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METHOD FOR CONCENTRATING THE TITANIUM OXIDE MINERALS IN BEACH SAND

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This invention relates to a method for concentrating the titanium oxide minerals in sand deposits which are usually known as beach sands. The invention also relates to a method for making a bulk separation of the heavy minerals in beach sands from the quartz.

Beach sands of the type with which the present invention is concerned may be found along the seashore, but are also found in large inland deposits in Florida and elsewhere. These sand beds or deposits are composed principally of quartz, while containing a small proportion of valuable minerals, and in particular titanium oxide minerals like ilmenite and rutile. Usually the content of quartz in these sands will be at least 90%, while the content of titanium oxide minerals ranges from 3% down to as little as .5%, with some sands falling outside of this range. For example, a typical Florida beach sand deposit may contain 94 to 96% quartz and from 1 to 2% of ilmenite and rutile. Small amounts of other titanium oxide minerals, such as leucoxene, may also be present, as well as a few percent of other heavy minerals. The most valuable product at present is the titanium oxide minerals, although other heavy minerals are of value, especially zircon and monazite.

At present titanium oxide minerals and other heavy minerals are being recovered from Florida beach sand deposits by a complicated and expensive procedure. The first step in the present process is to pass the beach sands through a series of spiral concentrators to make a rough separation of the titanium oxide and other heavy minerals from the quartz. Following the rough separation, there are cleaner and recleaner spiral circuits to upgrade the rough concentrate, and a large amount of the middling material is recycled through these circuits to increase recovery. The equipment for carrying out these steps is bulky and expensive, and there is a serious problem of wear because of the abrasion of the concentrators by the sand. The titanium minerals in the heavy mineral concentrate are then further separated and concentrated by electrostatic and magnetic separators.

For the reasons indicated above, there has been a manifest need for a simpler process of separating titanium oxide minerals from the quartz in beach sand. Efforts have been made to develop a flotation process which would produce this result, but heretofore such efforts have not met with success. This is somewhat surprising in view of the fact that the subdivided condition of beach sands is such as to make them a natural flotation feed. The mineral particles are completely liberated, and while the beach sands are composed of very fine particles, 90% of the particles are usually above 150 mesh. The problem, however, has been to provide a flotation method which would result in a sufficiently clean separation of the valuable mineral components in the beach sands from the quartz.

It is therefore a general object of this invention to provide an improved method for concentrating the

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titanium oxide minerals in beach sands, and specifically, to provide a flotation method for accomplishing this result. More specifically, it is an object to provide a flotation method by means of which the titanium minerals in beach sands can be separated from the quartz. It is also an object of this invention to provide a means for carrying out a bulk separation of the heavy minerals in beach sand from the quartz therein. Further objects and advantages will appear as the specification proceeds.

This invention is based in part on the discovery that beach sands of the type found in inland deposits in Florida have films of organic material on the particles therein which interfere with the separation of the valuable minerals from the quartz by flotation. These organic films can be observed when the beach sand particles are examined under a microscope. The beach sands may also contain some separate organic matter, but this is quite distinct from the films, since the separate organic material can be removed from the beach sands by ordinary desliming procedures.

In practicing the present invention, the beach sand is first treated to remove the organic films from the sand particles. Preferably, this is accomplished by scrubbing the beach sands with a caustic like sodium hydroxide or potassium hydroxide. Specifically, an aqueous pulp or slurry of the beach sand can be formed containing solids concentration of from 30 to 80%, and from 1/2 to 5 pounds of caustic added per ton of beach sand solids. This slurry or pulp is then mixed until the organic films have been removed from the particles, as can readily be determined by examining the particles under a microscope. Higher solids concentration up to at least 60 to 70% solids are preferred for caustic reagent economy, and if desired the treating step can be carried out in an attrition scrubber.

The removed organic material is then preferably separated from the beach sand before continuing with the recovery operation. This can be done by the usual desliming procedures. For example, the caustic-treated pulp or slurry can be charged to a hydro-classifier or any type of apparatus designed for turbulent washing of mineral particles. This desliming operation will also remove any larger organic particles which may have been present in the beach sand, in the event that the beach sand has not been subjected to a preliminary desliming operation before the caustic treatment. If desired the caustic scrubbing and desliming steps can be repeated.

Instead of sodium or potassium hydroxide, other inorganic alkaline reagents can be used which are capable of producing a pH above 8. Preferably, a pH from 9 to 14 is employed, although the pH is not particularly critical. The important point is to have a sufficient amount of the alkaline reagent present to completely liberate the organic films on the surfaces of the particles. Specifically, other alkali metal hydroxides can be used, as well as alkali metal carbonates and bicarbonates. The alkaline earth metal hydroxides, carbonates and bicarbonates can also be used with more or less success, and the mineral acids like sulfuric acid are of some value.

The caustic-treated, deslimed beach sand is then formed into a flotation feed. Preferably, an aqueous slurry is formed containing from 15 to 30% beach sand solids, although this concentration can be varied. To the flotation feed is added an amine collector and a fluorine-containing acid, and the pH of the aqueous feed is adjusted to an acidic pH below 5.0. Sodium fluoride and sulfuric acid may also be added. Any beach sands which are substantially free of the organic films discussed above, can be formed directly into a flotation feed in this man-

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ner and if desired beach sand concentrates can be used. For example, the beach sands could first be processed by a gravity method to upgrade the titanium minerals to 10% or more.

Any amine collector can be employed, and the specific amine collector is not critical. Preferably, however, the amine flotation agent is a primary amine containing a hydrophobic group of from 6 to 22 carbon atoms. Mixed amines like primary tallow and soya amines are suitable. Best results are achieved when the amine flotation agent is used in the form of a water-soluble salt thereof, such as an amine acetate, hydrochloride or phosphate salt. Both mono-amines and poly-amines can be used.

The fluorine-containing acid is preferably hydrofluoric acid, although other fluorine-containing acids can be substituted, as well as mixtures of hydrofluoric acid and

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pass out in the overflow, although these are of lesser importance than the titanium oxide minerals. However, it is significant that the method of this invention permits a clean separation to be made between all of the metal oxide and silicate minerals on the one hand and the quartz on the other.

This invention is further described in the following specific examples:

EXAMPLE I

Preparation.—Scrub 500 grams of beach sand (as received) at 30% solids in hard water (Chicago tap water—pH—7.9), with 4#/T NaOH. Deslime pulp twice and wash twice. One minute settling time allowed before each deslime or wash step. A Fagergren 500 gram cell was used for scrubbing and flotation. Temperature—30° C.

Reagents and conditions

Point of Addition	Conditions				Reagents #/T			
	Time Cond.	(Min.) Float	Percent Solids	pH	NaOH	HF 48%	Armac TD	MAAPO
Scrub.....	5	-----	30	7.8	4.0	-----	-----	-----
After Deslime.....	-----	-----	-----	3.1F	-----	-----	-----	-----
R ₁	1	2	20	3.2F	-----	2.08	0.35	0.1

MAAPO—Frother composed of 50-50 mixture of methyl amyl alcohol and pine oil.
Armac TD—Distilled primary amine acetate derived from tallow fatty acids.

other fluorine-containing acids. The hydrofluoric acid or other fluorine-containing acid acts as a depressant for the quartz.

The pH of the flotation slurry is critical, and should not exceed pH 5.0. Best results are achieved at pH's ranging from 3.0 to 4.0. Part of the necessary hydrogen ion concentration to achieve the desired pH can be supplied by the fluorine-containing acid, but it will usually be preferred to use an additional acid, such as sulfuric or hydrochloric acid to maintain the flotation circuit at an acidic pH below 5.0.

The production of a persistent froth of good selectivity and control is very important for a successful flotation operation. Therefore, it will be understood that a frother, such as pine oil or cresylic acid, will usually be incorporated in the flotation feed to produce the correct type of froth. Amine collectors impart some frothing in themselves and may in some cases be used alone. Good results can be obtained with a 50-50 mixture of pine oil

Metallurgical results

Product	Wt., Grams	Wt., Percent	Assay, Percent—Percent Heavy Mineral ¹	Distribution, Percent
R ₁	20.2	4.22	97.4	96.9
T.....	458.95	95.78	0.14	3.1
40 Composite.....	479.15	100.00	4.23	100.0

¹ Specific gravity analysis made in tetrabromoethane—sp. gr. 2.95.

EXAMPLE II

Preparation.—Scrub 500 grams of beach sand (as received) at 30% solids in hard water (Chicago tap water—pH—7.9), with 4#/T NaOH. Deslime pulp twice and wash twice. One minute settling time allowed before each deslime or wash step. A Fagergren 500 gram cell was used for scrubbing and flotation. Temperature—30° C.

Reagents and conditions

Point of Addition	Conditions				Reagents #/T				
	Time Cond.	(Min.) Float	Percent Solids	pH	NaOH	HF 48%	H ₂ SO ₄	Armac TD	MAAPO
Scrub.....	5	-----	30	7.8	4.0	-----	-----	-----	-----
After Deslime.....	-----	-----	-----	3.2F	-----	-----	-----	-----	-----
R ₁	1	2	20	3.4F	-----	0.312	1.0	0.35	0.1

MAAPO—Frother composed of 50-50 mixture of methyl amyl alcohol and pine oil.
Armac TD—Distilled primary amine acetate derived from tallow fatty acids.

and isopropanol. The flotation operation itself can be carried out in the usual type of flotation cells provided with means for supplying air to the lower portion of the cells. When the beach sand has been treated and conditioned as described and the flotation feed is at a pH below 5.0, the titanium oxide minerals in the beach sand can be readily floated away from the quartz. In other words, the titanium oxide minerals will be recovered in the overflow from the cells, while the quartz will be depressed and will pass out in the underflow from the cells. The other mineral constituents of the beach sand will also

Metallurgical results

Product	Wt., Grams	Wt., Percent	Assay, Percent—Percent Heavy Minerals ¹	Distribution, Percent
R ₁	18.25	3.81	97.7	92.3
T.....	460.5	96.19	0.32	7.7
Composite.....	478.75	100.0	4.08	100.0

¹ Specific gravity analysis made in tetrabromoethane, sp. gr. 2.95.

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EXAMPLE III

Preparation.—Scrub 500 grams of beach sand (as received—untreated) at 30% solids in soft water (pH 6.3—local water obtained at site) with 4#/T NaOH. Deslime twice and wash once. One minute settling time required before desliming or dewatering. A Fagergren 500-gram cell was used for scrubbing and flotation. Temperature 30° C.

Reagents and conditions

Point of Addition	Conditions				Reagents #/T				
	Time Cond.	(Min.) Float	Percent Solids	pH	NaOH	HF 48%	H ₂ SO ₄	Armac TD	MAAPO
Scrub.....	5		30		4.0				
After Deslime.....				5.5					
R ₁	1	2	20	{ 3.2I 3.4F }		0.416	0.4	0.2	0.1

MAAPO—Frother composed of 50-50 mixture methyl amyl alcohol and pine oil.
Armac TD—Distilled primary amine acetate derived from tallow fatty acids.

Metallurgical results

Product	Wt., Grams	Wt., Percent	Assay, Percent—Percent Heavy Mineral ¹	Distribution, Percent
R ₁	22.95	4.75	86.8	93.9
T.....	482.00	95.25	0.23	6.1
Composite.....	484.95	100.0	4.39	100.0

¹ Specific gravity analysis made in tetrabromoethane—sp. gr. 2.95.

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Metallurgical results

Product	Wt., Grams	Wt., Percent	Assay, Percent—Percent Heavy Mineral ¹	Distribution, Percent
R ₁	22.2	4.6	88.75	96.5
T.....	461.0	95.4	0.16	3.5
Composite.....	483.2	100.0	4.23	100.0

¹ Specific gravity analysis made in tetrabromoethane—sp. gr. 2.95.

EXAMPLE V

Preparation.—Scrub 500 grams of beach sand (as received) for two minutes at 30% solids in demineralized water (pH 6.7). Deslime pulp once and wash once. Scrub 5 minutes with ½ #/T NaOH. Deslime pulp once and wash once. One minute settling time allowed for each deslime and wash step. A Fagergren 500-gram cell was used for scrubbing and flotation. Temperature 30° C.

Reagents and conditions

Point of Addition	Conditions				Reagents				
	Time Cond.	(Min.) Float	Percent Solids	pH	NaOH	HF 48%	H ₂ SO ₄	Armac TD	MAAPO
Scrub.....	2		30						
Scrub.....	5		30		0.5				
After Deslime.....				5.6					
R ₁	1	1½	20	{ 3.15I 3.5F }		0.416	0.2	0.2	0.1
R ₂	1	1½	20	{ 3.5F 3.7 }				0.1	0.1

MAAPO—Frother composed of 50-50 mixture of methyl amyl alcohol and pine oil.
Armac TD—Distilled primary amine acetate derived from tallow fatty acids.

EXAMPLE IV

Preparation.—Scrub 500 grams of beach sand (as received) for two minutes at 30% solids in demineralized water (pH—6.7). Deslime pulp once and wash once. Scrub for 5 minutes at 30% solids in demineralized water with 1#/T NaOH. Deslime pulp once and wash once. One minute settling time was allowed for each deslime and washing step. A Fagergren 500-gram cell was used for scrubbing and flotation. Temperature 30° C.

Reagents and conditions

Point of Addition	Conditions				Reagents #/T				
	Time Cond.	(Min.) Float	Percent Solids	pH	NaOH	HF 48%	H ₂ SO ₄	Armac TD	MAAPO
Scrub.....	2		30						
Scrub.....	5		30		1.0				
After Deslime.....				5.6					
R ₁	1	2	20	{ 3.15I 3.45F }		0.416	0.2	0.2	0.1

MAAPO—Frother composed of 50-50 mixture methyl amyl alcohol and pine oil.
Armac TD—Distilled primary amine acetate derived from tallow fatty acids.

Metallurgical results

Product	Wt., Grams	Wt., Percent	Assay, Percent—Percent Heavy Mineral ¹	Distribution, Percent
R ₁	20.8	4.31	93.32	94.6
R ₂	1.7	0.35	26.48	2.1
T.....	460.0	95.34	0.15	3.3
Composite.....	482.5	100.0	4.25	100.0

¹ Specific gravity analysis made in tetrabromoethane—sp. gr. 2.95.

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Preparation.—Beach sands (as received) scrubbed in attrition scrubber at 76% solids for 3 minutes. Pulp deslimed once and washed once. Scrub pulp at 30% solids in soft water for 2 minutes with 1/3 #/T NaOH. Deslime pulp once and wash once. One minute settling time allowed for each deslime and wash step. A Fagergren 500-gram flotation cell was used for 2nd scrub and flotation. Temperature 30° C.

Reagents and conditions

Point of Addition	Conditions				Reagents				
	Time Cond.	(Min.) Float	Percent Solids	pH	NaOH	HF 48%	H ₂ SO ₄	Armac T	MAAPO
Attrition Scrub.	4		76						
Scrub	2		30		1/4				
After Deslime				5.7					
R ₁	1	2	20	{ 3.3I 3.5F }		0.312	0.3	0.15	0.05

MAAPO—Frother composed of 50-50 mixture of methyl amyl alcohol and pine oil.
Armac T—Technical primary amine acetate derived from tallow fatty acids.

Metallurgical results

Product	Wt., Grams	Wt., Percent	Assay, Percent—Percent Heavy Mineral ¹	Distribution, Percent
R ₁	21.0	4.30	94.0	96.4
T	459.0	95.70	0.16	3.6
Composite	480.0	100.0	4.20	100.0

¹ Specific gravity analysis made in tetrabromoethane—sp. gr. 2.95.

The method of this invention can also be advantageously used for the concentration of heavy minerals such as titanium oxide minerals from beach sand concentrates, as illustrated by the following example:

EXAMPLE VII

Preparation.—Scrub 500 grams of beach sand concentrate¹ (15% heavy mineral content and as received), at 30% solids in hard water (Chicago tap water) with 1 #/T H₂SO₄. One-half minute settling time allowed before single deslime and one wash step. A Fagergren 500-gram cell was used for scrubbing and flotation. Distilled water added to deslimed pulp for flotation. Temperature 25° C.

Reagents and conditions

Addition	Conditions				Reagents #/T		
	Time Cond.	(Min.) Float	Percent Solids	pH	HF 48%	Armac T	MAAPO
After deslime				6.5			
R ₁	1	2	20	{ 3.1I 3.3F 3.4F }	0.96	0.3	0.1
R ₂	1	2	20			0.2	0.1

MAAPO—Frother composed of 50-50 mixture of methyl amyl alcohol and pine oil.

Armac T—Primary amine acetate derived from tallow fatty acids.

¹ Composition of 15% HM Sand:

Zircon	1.1
Rutile	1.4
Ilmenite	4.1
Leucosine	Tr.
Monazite	3.5
Kyanite	1.9
Staurolite	1.9
Hematite	1.0
Misc.	2.0
HM total	15.0
Quartz	85.0
	100.0

8 Metallurgical results

Product	Wt., Grams	Wt., Percent	Assay, Percent—Percent Heavy Minerals	Distribution, Percent
R ₁	72	14.37	92.12	85.20
R ₂	32	6.39	31.38	12.93
T	397	79.24	0.36	1.87
Composite	501	100.0		100.0

Specific gravity analysis only for an additional test. Reagents and conditions similar to Example I.

Product	Wt., Grams	Wt., Percent	Assay, Percent—Percent Heavy Minerals	Distribution, Percent
R ₁	51	10.3	99.41	93.2
R ₂	2	0.4	58.87	2.2
T	442	89.3	0.57	4.6
Composite	495	100.0		100.0

While in the foregoing specification this invention has been described in relation to a specific embodiment thereof and many details have been set forth for this embodiment, it will be apparent to those skilled in the art that the invention is susceptible to other embodiments and that many of the details set forth herein can be varied widely without departing from the basic concepts of the invention.

I claim:

1. The method of concentrating titanium oxide minerals from beach sand having films of organic minerals on the particles therein and being composed principally of quartz particles while containing titanium oxide mineral particles, comprising removing the organic films from the particles of said sand, and then floating the titanium oxide mineral particles away from the quartz particles of said sand in water containing an amine collector and a fluorine-containing acid and being at a pH below 5.0.

2. The method of concentrating titanium oxide minerals from beach sand having films of organic minerals on the particles therein and being composed principally of quartz particles while containing titanium oxide mineral particles, comprising treating said beach sand with an inorganic alkaline reagent to remove the organic films from the particles of said sand, and then floating the titanium oxide mineral particles away from the quartz particles of said sand in water containing an amine collector and a fluorine-containing acid and being at a pH below 5.0.

3. The method of claim 2 in which said alkaline reagent is an alkali metal hydroxide.

4. The method of concentrating titanium oxide minerals from beach sand having films of organic minerals on the particles therein and being composed principally of quartz particles while containing titanium oxide mineral particles, comprising scrubbing said beach sand with caustic to remove the organic films from the particles

of said sand, separating the removed organic material from said sand, forming an aqueous flotation pulp of said sand containing an amine collector and a fluorine-containing acid, and separating the titanium oxide mineral particles from the quartz particles by subjecting said flotation pulp to froth flotation at a pH below 5.0.

5. The method of concentrating titanium oxide minerals from beach sand having films of organic materials on the particles therein and being composed of at least 90% quartz particles while containing a substantial amount of ilmenite and rutile particles, comprising removing the organic films from the particles of said sand, and then floating the ilmenite and rutile particles away from the quartz particles of said sand in water containing an amine collector and a fluorine-containing acid and being at a pH below 5.0.

6. The method of concentrating metal oxide and silicate minerals from beach sand having films of organic material on the particles therein, said beach sand containing at least 90% quartz particles and less than 10% metal oxide and silicate mineral particles, comprising scrubbing said sand with caustic to remove the organic films from the particles thereof, separating the removed organic material from the sand, forming an aqueous flotation pulp of the sand containing an amine collector and a fluorine-containing acid depressant, subjecting said pulp to froth flotation at a pH below 5.0, and removing substantially all of said metal oxide and silicate minerals

in the overflow while removing substantially all of the quartz in the underflow.

7. In a method of concentrating heavy minerals from beach sands composed principally of quartz particles while containing heavy mineral particles, the step of floating the heavy mineral particles away from the quartz particles of said sand in water containing an amine collector and a fluorine-containing acid and being at a pH below 5.0.

8. In a method of concentrating heavy minerals from beach sand concentrates containing quartz particles and heavy mineral particles, the step of floating the heavy mineral particles away from the quartz particles of said sand concentrate in water containing an amine collector and a fluorine-containing acid and being at a pH below 5.0.

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