all gave froth floats which contained lower amounts of BPL than the sulfuric acid check. The exception, Attasorb, which has a larger BPL value in the froth also had a much lower percent insol. in the concentrate so that weighing the two analytical results one can only reach the conclusion that Attasorb is at least equal to sulfuric acid as a deoiler for rougher phosphate concentrate.

In interpretation of the results of our use of activated clays and carbons for deoiling rougher phosphate concentrates, one should bear in mind that the deoiling and subsequent flotation with amine are two entirely separate procedures, even though they are shown as one in the reporting of our tests. A material that is a highly effective deoiling agent may have the disadvantage of not providing a residual effect which is helpful in the amine flotation step.

The foregoing tests merely demonstrate the deoiling properties of the materials tested and do not necessarily show the best flotation results obtainable by their use. Once an agent has been determined to be a good deoiler

which precede and follow the deoiling step, such agents being well known in this art. It will be appreciated further that our invention embraces the use of any finely divided water-insoluble solid which is capable of assisting the removal of the anionic agent left in or on the ore particles as a result of the anionic flotation step. A variety of finely divided solid deoiling agents have been mentioned but it is to be understood that our invention is not limited to such agents, excepting as may be required by the scope of the appended claims. Our invention embraces all finely divided solid materials which are capable upon being mixed with a phosphate ore having an anionic agent thereon of being washed out of the ore and of facilitating the simultaneous removal of the anionic agent from the ore. In general the deoiling agents of the invention are finely divided chemically inert solids—less than 200 mesh, having absorptive or adsorptive surfaces.

The deoiling agent may be applied as described above by mixing with an ore-water mixture containing 75–80% by weight of the ore but they may be applied by mixing with the dry ore or with more dilute ore-water mixtures.

The pH values of the ore-water mixtures to which the deoiling agents are added have been observed and have not been found to have an appreciable effect. It may be said that a pH within the range from 7 to 8 gives satisfactory results.

The quantity of deoiling agent to be used in any particular instance readily may be determined by a series of tests. As shown by the tests of the table about 100 pounds of deoiling agent per ton of ore generally gives satisfactory results but the quantity used may vary within the range from about 10 pounds or even less upward.

As stated above the degree of deoiling or the effectiveness of deoiling is measured by the results produced in the subsequent cationic flotation and as is obvious need not involve a complete removal of the anionic flotation agent. The deoiling process of our invention may therefore be employed in any process in which deoiling is desired such as in the retarded float process of U. S. Patent No. 2,661,842.

We claim:

1. In a process for the beneficiation of phosphate ore containing silicious impurity involving the steps in sequence of anionic flotation, deoiling the resulting concentrate and cationic flotation of the deoiled concentrate, the improvement which consists in deoiling the concentrate produced by the anionic flotation by mixing it with a finely divided solid water-insoluble material in the presence of water and washing the resulting mixture with water.

2. Process as defined in claim 1 in which the finely divided solid water-insoluble material is a member of the group consisting of activated carbons, fuller's earths, activated clays, diatomaceous earth, phosphate ore slimes, kaolin, bentonite, pyrophyllite, talc, kieselguhr, gypsum, sulfur, slate dust and starch.

3. Process as defined in claim 1 in which the finely divided solid water-insoluble material is a phosphate ore slime.

4. Process as defined in claim 3 in which the slime is matrix zone slime.

5. Process as defined in claim 3 in which the slime is leached zone slime.

6. Process as defined in claim 1 in which the finely divided solid water-insoluble material has a particle size less than 200 mesh.

7. Process as defined in claim 1 in which a mixture of about 2000 parts by weight of ore and about 700 parts by weight of water is stirred with about 100 parts by weight of the finely divided water-insoluble solid material.

References Cited in the file of this patent

UNITED STATES PATENTS

1,261,810 Hebbard _______________ Apr. 9, 1918