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FLOTATION OF ILMENITE ORES

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1 Claim. (Cl. 209—166)

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This invention relates to the beneficiation of metallic-oxide minerals from those ores containing excessive amounts of phosphorous-bearing gangue. More particularly, it is concerned with the separation by froth flotation of titanium oxide minerals from low-grade ores containing excessive amounts of such phosphate-bearing minerals as apatite and the like.

Titanium oxides have become increasingly important in use, and accordingly, the demand for high-grade ore from which they may be chemically recovered is steadily increasing. Unfortunately, while natural deposits of titanium-bearing minerals are not infrequent, such ores are usually of too low grade for commercial recovery of titanium oxides directly therefrom. If they are to be effectively utilized, the ore must be beneficiated to increase the titaniferous content. Another source of titanium oxides are various incidental, or by-product, ilmenite concentrates obtained in working an ore primarily for some other purpose. They too, usually require beneficiation.

The term "ore" is used herein in its ordinary sense to include both ore as mined and minerals mixtures in such partially beneficiated concentrates. Such ores frequently contain, as a gangue constituent, quantities of phosphorous-bearing minerals, apatite, for example, being very commonly found. The P_2O_5 assay may vary from less than 1% in ilmenite concentrates which have been obtained from ores worked primarily for other constituents, to as high as 12 to 15% as found in ores such as "nelsonite" and the like. This is particularly unfortunate since a P_2O_5 assay in excess of about 0.2% is unacceptable in the production of titanium oxide pigments. Below 0.13% is desirable, particularly in the anatase crystal form production.

For various reasons, largely procedural and economic, it is desirable to use an anionic-type of promoter for the metal oxide minerals. Unfortunately, many phosphate-bearing minerals, apatite, for example, float readily in the presence of most such promoters. Effective depressants for the apatite which do not also depress ilmenite have not have been known. As a result, most beneficiation procedures used with such were unsatisfactory either as to the grade or the recovery or both.

Accordingly, it is highly desirable to find a beneficiation procedure, involving only a single operation capable of producing an ilmenite concentrate of sufficiently low P_2O_5 content and in high recovery. It is, therefore, the principal object of the present invention to produce such an adaptation and to develop a suitable reagent combination therefor. Such a process should enable the use of a single operation of rougher and cleaner flotations to produce an ilmenite concentrate of such grade as to be capable of utilization in a pigment production.

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Surprisingly, the desired objects of the invention are quite simply accomplished by the use of novel fluoride or fluosilicate conditioning agents under acidic conditions. The mechanical handling is simple and effective. An aqueous pulp of the ore is conditioned with a reagents combination capable of maintaining an acid pH and free fluoride and/or silicofluoride ions in the circuit. This may be done prior to or concurrently with conditioning with the promoter. The ilmenite concentrate is then taken directly therefrom. Effective and highly selective depression of the phosphorous-bearing minerals is obtained. Using this reagent combination in a single operation comprising a rougher and one or more cleaner flotations produces efficient recovery of the TiO_2 content, accompanied by a reduction in the P_2O_5 content to or below the 0.12% level.

It is an advantage of the present invention that it does not require any excessive pretreatment of the ore. Usually these ores require quite fine size reduction, usually to below —28 mesh and often to —65 mesh, to unlock the mineral values from the gangue constituents. Any crushing or grinding, which is sufficient to unlock the mineral values, is, in general, adequate for the purposes of the flotation operation.

Since many titanium ores slime freely, a desliming operation is helpful. It is advantageous that rough desliming is ordinarily sufficient, it being wholly unnecessary to attempt to carry out a quantitativve desliming. A good general practice is to first rough crush the ore to a suitable degree, for example about —1.0 to —0.5 inch. This material is then washed, ground to a suitable size, and then finally deslimed. Desliming is usually done by hydraulic classification. Screening may be used but is not as generally practical in use because only the material below about 10–20 microns is ordinarily discarded.

This partially deslimed ore may then be fed directly to the treatment of the present invention. However, if so desired, the coarser sizes may be separated out and treated in any other desired manner as by tabling, jigging, and the like. This again is not necessary. The choice is based on considerations other than the ability of the present process to concentrate the ore. Whatever procedure is chosen, that fraction of the ore to be treated by froth flotation is made up into a pulp with water and conditioned with the reagents and floated.

Preferably, the pulp should be conditioned with the reagents at a higher density than that normally used in the flotation cells. This high-solids conditioning aids in insuring thorough dissemination of the reagents, at least a major portion of which are generally added at this stage. A solids content of 30–40% is good practice, with even higher solids content being used if the necessary apparatus for its handling is available. Where conditioning at high solids, or even con-

ditioning prior to flotation cannot be employed, it is possible to add the reagents to the flotation cell. This practice is undesirable and should be avoided if possible, since it requires more reagent and/or longer treatment in the cells, and even then is not as satisfactory.

It is also an advantage of the present invention that it permits the use of readily-available anionic-type promoters for metallic oxide minerals. These include, for example, the higher fatty acids; oleic, ricinoleic, stearic, palmitic, fish-oil fatty acids, corn-oil fatty acids, and the like, as well as the various commercial mixtures thereof. In addition, certain naphthenic acids may be used, alone or in combination with the fatty acids. Such naturally-occurring mixtures of fatty and resin acids as found in talloel are also satisfactory. The promoter is preferably added as the free acid. If necessary it may be used as a sodium, potassium or ammonium neutralized soap thereof but the latter procedure is not to be preferred. The flotation circuit will be acidic and the presence of alkali soap-forming ions makes control less certain. Sulfates and/or sulfonates such as found in certain of the sulfonated petroleum hydrocarbon reagents should not be used since the depression of apatite as done in this invention is not effective in their presence.

The amount of promoter used will vary with the nature of the ore, the water conditions, i. e., temperature, acidity, hardness, etc. of the water and the average particle size mineral and content of the feed being treated. In general, amounts ranging from 0.5 to 10 lbs.+ton of ore treated, with an average of about 1.5 to 3.0 lbs./ton constituting the average practice will be necessary. In some cases a frother may be helpful. Where a frother is desirable or necessary, any suitable type such as pine oil, cresylic acids, and the commercial higher-alcohol frothers may be used. Frothers of the sulfated alcohol type should not be used as they tend to adversely effect the depression of apatite.

Of primary importance is the use of the novel depressant of the present invention. As noted above, this depressant should be an effective source of fluoride and/or fluosilicate ions. The particular source may be varied. The necessary ions may be provided, for example, by adding fluosilicic acid, per se or as a soluble salt thereof. Where the circuit itself is not normally acidic it should be made so. This may be done by adding an acid such as HF or H_2SiF_6. It may also be done by adding a soluble fluosilicate, such as that of sodium or potassium, since these salts have an acid reaction. Similarly a combination of a mineral acid, sulfuric, hydrochloric or the like may be used with a soluble fluoride or acid fluoride such as those of sodium, potassium or ammonium. Although certain sulfate containing reagents should not be used, as noted above, sulfuric acid does not affect the apatite depression. When used with a soluble fluoride as a source of fluoride ions the procedure is wholly successful.

As to the amount of depressant used, the demand may be quite flexible, depending upon the nature of the ore, the temperature, acidity, hardness etc., of the process water and the particular agent used. Smaller amounts of phosphate mineral, obviously require smaller amounts of depressant. In general, the amount used will vary from about 0.1 to about 4.0 lbs./ton of feed. A good general practice is to add about 1.5 to 2.0 lbs./ton in the initial conditioning operation, or to the

cells during the rougher flotation if preconditioning is not used. A part may be withheld and added during cleaning or an additional amount or amounts may be so added if desired.

Actually, numerical weight limitations are not as helpful as a consideration of the pH during flotation. As noted, definitely acidic conditions, a pH less than 6.8, are necessary. A pH below 6.0 is better. Dropping below about 4.5 does appear to help although a lower pH may be reached as a result of other conditions and does no harm. Soluble fluosilicates make excellent reagents for this reason. They are not only acid in reaction but appear to be somewhat self-buffering, producing a pH of about 4.5–5.5 as long as there is a sufficient amount present. In using the fluosilicates one precaution should be taken. If the process water is very cold it is helpful to warm it slightly since the solubility of the salt increases rapidly above about 20° C.

The lower pH values may be produced directly in the conditioning step or in the cell during the rougher flotation. When this is done, any rise in pH through dilution in the cleaner step or steps may be ignored. This procedure being the simplest is perhaps preferable. On the other hand, it may be desirable to conduct the rougher float at a higher pH, i. e., 5.5–6.8, and drop down to the lower pH during cleaning by subsequent acid addition. Either procedure is effective in obtaining the desired result.

This invention will be further illustrated in conjunction with the following examples which are intended as illustrative only. All parts are by weight unless otherwise noted.

EXAMPLE 1

A sample of primary "Nelsonite" ore, comprising ilmenite with an apatite gangue was given a preliminary treatment by rough crushing to minus ½", washing, grinding to minus 65 mesh, and rough desliming. A pulp of the partially deslimed ore comprising about 30% solids in water was conditioned for ten minutes with 2.5 lbs./ton of talloel and 2.0 lbs./ton of sodium silicofluoride (Na_2SiF_6) at a pulp temperature of about 30° C. This conditioned pulp was then reduced to about 20% solids, the ilmenite concentrate floated, and the concentrate was cleaned and recleaned, and the cleaner tailings were combined for analysis. Average results are shown in the following table.

Table I

Product	Assay			Distribution	
	Per Cent Wt.	Per Cent TiO_2	Per Cent P_2O_5	TiO_2	P_2O_5
Head (deslimed)	100.0	22.47	7.78	100.0	100.0
Ilmenite Concentrate	40.8	42.40	0.12	77.0	0.6
Cleaner Tailings (combined)	9.1	30.06	1.00	12.2	1.2
Rougher Tailing	50.1	4.85	15.25	10.8	98.2

Conditioned pulp before dilution, pH=4.9.

EXAMPLE 2

Another ore sample, prepared and deslimed as in Example 1, was pulped with water to 30% solids and conditioned for 10 minutes at 30° C. with 2.5 lbs./ton of crude naphthenic acids and 2 lbs./ton of Na_2SiF_6. The conditioned pulp was diluted to about 20% solids and floated for 4 minutes to obtain the rougher ilmenite concentrate. This concentrate was given a cleaning and recleaning of 3 minutes each. The cleaner

tails were combined. Typical results are shown in the following Table II.

Table II

Product	Assay			Distribution	
	Per Cent Weight	Per Cent TiO_2	Per Cent P_2O_5	TiO_2	P_2O_5
Head (deslimed)	100.0	24.36	9.25	100.0	100.0
Ilmenite Concentrate	28.6	42.87	0.12	50.3	0.4
Cleaner Tails (combined)	22.4	32.15	5.87	29.6	14.2
Rougher Tailings	49.0	10.00	16.12	20.1	85.4

EXAMPLE 3

An apatite-ilmenite concentrate produced by gravity concentration and analyzing 38% TiO_2 and 6% P_2O_5 was ground to pass a 65 mesh screen, deslimed and made up into a pulp at about 65% solids. This pulp was conditioned for 10 minutes with 1 lb./ton of sulfuric acid, 2 lbs./ton of sodium fluoride, 1.5 lbs./ton of oleic acid and 0.1 lb./ton of an alcoholic frother. The conditioned pulp was diluted to 22% solids and an ilmenite concentrate floated for 5 minutes. This concentrate was given a single 4 minute cleaning. The cleaned concentrate constituted 70% by weight of the feed, contained 82% of the ilmenite and assayed 45% TiO_2. 96.5% of the P_2O_5 content was removed in the rougher tail and an additional 1.4% in the cleaner tail.

In the foregoing examples it has been shown that the procedure of the present invention is wholly effective in reducing the P_2O_5 assay. For some purposes, particularly for the manufacture of the anatase crystal form it may be desirable further to reduce the P_2O_5 content. This can be done in any of several ways.

One effective procedure is to repeat the treatment of the present invention on a cleaned concentrate previously obtained. This operation again is simple. The pulp of the ore is conditioned with additional amounts of the depressant reagent and promoter. This conditioned pulp is floated and the concentrate cleaned in the usual manner. An illustration of this procedure is shown in the following example.

EXAMPLE 4

The ilmenite concentrate obtained in Example 1 was repulped with water to about 30% solids and conditioned for 5 minutes with 1 lb./ton of Na_2SiF_6. The conditioned pulp was diluted to about 20% solids and the ilmenite concentrate flotation made using 1.0 lb./ton of talloel as the promoter. The results are shown in the following table.

Table III

Product	Assay			Distribution	
	Per Cent Weight	Per Cent TiO_2	Per Cent P_2O_5	TiO_2	P_2O_5
Original Ilmenite Concentrate (Flotation Feed)	40.8	42.40	0.12	77.0	0.6
Final Ilmenite	36.1	43.96	0.06	70.6	0.2
Final Tailing	4.7	30.4	0.61	6.4	0.4

In the preceding example the procedure is in effect a multiple stage operation in which the apatite depressant reagents of the present invention are added in each stage. So used, the process of the present invention is very effective in producing very low P_2O_5 assay concentrates. However, the procedure of the present invention may be used as a pretreatment for certain other apatite-ilmenite separating processes. One such process is that disclosed in the application for U. S. Letters Patent of McMurray and Moyer, Serial No. 636,228, filed December 20, 1945, now Patent Number 2,525,146 in which caustic starch is used to depress ilmenite, and apatite is floated therefrom with an anionic promoter such as a soap of talloel or a fatty acid.

This latter procedure is particularly effective as an after treatment in conjunction with the present process. In the instant application is shown a process which makes a good concentration of ilmenite with high recovery in a product containing only a small amount of the phosphate. Instead of repeating the operation, that is, again floating ilmenite from apatite, to reduce the P_2O_5 assay, a pulp of this concentrate may be neutralized and then treated in accordance with the above mentioned procedure of McMurray and Moyer. In this way a major portion of the residual small amount of phosphate-bearing minerals may be readily floated away from the titanium-bearing minerals. In some instances this combined operation has the advantages that overall reagent consumption may be reduced, and the pretreatment need not be so carefully controlled to reject P_2O_5 content and the final ilmenite concentrate is of extremely high grade. This procedure is shown in the following example.

EXAMPLE 5

A sample of nelsonite ore was prepared in accordance with the procedure shown in Example 1. After desliming, a pulp of the ore at about 30% solids, was conditioned for 5 minutes with 2 lbs./ton of sodium silicofluoride and then an additional 5 minutes with 3 lbs./ton of talloel. The conditioned pulp was diluted to 20% solids and a rougher ilmenite concentrate taken for 4 minutes. This concentrate was given a cleaner and recleaner flotation of 3 minutes each without additional reagents. This procedure produced a recleaner concentrate containing 81% of the ilmenite, assaying 41% TiO_2 and 0.19% TiO_2. This concentrate was pulped with water to 68% solids and conditioned for 10 minutes with a combination of 3 lbs./ton of caustic starch and 2 lbs./ton of sodium silicate. The conditioned pulp was diluted to about 20% solids and apatite concentrate taken for 3 minutes using 0.5 lbs./ton of sodium saponified talloel. An extremely low P_2O_5 content ilmenite concentrate was produced as machine discharge. Detailed results of this test are shown in the following Table IV.

Table IV

Product	Assay			Distribution	
	Per Cent Weight	Per Cent TiO_2	Per Cent P_2O_5	Per Cent TiO_2	Per Cent P_2O_5
Head (deslimed)	100.0	17.40	7.36	100.0	100.0
Rgh. Apatite Ct.	6.2	29.89	10.18	10.6	8.6
Final Ilmenite Ct. or Machine Discharge	28.3	43.20	0.05	70.3	0.2
Calc. Recleaned Ilmenite Ct.	34.5	40.81	0.19	80.9	8.8
Recleaner Tailing	3.6	30.98	1.77	6.4	0.9
Cleaner Tailing	5.3	18.42	2.02	5.6	1.5
Rougher Tailing	56.6	2.18	11.56	7.1	88.8

I claim :

A process of beneficiating mineral mixtures comprising at least ilmenite and an excessive amount of apatite as gangue, said mixture being in particle sizes suitable for froth flotation feed, which comprises the steps of forming an aqueous pulp of the mixture, subjecting said aqueous pulp to froth flotation at a pH less than 6.8 in the presence of an anionic promoter selected from the group consisting of the sulfate and sulfonate-free higher fatty acids, resin acids, naphthenic acids, talloel, mixtures thereof, and the sodium, potassium, and ammonium soaps of these materials and a selective depressant for the apatite containing a source of free ions selected from the group consisting of fluoride and fluosilicate ions, and collecting the resultant ilmenite-bearing froth concentrate, whereby a concentrate of increased TiO_2 and decreased P_2O_5 assay is obtained.

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