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FLOTATION PROCEDURES

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This invention relates to a novel process for separating mineral constituents from at least one mineral in the group consisting of calcite, fluorite, chalcopryrite, and monazite.

In the treatment of ores by flotation for the selective separation of certain components, the crude material is first crushed and ground and then formed into a slurry. At least one flotation reagent is then added to the slurry during the conditioning period for the purpose of improving separation. The mechanism by which the reagents are believed to enhance selectivity, stated in its simplest form, is that certain constituents of the ore are preferentially coated with a film, and some particles remain uncoated. When a froth producer is then introduced and flotation is under way, the coated particles, now hydrophobic, are repelled by the water and adhere to the gas or air bubbles; after rising to the surface of the bath, they are removed for further treatment. The components of the crude ore which were not coated remain in suspension and, depending on their commercial value, are treated further or discarded.

A great variety of reagents are known and commercially employed, each reagent being particularly applicable to, and having a marked preference for, a certain type or class of mineral or even a specific compound. New reagents, however, are constantly being sought which react with constituent ore particles for which no reagent is as yet known, or which exhibit greater selectivity for a specific type of material than those previously employed.

By way of example, crude tungsten ore presently being processed for tungsten recovery is composed primarily of quartz (SiO_2), calcite (CaCO_3) and fluorite (CaF_2); also present are apatite; garnet; copper, molybdenum, and iron sulfides; minor silicates and approximately 0.5 percent WO_3 in the form of scheelite.

Current practice in processing an ore of this type calls for flotation using xanthate to recover the sulfide constituents of the crushed and ground ore. The tailings from this process are then subjected to a preliminary (rougher) flotation treatment for tungsten recovery. In this step, fatty acids having long-chained molecules (impure commercial soaps) are employed along with other compounds as flotation reagents. The soap is adsorbed on the surface of the scheelite particles, rendering them hydrophobic, so that during flotation the coated particles attach themselves to the air bubbles and are thus separated from the gangue. Unfortunately, the selectivity of the soap is not limited to scheelite alone, since the other calcium components present as components of the ore, calcite and fluorite, are also coated to an appreciable extent and recovered, in part, as a floated product. Also important is the fact that considerable soap is carried over as a coating on the floated particles, and as precipitated-and-floated calcium soaps.

The product resulting from the rougher treatment is a tungsten concentrate containing on the order of about 10 percent WO_3 . Although this represents about 90 percent tungsten recovery from the original feed material, approximately 30 to 35 percent calcite is also recovered. This material, along with fluorite and portions of other constituents of the crushed ore, comprises the major components of the rougher concentrate.

This low-grade concentrate is later subjected to pres-

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sure leaches or other treatments for the eventual recovery of tungsten either as pure scheelite, ammonium paratungstate, or WO_3 . Since tungsten is the sought-after constituent of the crude ore, it can be readily understood that any improvement which could be made in ore processing which would result in higher concentrations of tungsten would be most desirable. For instance, a six-fold excess of sodium carbonate is customarily employed when leaching the 10 percent WO_3 concentrate. A higher-grade concentrate on the order of 50 percent WO_3 would require at the most a twofold excess of Na_2CO_3 and might even be economically upgraded by an acid leach. The rejection of calcite, particularly, during flotation, and fluorite as well, would, therefore, serve materially to produce higher concentrations of tungsten, thereby permitting more effective use of the leaching reagent in the recovery of the tungsten values from the concentrate.

Most efforts expended to increase the extent to which calcite and fluorite may be depressed have met with little success. The one method by which calcite recovery was appreciably depressed, that of adding sodium silicate to the slurry, resulted in a corresponding decrease in tungsten recovery as well. Similar failure resulted from attempts to reject fluorite, which component would be deemed as objectionable as calcite in the final product but for the fact that it is present in lesser quantities.

Another major difficulty that arises from the use of sodium silicate as a calcite depressant is due to the presence of soap in the slurry. When sodium silicate is added to the slurry in quantities sufficient to depress calcite significantly, not only is tungsten recovery materially lowered, but, even more important, an overabundance of very fine bubbles and an excessive froth are produced. The froth, in fact, becomes so voluminous when sodium silicate is increased as to become entirely unmanageable.

The effectiveness of sodium silicate in preventing the flotation of calcite, however, is distinctly advantageous. Since an unmanageable froth results from its use even when quantities are employed wherein no tungsten losses are incurred, it can be readily appreciated that any means which would make possible the use of sodium silicate to depress calcite without producing an unmanageable volume of froth, would be a decided advance in the technique for processing tungsten ores.

It is an object of the present invention to provide an improved process for the flotation separation of minerals from at least one mineral in the group consisting of calcite, fluorite, chalcopryrite, and monazite.

It is another object of the present invention to provide an improved process for the flotation separation of minerals from at least one mineral in the group consisting of calcite, fluorite, chalcopryrite, and monazite wherein sodium silicate may be employed as a calcite depressant without the interference of the excessive froth normally present during such calcite depression.

Other objects will be apparent from the subsequent disclosure and appended claims.

The objects are achieved by employing sodium or potassium permanganate (KMnO_4) as a treating reagent in the beneficiation of crude ores or flotation concentrates by flotation techniques.

Although the exact mechanism by which the permanganate performs its useful functions in the process is not fully understood, it is believed that, among other attributes, this compound has excellent oxidizing characteristics in flotation applications. In the treatment of flotation concentrates where films of soap or other reagents are still present on the surfaces of the floated product, further treatment of the concentrate may be accomplished by the use of KMnO_4 to oxidize the organic surfaces of some of the constituents and render some of the floated particles non-floatable, thereby achieving separa-

tion of ore components more efficiently and at less cost than was previously possible. In addition to its tendency to oxidize selectively, potassium permanganate, when chemically reduced, is also thought to form a hydrous manganese oxide ($MnOx \cdot xH_2O$), which product may precipitate on the surfaces of certain components of the concentrate and thereby further serve to depress the floatability of these components.

Particularly in connection with the recovery of scheelite, potassium permanganate is most effective when used jointly with sodium silicate. In accordance with the present invention, the $KMnO_4$ is added to a flotation slurry of low-grade tungsten concentrate, in which sodium silicate is also present, in a sufficient quantity to oxidize the residual and some of the adsorbed soap. The $KMnO_4$ is preferably added in stages but may also be introduced as a single addition. The invention is based partly on the hypothesis that the concentration of the soap ions in solution, which in turn ties into the adsorption density of the soap coatings on all minerals, is thereby controlled. Furthermore, it is believed that the silicate ions compete with the soap ions for the surfaces of the calcium mineral particles and that the destruction of the excess soap would result in the elimination of excessive foaminess since, in the absence of soap, the sodium silicate would clean the surfaces of the mineral particles.

In practicing the invention, a dilute $KMnO_4$ solution is added in stages to a slurry in a flotation cell in a total quantity equivalent to about 15 to 20 pounds per ton of solids being treated, and into which was previously introduced the equivalent of approximately 30 pounds of sodium silicate per ton of solids. The above figures are particularly relevant to a low-grade tungsten concentrate containing on the order of about 10 percent to 15 percent WO_3 , the balance being predominantly calcite and fluorite, and in which slurry are also present remnants of impure commercial soap employed in the initial rougher flotation treatment of the crude ore. Operating conditions under which the slurry is so heated to from 50° C. to 60° C. appear to yield optimum results although the beneficial effects are obtainable even at room temperature. A slurry containing from 20 percent to 25 percent solids has also been found to be satisfactory.

Observation of the reaction when potassium permanganate is added indicates clearly its oxidizing action and its eventual consumption by a constituent of the pulp until the oxidizing component of the permanganate is all gone. The mineral particles in the slurry progressively turn yellow, brown, and finally dark brown, with the pulp, initially in a dispersed state, becoming flocculated. After the soap is oxidized, the scheelite is floated in the usual fashion as a cream-colored or white float with bubbles of moderate size. The extreme frothiness that is generally associated with the addition of sodium silicate alone is not present when potassium permanganate is simultaneously employed as a reagent and, indeed, the froth may disappear so completely that additional frothing agents, such as heptanol or pine oil, or even a collector such as oleic acid, may be required. Improved results may be had if additional flotation reagent is added after the permanganate treatment.

As stated previously, the exact mechanism of the reaction is not thoroughly understood but it is postulated that the potassium permanganate reacts with the soap either at the surface of the calcite and possibly the fluorite particles, or in solution, with the permanganate being reduced from the Mn^{+7} to Mn^{+4} state, forming hydrous manganese dioxide.

The optimum temperature of operation appears to be about 60° C., the rate of reaction at this temperature being several times faster than at room temperature. A slurry containing approximately 20 percent to 25 percent solids and having a pH of about 11 has been found to be suitable for treatment in accordance with the invention.

As originally stated, potassium permanganate is ex-

tremely effective as a reagent in the treatment of a wide variety of ores. The following examples will serve to illustrate the process of the invention and the benefits derived from the use of $KMnO_4$ in the flotation of scheelite and the separation of other closely allied components of ores and concentrates.

Example I

A scheelite concentrate containing about 14 percent calcium tungstate, expressed as tungsten trioxide and containing residual xanthate flotation reagent for the initial concentration, was introduced into a flotation cell containing sufficient water to form a slurry containing approximately 25 percent solids. The temperature of the slurry was increased to about 60° C. and 1.5 parts by weight of sodium silicate were added per 100 parts by weight of solids. A 5 percent solution of potassium permanganate was added to a mixture in three increments of 0.25 part by weight of potassium permanganate per 100 parts by weight of solids. The slurry was then subjected to normal froth flotation separation to produce a froth concentrate containing 71.39 percent by weight of calcium tungstate expressed as tungsten trioxide and a tailings containing about 6.65 percent calcium tungstate expressed as tungsten trioxide.

Example II

Following identically the same procedure of Example I a calcium tungstate concentrate containing 71.8 percent calcium tungstate expressed as tungsten trioxide was obtained.

Example III

Slurries containing residual xanthate flotation reagent from a prior treatment, and consisting predominantly of calcite and fluorite and approximately 10 percent calcium tungstate, expressed as tungsten trioxide, were treated with 1.5 parts by weight of sodium silicate and 1 part by weight of potassium permanganate per 100 parts by weight of solids in the slurry. The permanganate was added as a 5 percent aqueous solution. Concentrates containing from 50 percent to 70 percent calcium tungstate were obtained. As little as 4.5 percent of calcite and 9.0 percent of fluorite were present in the final concentrate.

Example IV

The float concentrate obtained from the xanthate flotation of crude calcium tungstate ore and comprising primarily molybdenite (20 percent Mo) and chalcopryrite (20 percent Cu) was slurried with water containing 1.0 to 1.5 parts of potassium permanganate per 100 parts of solids treated and subjected to further flotation treatment. Practically pure molybdenite was recovered as a floated product, the chalcopryrite being removed as tailings.

Example V

Two 500 gram samples of beach sand were treated by flotation in exactly the same manner to produce zircon-monzite concentrates containing 79 percent zircon and 19 percent monazite. No further treatment was provided for one of the concentrates. The second concentrate was treated with 1 part by weight of potassium permanganate per 100 parts of solids and six increments of oleic acid totalling 0.32 part by weight per 100 parts of solids. Air was passed through the slurry. The zircon floated to the surface with the froth but the potassium permanganate completely depressed the monazite. Thus a zircon flotation concentrate of high purity was obtained.

In the preferred form of the invention .75 to 1.0 part by weight of potassium permanganate is employed per 100 parts by weight of solids being treated. The permanganate is added preferably as a dilute aqueous solution in several increments. By adding the permanganate in this manner, not only is the degree of concentration high but the recovery of the floatable mineral is also improved over the procedure of adding the permanganate all at once. This may be illustrated by Example VI.

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Example VI

A calcium tungstate concentrate containing residual xanthate flotation reagent from the initial concentration and containing 10.29 percent by weight of calcium tungstate, expressed as tungsten trioxide, was pulped in water to produce an aqueous slurry containing 25 percent solids; this slurry was treated with two equal incremental portions of sodium silicate (a total of 1.6 parts by weight of sodium silicate per 100 parts by weight of solids), three 3-parts-by-weight increments, and two, 6-parts-by-weight increments, of potassium permanganate, per 100 parts of solids. The incremental additions were spaced over an 11 minute conditioning period during which time the temperature of the slurry was gradually increased to 53° C. and the pH to 10.7. Air was passed through the slurry and the froth was removed. The flotation concentrate contained 52.30 percent calcium tungstate expressed as tungsten trioxide. Calcium carbonate (calcite) in the amount of 4.46 percent and 8.93 percent calcium fluoride (fluorite) had a calcium tungstate recovery of 80 percent. This recovery is to be compared to the recovery obtained in Examples I and II wherein the recovery was of the order of 58 to 65 percent.

It has been found to be most advantageous to heat the slurry to a temperature in the range of 50° C. to 60° C. during flotation for maximum efficiency of operation. Similarly, it has been found most advantageous to treat the slurry containing from 20 to 25 parts of solids.

The optimum conditions of operation are as follows: temperature of slurry: about 60° C.; pH of slurry: about 11; slurry concentration: approximately 20-25 percent solids. When calcite is one of the minerals to be depressed in the flotation procedure the inclusion of approximately 1.5 parts by weight of sodium silicate per 100 parts by weight of solids has been found to be most advantageous.

While the foregoing examples illustrate specific separations, the process is applicable to any separation process wherein a mineral is separated from calcite, fluorite, chalcopryrite or monazite by the flotation of that mineral. The permanganate increases the degree of flotability between the mineral to be floated and the calcite, fluorite, chalcopryrite, or monazite, thereby increasing the sharpness of separation.

What is claimed is:

1. In a flotation process wherein calcium tungstate is separated from a mixture of said mineral with a gangue

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containing at least one mineral of the group consisting of calcite and fluorite by the addition to an aqueous slurry of said mixture of an organic flotation reagent whereby the major portion of said calcium tungstate is floated to the surface of said slurry and removed therefrom, and the major portion of said gangue remains in said slurry, the improvement which comprises adding to said slurry at least a substantial portion of at least one water-soluble permanganate selected from the group consisting of sodium permanganate and potassium permanganate, whereby the propensity of said gangue to float with said calcium tungstate is substantially decreased.

2. A process in accordance with claim 1 wherein at least a substantial amount of flotation reagent is added to said slurry subsequent to said permanganate addition.

3. A process in accordance with claim 1 wherein a substantial amount of sodium silicate is added to said slurry prior to said flotation.

4. A process in accordance with claim 3 wherein at least a substantial amount of flotation reagent is added to said slurry subsequent to said permanganate addition.

5. In a flotation process wherein zircon is separated from a mixture thereof with monazite by the addition to an aqueous slurry of said mixture of an organic flotation reagent whereby the major portion of said zircon is floated to the surface of said slurry and the major portion of said monazite remains in said slurry, the improvement which comprises adding to said slurry at least a substantial portion of at least one water-soluble permanganate selected from the group consisting of sodium permanganate and potassium permanganate, whereby the propensity of said monazite to float with said zircon is substantially decreased.

6. A process in accordance with claim 5 wherein a substantial amount of flotation reagent is added to said slurry subsequent to said permanganate addition.

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