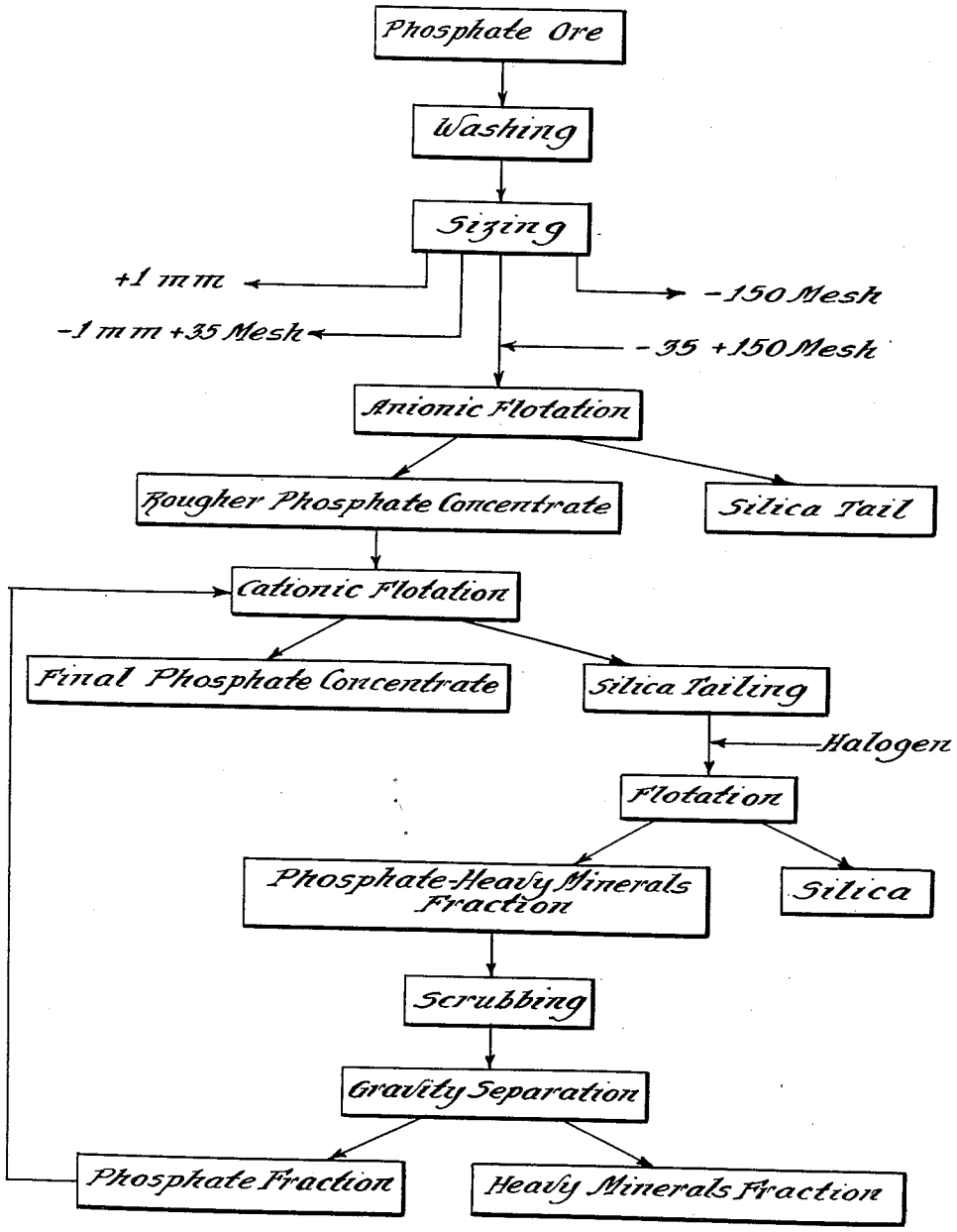
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METHOD OF RECOVERING MINERAL VALUES FROM ORE

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Inventor:
Douglas H. Fenske
By: Ernest V. Haines
Attorney

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METHOD OF RECOVERING MINERAL VALUES FROM ORE

Douglas H. Fenske, Lakeland, Fla., assignor to International Minerals & Chemical Corporation, a corporation of New York

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This invention relates to the recovery of phosphate and other mineral constituents from ores containing the same. More particularly, the invention relates to the recovery of phosphate and metallic minerals such as ilmenite, rutile, zircon, monazite and the like. Still more particularly, it relates to the recovery of an appreciable amount of the phosphate normally lost in the general mill tails.

Phosphate ore from the central district of Florida is subjected to flotation operations to produce high grade phosphate concentrates. The flotation procedure usually involves a rougher flotation operation whereby the phosphate is floated utilizing anionic reagents such as fatty acids. Phosphate intermediate concentrate is upgraded to a final concentrate of a grade between about 72% and 78% BPL by flotation with cationic reagents such as long chain aliphatic amine acid addition salts. The froth product from the amine flotation is a predominantly silica product containing from about 8 to 20% BPL product which in so-called open circuit operation is discharged to waste and in closed circuit carries so much material such as heavy minerals that the circuit periodically must be purged with consequent losses.

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

It is another object of the invention to provide a process wherein an appreciable portion of the phosphate formerly discharged to waste in the silica tailings is recovered.

It is still another object of the invention to provide an improved process permitting recovery of the heavy minerals as a bulk concentrate.

It is a further object of the invention to provide a relatively inexpensive method of preferentially depressing silica in a phosphate flotation operation following amine flotation.

It is still a further object of the invention to provide a method for rendering amine flotation agents ineffective in subsequent flotation operations on the products of amine flotation.

Now it has been discovered that, for example, the froth overflow product, containing phosphate and heavy minerals and predominating in silica, obtained by flotation of nitrogenous positive ion reagent treated phosphate concentrate can be subjected to a further flotation operation without addition of flotation reagents but in the presence of controlled amounts of halogen oxidizing agents to effectively separate silica, leaving a predominantly phosphate-heavy minerals fraction from which both components can be recovered.

The appended drawing is a flowsheet showing the method of the present invention as an improvement on the prior art method of concentrating phosphatic ores by anionic flotation to produce a rougher phosphate concentrate, followed by cationic flotation of the concentrate.

In this new and novel process, the predominantly silica froth overflowing the nitrogenous positive ion reagent

or amine reagent flotation cell is accumulated in a sump or passed directly to a flotation cell. To the froth product in the sump or in the cell is added between about 0.05 pound of halogen and about 1.5 pounds of halogen per ton of reagentized solids to be subjected to agitation and aeration in the flotation operation with about 0.3 pound to about 1.0 pound preferred.

Halogen may be added in the form of gaseous chlorine or gaseous bromine in the form of solution such as diluting water containing halogen in solution or sodium hypochlorite or similar materials in solution or solid-halogen-bearing materials such as sodium hypochlorite, potassium hypochlorite, calcium hypochlorite and the like.

In carrying out the process for recovery of phosphates and heavy minerals, the phosphatic ore is subjected to a washing operation in order to remove slime and other organic matter. The washed rock in an aqueous pulp form is subjected to screening or hydraulic sizing operation whereby the pebble or larger particles of phosphate rock are segregated from material which is approximately +1 mm. size. The —1 mm. size material is subjected to further washing for complete desliming, which desliming is produced by separating the —150 mesh size material from the +150 mesh size material. The +150 mesh size material called sand is subjected to a screening operation to produce a +35 mesh size fraction which is passed to spiral for concentration and a —35 mesh size fraction which is the feed to the flotation circuit. The major portion of the heavy mineral in this phosphate material reports in this —35 +150 mesh size fraction.

In the phosphate flotation operation, the —35 mesh fraction of the ore is mixed with anionic reagents which have an affinity for phosphate material and the heavy minerals. The reagentized mixture is subjected to flotation under conditions giving high recovery and selectivity permitting production of a throw-away silica tail product.

Anionic or carboxyl containing negative ion agents which are useful in the first or rougher stage of phosphate concentration are for example, the higher fatty acids, i.e., oleic, linoleic, and abietic acids, natural resin acid, tall oil, naphthenic acids, alkyl sulphonated fatty acids, acid esters of high molecular weight aliphatic alcohols and the soaps of such materials. Included within the term soaps of such negative ion or anionic type reagents, are the alkali metal and alkaline earth metal soaps such as sodium, potassium, aluminum, calcium and magnesium soaps. Soaps may also be formed by reacting such reagents with ammonia or aqueous solutions thereof. The metallic mineral-containing ore and phosphate having a —35 mesh particle size, is reagentized with one or more of these reagents in the presence of water by agitating the mixture at a solids content between about 50% and about 75% by weight, following which the slurry is diluted to a concentration suitable for introduction into the flotation cells. In these cells a froth is formed which carries the phosphate and heavy mineral to the top where this fraction is removed by overflow. This ore product, overflowing from the anionic flotation cell, is recovered for further processing as follows: The anionic reagents are removed from the solids by scrubbing with sulfuric acid. After scrubbing, the solids are washed free of reagents and acid by agitation with wash water. The washed solids are then reagentized with a cationic flotation reagent designed to remove the minor component of the concentrate, i.e., silica, and the heavy mineral. Useful cationic or positive ion reagents for this stage of the flotation procedure are the nitrogenous positive ion agents such as the higher molecular weight aliphatic amines containing at least one alkyl group having 12 to 20 carbon atoms and their water-soluble addition

salts with mineral and organic acids, esters of amino alcohol with higher molecular weight fatty acids, and higher alkyl substituted isoureas and their water-soluble salts, alkyl substituted pyridinium and quinolinium water-soluble salts and the like.

One of the products of this cationic flotation operation is a final phosphate concentrate which is the underflow from the flotation cells. The froth overflow from the cationic flotation is a mixture of silica, phosphate, and heavy minerals.

The froth mixture or slurry which usually contains between about 20% and about 30% of solids is generally accumulated in a sump, slurried with water to form a pulp containing about 10 to 25% by weight of solids and for example, sodium hypochlorite solution of 5% strength is added at a rate of about 0.5 to 2.0 pounds per ton of froth mixture. From this sump the slurry is pumped directly to a flotation cell of the Fagergren, Denver, or similar type for agitation and aeration. The underflow product from this flotation operation is predominantly silica whose phosphate content is about 1/5 to 1/2 that of the froth of the cationic flotation running about 2 to 8 BPL and 0.2% to 2.0% heavy minerals as against 10% to about 25% BPL and 3% to 5% heavy minerals in the froth feed.

Phosphate-heavy mineral froth overflowing the cell generally will contain 30 to 50% BPL and 5 to 15% heavy minerals and will require scrubbing treatment such as washing with sulfuric acid before subsequent processing to separate phosphates and heavy minerals unless the froth is to be recycled for mixing with feed to the rougher flotation operation. Generally, the phosphate-heavy minerals fraction is de-reagentized and subjected to gravity separation operations either in spirals or on tables or the like. The heavy mineral fraction separated in this manner will usually be a bulk concentrate containing about 85 to 95% of heavy minerals. Phosphate fraction recovered in the gravity separation is usually of the order of 38% to about 55% BPL which can be recycled to the positive ion agent flotation where a final phosphate concentrate is being produced and permitting recovery of 50% to 75% formerly lost in the general mill tail.

When feeding through this process a −35 mesh phosphate feed of approximately 31.1% BPL, .4% heavy minerals, at a rate of 600 parts by weight per hour, a separation is made in the rougher flotation cells which produces a phosphate concentrate assaying about 68% BPL and 1.0% heavy minerals containing about 250 parts by weight of the feed. The throw-away tail fraction consists of about 350 parts by weight of the feed and assays 93% silica and about 5% BPL.

The phosphate concentrate is separated in the amine flotation cell to recover a concentrate containing about 180 parts by weight per hour and a froth flotation product containing about 70 parts by weight per hour. The concentrate from the amine flotation will assay about 77% BPL and the amine froth product will assay 76.3% silica, 14.5% BPL and 5.0% heavy mineral.

The invention will be more fully understood from a study of the following example which is given by way of illustration of the preferred embodiment of the invention, and without any intention that the invention be limited thereto.

Example

A phosphate rock of the type found in phosphate pebble fields of Florida is subjected to a washing operation in order to remove slimes and other organic matter. The washed rock in an aqueous pulp is subjected to a screening or hydraulic sizing operation whereby the larger particles of rock are segregated from material which is approximately −35 mesh standard screen size. The latter material is then reagentized in an aqueous pulp containing about 70% solids with about one pound of a reagent comprising about 88% tall oil and about 12% kerosene per ton of ore treated. About 2 to 4 pounds of fuel oil is added and sufficient caustic soda is mixed into the mixture to give the latter a pH of about 8 to 9. The resultant pulp is then subjected to a flotation operation at a solids content of about 25 to 40% by weight in a Fagergren machine and a float product is recovered containing approximately 60% tricalcium phosphate, about 20% silica, and about 1.0% of metallic mineral. This phosphatic product is then treated with about 5 pounds per ton of solids of sulfuric acid (60° Bé.) in order to remove the reagents therefrom. The acid-treated product is washed until it is substantially neutral and is then reagentized in an aqueous pulp with a mixture of long-chain aliphatic amine, the latter comprising a mixture of about 73% of monooctadecyl amine and about 24% monohexadecyl amine, together with small quantities of secondary and tertiary amines whose aliphatic groups contain between about 12 and 18 carbon atoms. This reagent is preferably added in the form of acetic acid addition salt. The reagentized product is then subjected to a flotation operation at a solids content as previously described. The resultant froth product from this flotation contains a majority of the silica and about 2 to 6% by weight of metallic minerals. This siliceous float was slurried with water to form a pulp containing about 20% by weight of solids.

The amine float product was conducted directly to a Denver flotation cell and 24.2 pounds of sodium hypochlorite solution was added per ton of feed solids as a solution containing .042 pound/gallon of chlorine and introducing halogen in an amount corresponding 0.47 pound of chlorine per ton of feed solids.

Results of this flotation was as follows:

	Percent BPL	Percent Insol.	Percent H.M.
Feed	14.54	81.3	4.98
Underflow Tail	5.85	92.5	2.34
Concentrate	45.56	41.4	14.39

Concentrate from this flotation, corresponding to about 13 parts by weight per hour, was scrubbed with 2 pounds of sulfuric acid (60° Bé.) for 3 minutes and the concentrate washed to neutrality. In a spiral separation, the solids flowing at the rate of 1 ton of solid per hour, a separation was made as follows:

	Percent BPL	Percent Insol.	Percent H.M.
Feed	45.6	41.4	14.4
Heavy Mineral Tail	52.9	32.0	2.2
Heavy Mineral Concentrate	12.1	84.5	70.0

Having thus described this invention, what is desired to be secured by Letters Patent is:

1. In a flotation process wherein a phosphate ore containing silica and heavy minerals is subjected to anionic flotation to separate a float concentrate comprising silica and heavy minerals and predominating in phosphate, and the said anionic concentrate is subjected to cationic flotation to separate a float concentrate containing phosphate and heavy minerals and predominating in silica, the steps which comprise adding to said cationic float concentrate a halogen substance selected from the group consisting of chlorine, bromine, hypochlorites, hypobromites and mixtures thereof in a proportion equivalent to between about 0.05 and about 1.5 pounds of halogen per ton of solids, and subjecting said cationic float concentrate to further flotation without further reagentizing to separate a float concentrate comprising predominately phosphate and heavy minerals.

2. The process of claim 1 wherein the proportion of said halogen substance added to said cationic float concentrate is equivalent to between about 0.3 pound and about 1.0 pound of halogen per ton of solids.

3. The process of claim 1 wherein said halogen substance is chlorine.

4. The process of claim 1 wherein said halogen substance is added in the form of sodium hypochlorite, the proportion of sodium hypochlorite being between about 0.5 pound and about 2 pounds per ton of solids.

5. The process of claim 1 wherein said float concentrate comprising predominately phosphate and heavy minerals is admixed with sufficient acid to remove flotation reagents therefrom, and the dereagentized solids are subjected to gravity separation, whereby a phosphate concentrate and a heavy minerals concentrate are separately recovered.

6. The process of claim 5 wherein said phosphate concentrate recovered from said gravity separation is recycled to said cationic flotation.

7. In a flotation process wherein a phosphate ore containing silica and heavy minerals is subjected to anionic flotation with a fatty acid to separate a float concentrate comprising silica and heavy minerals and predominating in phosphate, and the said anionic concentrate is subjected to cationic flotation with a long chain aliphatic amine acid addition salt to separate a float concentrate containing phosphate and heavy minerals and predominating in silica, the steps which comprise adding to said cationic float concentrate between about 0.5 pound and about 2 pounds of sodium hypochlorite per ton of solids, and subjecting said cationic float concentrate to further flotation without further reagentizing to separate a float concentrate comprising predominately phosphate and heavy minerals.

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