

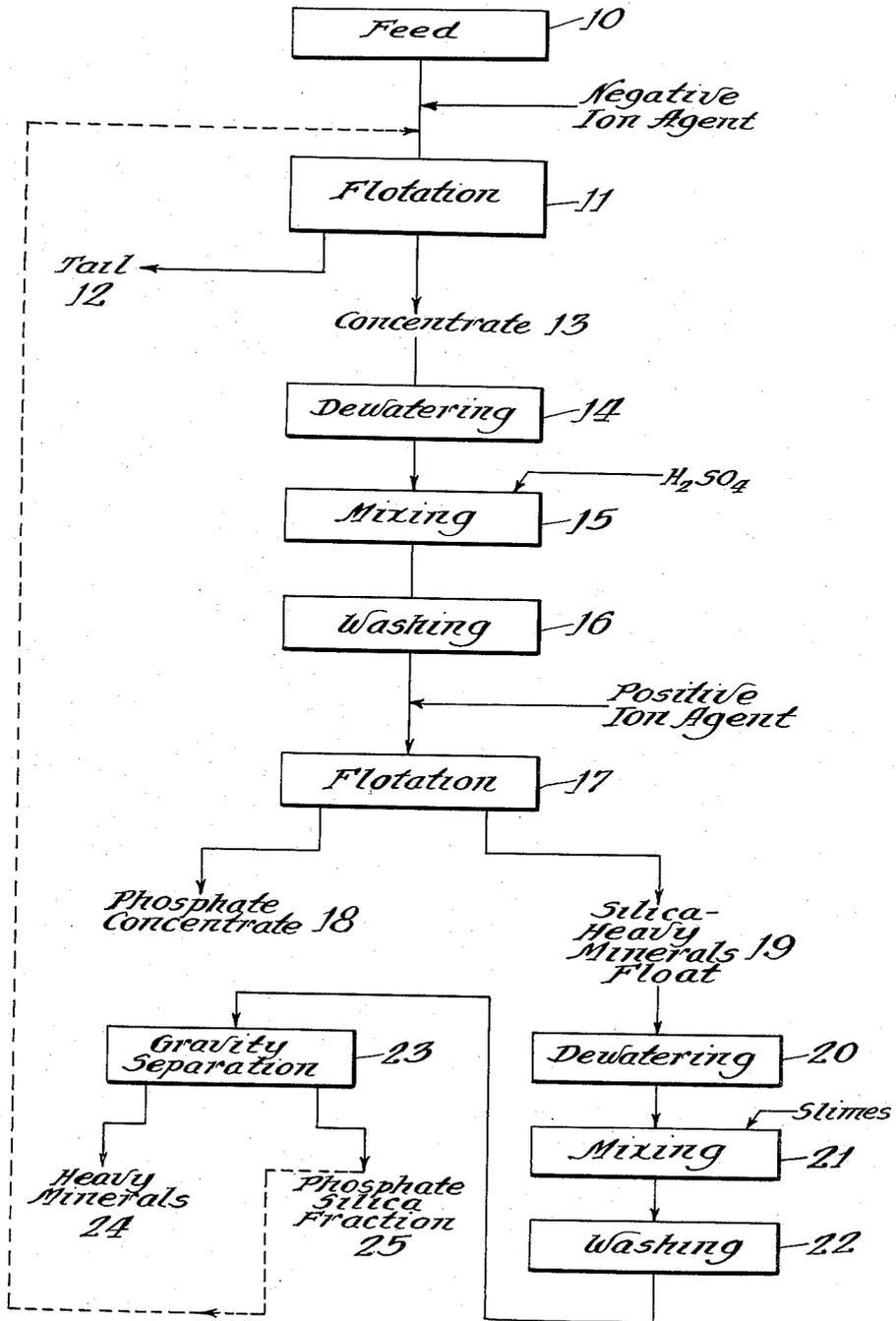
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METHOD FOR RECOVERY OF MINERALS

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METHOD FOR RECOVERY OF MINERALS

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This invention relates to the recovery of certain valuable mineral constituents from ores containing the same. More particularly, the invention relates to the recovery of metallic minerals such as ilmenite, rutile, zircon, as well as certain other minerals from ores containing substantial amounts of phosphate rock and siliceous material.

The occurrence of minerals such as ilmenite (FeTiO_3), zircon (ZrSiO_4), and rutile (TiO_2), is widespread. Up to the present time, it has been common practice to process or beneficiate only those ores which contain a rather high percentage of such valuable minerals. For example, it has been found that the raw material usually must be upgraded from about 5% to about 40% by weight of such mineral in order to be amenable to flotation procedure, whereby the desired constituents of the ore are floated away from siliceous gangue, or silica is floated away from the desired mineral constituents. Several flotation processes have been developed whereby flotation procedures have been adapted to the recovery of these so-called heavy minerals from ores.

Traces of certain metallic minerals such as ilmenite, rutile, zircon, sillimanite as well as minor amounts of garnet, tourmaline and monazite are known to occur in association with silica and phosphatic rock in the Florida phosphate field. As distinguished from their occurrence in various Florida or Australian sands, the heavy minerals are present in the phosphate matrix in quantities of less than about 0.1% by weight. By subjecting phosphate material to flotation operation for the recovery of the phosphatic values contained therein, according to the flotation processes heretofore in use, the metallic mineral content of the phosphate ore may be gathered together into a heavy mineral concentrate having a heavy mineral content of 2 to 4% by weight. In the past, the silica concentrates produced in the flotation of phosphatic ores have been discarded. This product, it has been found, contains the 2 to 4% by weight of heavy mineral as a result of treatment of the ore with cationic reagents. The composition of the silica concentrate produced by this method averages about 60 to 70% by weight of silica, about 10 to 20% by weight of tricalcium phosphate, the remainder consisting of the aforementioned heavy minerals together with other gangue impurities. A silica fraction containing only 2 to 4% by weight of metallic minerals is not commercially adaptable to industrial recovery processes and requires elaborate flotation operation with consequent capital investment to recover the heavy mineral in the form of a concentrate adaptable to industrial processes. It is the primary object of this invention to provide a new and novel process eliminating the disadvantages and shortcomings of processes heretofore in use.

It is an object of this invention to provide a novel and simplified process for the recovery of metallic mineral values from phosphatic ores.

It is another object of this invention to provide a novel process whereby the phosphate in the concentrate is re-

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covered in higher purity and with more complete recovery and metallic minerals recovered in commercially acceptable concentrations.

It is still another object of this invention to provide a process which eliminates a large number of flotation operations of the processes heretofore known.

It is still a further object of this invention to provide a process whereby the metallic minerals are accumulated in a predominantly silica fraction which formerly was discharged to waste, and the silica fraction processed to recover the minerals and phosphate therefrom.

These and other objects of the invention are accomplished by subjecting a finely divided phosphatic-siliceous ore which contains base metal oxide type metallic minerals to at least one flotation operation in the presence of anionic flotation agents having an affinity for phosphate value and nitrogenous cationic agents having an affinity for siliceous gangue, separating out a predominately siliceous fraction rich in metallic minerals, removing the amine flotation reagent, i.e., nitrogenous cationic agent, from said siliceous fraction, slurring the de-reagentized siliceous material with water, separating the heavy minerals from silica and phosphate on the basis of difference of specific gravity and recycling the silica-phosphate fraction to the flotation system.

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 a 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, stearic, and palmitic 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 25% and about 50% 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

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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, high molecular weight aliphatic quaternary ammonium bases and their water-soluble salts, alkyl-substituted pyridinium and quinolineum 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 overflow from the cationic flotation is a mixture of silica and heavy minerals. This mixture is freed of amine reagents by any one of a number of treatments. The mixture may be "de-reagentized" by treating it with an acid material such as a mineral acid, for example, sulfuric acid; following which the acid-treated material is washed with water until it is substantially neutral. The amine reagent may also be removed by treating the slurry mixture overflowing from the cationic flotation operation with sodium hypochlorite and the like, or chlorine water with or without subsequent washing operations. In still another method of cationic reagent removal, the froth slurry is mixed with slime previously removed in the washing of the ore. Following agitation in the presence of the slime, the mixture is subjected to classification as in a hydroseparator to float the slime material away from the sand. The sands are then washed with water and are ready for further processing. The de-reagentized mixture of silica, phosphate, and heavy mineral is next subjected to separation on the basis of specific gravity differences of the various materials. This specific gravity separation may be effected on the Wilfley tables but preferably is carried out in spirals where a slurry of the mixture is flowed by gravity through a trough having a spiral port adapted for drop out of the heavy minerals of highest specific gravity along the inside of trough whereas the lighter specific gravity materials continue to flow in a path adjacent to the outer perimeter of the spiral and are recovered from the bottom of the spiral. Specific gravity differences between the heavy mineral and silica and phosphate are such that in a specific gravity separation a concentrate of heavy minerals may be produced of between 80 and 95% by weight of heavy mineral. The tail product from the specific gravity separation consisting predominately of silica and phosphate, may then be recycled to the rougher flotation feed.

The metallic mineral concentrate produced in accordance with the instant novel process is a bulk product containing all of the various heavy minerals present and may be subsequently dried and subjected to further concentration by suitable means.

Reference has been made herein to rougher separation of materials treated with anionic reagents followed by further separation of the phosphate concentrate by flotation under cationic flotation conditions as though these operations were performed in a single flotation stage. A single flotation stage in each instance is the preferred embodiment of the process but it is not meant to exclude the possibility that each of these stages may be carried out in a multiplicity of stages.

The invention will be more fully understood from a study of the figure which illustrates the preferred embodiment of this process. Referring to the flowsheet, deslimed phosphate ore of about -35 mesh size is indicated by the numeral 10. This material is mixed with flotation

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agent composition containing a negative ion agent such as tall oil and delivered to flotation unit 11 from which is recovered a throw-away silica tail 12 and a phosphate rock concentrate 13 containing the so-called heavy mineral. The concentrate 13 is a slurry which is raised to a solids content of about 75% at a dewatering station 14. Dewatered concentrate is conveyed to a mixing station 15 where sulfuric acid is added to remove the anionic flotation reagents. Concentrate is washed to neutrality at washing station 16. Following washing, the concentrate is delivered to a second flotation unit 17 where it is mixed with a positive ion flotation agent such as a long chain aliphatic amine, and aerated and agitated to cause formation of a froth which can be overflowed from the flotation cell. From this flotation is recovered a phosphate concentrate or underflow fraction 18 and a silica float 19 containing said heavy minerals. Silica float 19 is conducted to a dewatering station 20 and then to a de-reagentizing unit consisting of a mixing station 21 where either slimes or chlorine water is added and then to washing station 22 where water is added until the slimes or chlorine water is washed out of the slurry being treated. De-reagentized silica fraction is delivered from washing station 22 to a gravity separation unit 23 where the slurry of the de-reagentizing fraction is flowed in a spiral or elliptical path. From the ports in this elliptical path is recovered the heavy mineral fraction 24 and the silica-phosphate fraction 25. The silica-phosphate fraction 25 is then preferably recycled for combining with the rougher feed.

The nature and character of the invention is further illustrated by reference to the preferred embodiment of the invention 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 60% 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 30% silica, and about 0.5% of metallic mineral. This phosphatic product is then treated with about 2 pounds 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 mono-octadecyl amine and about 24% mono-hexadecyl 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 4% by weight of metallic mineral. This froth product was mixed with slime material in proportions of approximately 5 pounds of slime solids per ton of amine flotation silica product, the slimes being the fine material obtained from the hydroseparator in the washing of phosphate ore. The solids mixture was agitated for about 2 minutes and then deslimed by decanta-

tion. This de-reagentized siliceous material is then slurried with water to adjust the solids content of the slurry to approximately 50 to 60% by weight of solids and the slurry is fed through a distributor which introduces into each spiral about 5 tons per hours of solids. From the draw-off ports in each spiral is recovered the bulk heavy mineral fraction and from the end of the spiral is obtained a silica-phosphate slurry.

When feeding through this process a -35 mesh phosphate feed of approximately 31.1% BPL, 0.4% 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% heavy minerals and 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 91% silica and about 6% 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 53% silica, 38% BPL, and 7% heavy mineral. In the spiral, this froth product from the amine flotation will be separated to produce about one ton per hour of heavy mineral assaying 70% heavy mineral, 19% BPL, and a tail fraction of 75 parts by weight per hour assaying 60% silica and about 30% BPL. This silica-phosphate fraction, having the same concentration of phosphate as the feed, is mixed therewith.

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

1. A process for the recovery of base metal oxide type metallic mineral from phosphate-silica ores containing the metallic minerals in minor amounts which comprises subjecting the ore in a finely divided state to a flotation operation employing anionic reagents having an affinity for phosphate to recover a phosphate-metallic mineral concentrate and a throwaway silica tail, removing the anionic reagents from said phosphate concentrate, subjecting the phosphate concentrate after removing the anionic reagents to a flotation operation employing cationic reagents to recover a final phosphate concentrate and a silica-metallic mineral froth product, removing said cationic reagents from said silica-metallic mineral product, diluting the silica-metallic minerals product after removing said cationic reagents with water, subjecting the diluted silica-metallic mineral product to gravitational separation thereby stratifying the minerals according to their specific gravities, recovering a strata rich in metallic minerals, and recycling the silica-phosphate strata to the feed to the anionic flotation.

2. A process for the recovery of base metal oxide type metallic mineral from phosphate-silica ores containing the metallic minerals in minor amounts which comprises subjecting the ore in a finely divided state to a flotation operation employing carboxy-containing negative ion agent having an affinity for phosphate to recover a phosphate-metallic mineral concentrate and a throw-away silica tail, removing the carboxy-containing negative ion agent from said phosphate concentrate, subjecting the phosphate concentrate after removing the carboxy-containing negative ion agent to a flotation operation employing nitrogenous positive ion agent to recover a final phosphate concentrate and a silica-metallic mineral froth product, removing said nitrogenous positive ion agents from said silica-metallic mineral product, diluting the silica-metallic minerals product after removing said nitrogenous positive ion agent with water, subjecting the diluted silica-metallic mineral product to gravitational separation thereby stratifying the minerals according to their specific gravities, recovering a strata rich in metallic minerals and recycling the silica-phosphate strata

to the feed to the carboxy-containing negative ion agent flotation.

3. A process for the recovery of base metal oxide type metallic mineral from phosphate-silica ores containing the metallic minerals in minor amounts which comprises subjecting the ore in a finely divided state to a flotation operation employing anionic reagents having an affinity for phosphate to recover a phosphate-metallic mineral concentrate and a throw-away silica tail, removing the anionic reagents from said phosphate concentrate, subjecting the phosphate concentrate after the removal of said anionic reagents to a flotation operation employing cationic reagents to recover a final phosphate concentrate and a silica-metallic mineral froth product, removing said cationic reagents from said silica-metallic mineral product, diluting the silica-metallic minerals product after the removal of said cationic reagents with water, subjecting the diluted silica-metallic mineral product to spiral separation thereby stratifying the minerals according to their specific gravities, recovering a strata rich in metallic minerals, and recycling the silica-phosphate strata to the feed to the anionic flotation.

4. A process for the recovery of base metal oxide type metallic mineral from phosphate-silica ores containing the metallic minerals in minor amounts which comprises subjecting the ore in a finely divided state to a flotation operation at a pH in the range between about 8 and 9, employing carboxy-containing negative ion agent having an affinity for phosphate to recover a phosphate-metallic mineral concentrate and a throw-away silica tail, removing the carboxy-containing negative ion agent from said phosphate concentrate, subjecting the phosphate concentrate after the removal of carboxy-containing negative ion agent to a flotation operation employing nitrogenous positive ion agent to recover a final phosphate concentrate and a silica-metallic mineral froth product, removing nitrogenous positive ion agents from said silica-metallic mineral product, diluting the silica-metallic minerals product after the removal of said nitrogenous positive ion agent with water, subjecting the diluted silica-metallic mineral product to gravitational separation thereby stratifying the minerals according to their specific gravities, recovering a strata rich in metallic minerals and recycling the silica-phosphate strata to the feed to the carboxy-containing negative ion agent flotation.

5. A process for the recovery of base metal oxide type metallic mineral from phosphate-silica ores containing the metallic minerals in minor amounts which comprises subjecting the ore in a finely divided state to a flotation operation employing anionic reagents having an affinity for phosphate to recover a phosphate-metallic mineral concentrate and a throw-away silica tail, removing the anionic reagents from said phosphate concentrate by adding sulfuric acid to a slurry of said concentrate and agitating the mixture, washing the concentrate to a substantially neutral pH, subjecting the phosphate concentrate after washing to a flotation operation employing cationic reagents to recover a final phosphate concentrate and a silica-metallic mineral froth product, removing cationic reagents from said silica-metallic mineral product, diluting the silica-metallic minerals product with water, subjecting the diluted silica-metallic mineral product to gravitational separation thereby stratifying the minerals according to their specific gravities, recovering a strata rich in metallic minerals, and recycling the silica-phosphate strata to the feed to the anionic flotation.

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