

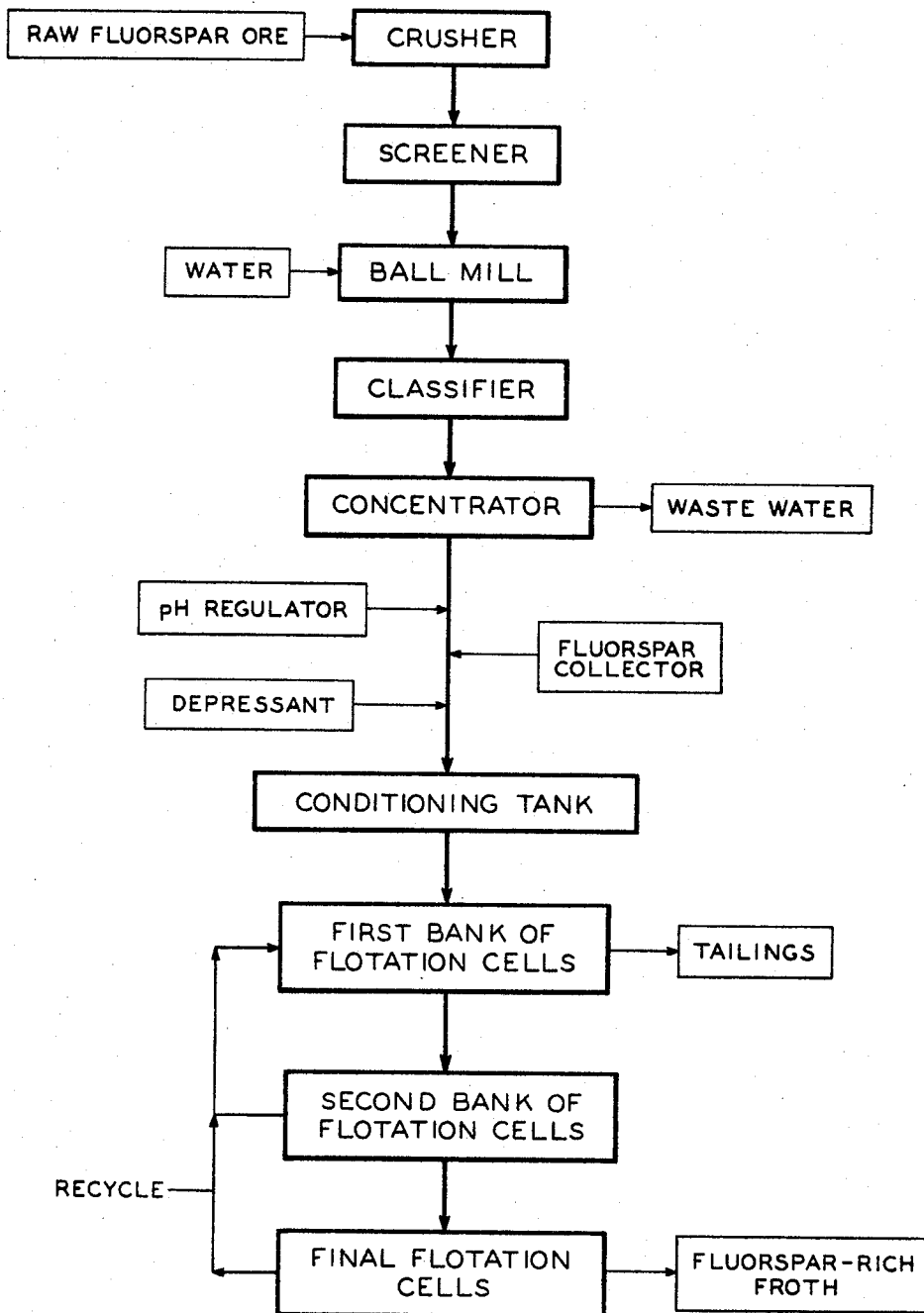
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BENEFICIATION OF FLUORSPAR ORES

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BENEFICIATION OF FLUORSPAR ORES

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ABSTRACT OF THE DISCLOSURE

"Acid-grade" fluor spar is recovered from fluor spar ores containing appreciable amounts of gangue minerals and metallic sulfides by a froth flotation treatment which comprises the following steps: (a) mixing crude fluor spar ore with water to form an aqueous pulp, (b) adding to the pulp a collector for fluor spar selected from the group consisting of saturated fatty acids and mixtures of saturated and unsaturated fatty acids wherein the saturated fatty acid content of the mixture comprises at least about 40% of the total quantity of collector, or soaps of these acids or acid mixtures, (c) further adding to the pulp a depressant for gangue minerals selected from the group consisting of alkali metal silicates and alkali metal metasilicates, (d) subjecting the pulp to a conditioning treatment which comprises heating the pulp to its boiling point with agitation while maintaining the pulp at a pH between about 8.0 and 9.0, (e) subjecting the conditioned pulp to froth flotation and (f) recovering fluor spar enriched concentrate from the froth.

The present invention relates to the beneficiation of fluor spar ores and more particularly to a froth flotation treatment whereby fluor spar of a high degree of purity is obtained.

"Acid grade" fluor spar, a term generally utilized to designate a concentrate containing at least 97% fluor spar (CaF₂), is used in various chemical processes as a source of fluorine and hydrogen fluoride. The specifications as to allowable impurities vary with the industry but, in general, it is required that the fluor spar product be relatively free of gangue minerals such as quartz, calcite, clays and barite, as well as other accessory minerals including various sulfides such as galena, sphalerite, pyrite and chalcopryrite. Fluor spar ores as mined seldom meet the specifications either with respect to fluor spar content or freedom from impurities and suitable methods of concentration and ore separation must be employed to recover commercial "acid grade" products from fluor spar ore. Although the beneficiation of fluor spar ores is readily effected by use of so-called "anionic" flotation reagents such as fatty acids, tall oils and the like, as well as various soaps thereof, the elimination of certain mineral impurities from the concentrate, thereby improving fluor spar grade, has been a difficult and costly task.

In the removal of sulfides from fluor spar ores the most commonly employed method is to first float the sulfide minerals, as by use of sulfhydryl or xanthate collectors in combination with metallic salts which serve as activators in sulfide flotation such as copper and zinc sulfate, and then to float the fluor spar with a fatty acid collector containing a high percentage of unsaturated fatty acids. The metallic salts used for the flotation of sulfide minerals under most conditions interfere with the subsequent flotation of fluor spar and thus, additional reagents are normally required to complex or precipitate the metallic salts, thereby overcoming any deleterious effect these salts may exert in fluor spar flotation. Although flotation of alkaline earth minerals with carboxylic acid collectors, while depressing the sulfide minerals with sulfide, hydro-

sulfide or cyanide ions, has been suggested in the prior art as another method for elimination of sulfide minerals, "acid grade" fluor spar cannot be obtained from most ores by such a one-step flotation process. In fact, the most common practice is to combine these two methods, thus, first floating sulfide minerals capable of being directly floated and then floating the fluor spar in the presence of depressants for the sulfide minerals. Employment of the primary sulfide flotation circuit, necessitating additional equipment in the form of sulfide flotation cells and increased power consumption, as well as additional reagents, has contributed substantially to high milling costs in recovering fluor spar having the desired high purity. Moreover, mining methods which require that the crude broken fluor spar ore be stored underground, render recovery of an "acid grade" fluor spar difficult even when the primary sulfide flotation circuit is employed. Apparently, under these conditions, the ore is oxidized to form complex metallic salt contaminants which are solubilized in the flotation process. In this form, these contaminants interfere not only with the effective removal of sulfide minerals in the primary sulfide flotation circuit, but also preclude selective flotation of the fluor spar in subsequent flotation circuits.

Furthermore, even after sulfide minerals have been sufficiently reduced to obtain an ore meeting specification requirements, gangue minerals such as quartz and calcite must be eliminated to effect the desired degree of concentration of the ore. Prior art practices generally require retardation of the gangue minerals by the addition of one or more depressants for these minerals such as lignin sulfonates, soluble fluorides, gelatinized or dextrinized starch and cresylic acid. In addition to the increased cost of using these reagents, specialized procedures must generally be employed in their preparation; for example, the starch must be heat treated or oxidized to rupture the starch granules, thereby increasing their water solubility.

Accordingly, one object of the present invention is to provide a froth flotation process for the concentration of natural fluor spar ores whereby "acid grade" fluor spar is obtained.

Another object of the invention is to provide a froth flotation process for the concentration of crude fluor spar ores whereby high recoveries of the fluor spar content of the crude ores are effected.

A further object of the present invention is to provide an improved one-step flotation process for producing a fluor spar enriched concentrate of "acid grade" quality from fluor spar ores containing substantial quantities of metallic sulfides without preliminary flotation of the sulfide minerals thereby effecting greater operating economies.

A still further object of the present invention is the provision of a froth flotation process for producing a fluor spar enriched concentrate of "acid grade" quality from fluor spar ores contaminated with complex metallic salts.

It has now been discovered that fluor spar ores containing in addition to fluor spar values appreciable quantities of sulfide minerals may be concentrated to produce a fluor spar enriched concentrate having a fluor spar concentration of at least 97% by a single step selective froth flotation treatment of aqueous pulps thereof provided the pulp is conditioned prior to its collection under particular alkaline conditions at elevated temperatures in the presence of a certain saturated fatty acid collector and in the further presence of a depressant for gangue minerals normally associated with such ores. When an aqueous pulp containing fluor spar values is conditioned in the presence of a combination of these reagents at the specific conditions required by the present process, a froth

rich in fluorspar is selectively formed in the froth flotation process while sulfide minerals such as galena, sphalerite and pyrite are left behind in the aqueous pulp as tailings, and the use of a preliminary sulfide flotation circuit, together with the additional reagents required therein, is eliminated. Furthermore, conditioning of the pulp under the conditions of the present invention results in effective retardation and/or dispersion of gangue materials and inhibits interference by the solubilized complex metallic salt contaminants associated with the crude ore when fluorspar is attempted to be selectively floated, thereby permitting for recovery of an "acid grade" fluorspar concentrate.

In accordance with the present invention, a fluorspar enriched concentrate having a fluorspar content of at least 97% is obtained from crude fluorspar ores containing in addition to fluorspar appreciable amounts of metallic sulfides and gangue minerals by mixing the crude ore with water to form an aqueous pulp, adding to said pulp a collector for fluorspar selected from the group consisting of saturated fatty acids, mixtures of saturated and unsaturated fatty acids wherein the saturated fatty acid content of the mixture comprises at least about 40 percent of the total quantity of collector present and soaps thereof and a depressant for gangue minerals selected from the group consisting of alkali metal silicates and alkali metal metasilicates, heating the pulp with agitation at its boiling temperature while maintaining said pulp at a pH between about 8.0 and 9.0, subjecting said pulp to froth flotation thereby forming a froth rich in fluorspar and recovering said fluorspar concentrate from the froth. The crude fluorspar ore subjectable to the present process may additionally have associated therewith complex metallic salts which are formed in underground storage of such ores.

In this novel process the fluorspar collector must be comprised, at least in part, of a saturated fatty acid or soap thereof if selective flotation of "acid grade" fluorspar is to be effected without preliminary flotation of sulfide minerals. Contrary to prior art procedures in which fatty acid collectors having a relatively high unsaturated fatty acid content such as oleic acid and tall oil acids are conventionally employed, we have found that conditioning of the aqueous pulp in the presence of fully saturated fatty acid collectors or soaps thereof, present in an amount of at least 1.5 pounds per ton of ore milled, is essential in obtaining a fluorspar product of desired "acid grade" purity. If desired, a portion of the saturated fatty acid collector may be replaced with an unsaturated fatty acid or soap thereof, provided that the saturated fatty acid content of the collector comprises at least about 40 percent, preferably between about 40 and 60 percent, of the total quantity of collector present. Moreover, by employing a saturated fatty acid collector, high recoveries, generally in excess of 80% of the fluorspar content present in the crude ore is effected. If the aqueous pulp is conditioned in the presence of unsaturated fatty acid collectors alone, such as oleic acid, or in the presence of a commercial preparation containing predominantly unsaturated fatty acids, substantially lower recoveries of the fluorspar content of the crude ore are obtained and the fluorspar concentrate resulting from such a one-step flotation procedure is contaminated with excessive amounts of sulfide minerals, precluding obtainment of an "acid grade" product.

The fatty acids and soaps thereof employable as collectors in the present process are well-known materials. Included within the term soaps are the alkali metal and alkaline earth metal soaps such as sodium, potassium, calcium, magnesium and aluminum soaps. Suitable saturated fatty acids include acids containing from about 4 to 22 carbon atoms, preferably 12 to 18 carbon atoms, in the molecule such as palmitic acid, lauric acid, stearic acid, commercially available preparations containing minor amounts of unsaturated fatty acids such as Hyfac 423, Hyfac 425, Hyfac 400 made by Emery Industries, Inc.;

and Swift 55, Swift 62, Swift RG made by Swift and Company, etc., all of which contain at least about 80% saturated fatty acids. Accordingly, as used in the present case, the term "saturated fatty acid" is intended to include such mixtures of fatty acids as are found in commercial products. If desired, unsaturated fatty acids containing from about 12 to 20 carbon atoms in the molecule such as crude and purified oleic acid, palmitoleic acid, linoleic acid, distilled tall oils, commercial preparations containing a major amount of unsaturated fatty acids such as Acintol FA1 tall oil fatty acid and Acintol FA2 tall oil fatty acid produced by the Arizona Chemical Company; Emersol 211 low-titer oleic acid, Emersol 531 distilled tallow fatty acid and Emtall 665 fractionated tall fatty acid made by Emery Industries, Inc., etc., may be used in conjunction with the saturated fatty acids. Although the amount of fatty acid collector used may be varied widely, amounts of about 1.5 to 5 pounds per ton of ore milled are generally satisfactory. It is necessary however, when commercial saturated fatty acid preparations and mixtures of saturated and unsaturated fatty acids are employed that the saturated fatty acid content of the collector comprise at least about 40 percent, preferably between about 40 and 60 percent, of the total quantity of collector present to effect selective flotation of the fluorspar values contained in the ore. The preferred collector is comprised of mixtures of saturated and unsaturated fatty acids having from 12 to 18 carbon atoms and having a saturated fatty acid content between about 40 and 60 percent.

It has been moreover ascertained that conditioning of the aqueous pulp must be effected at its boiling temperature at a pH in the range of about 8.0 to 9.0, preferably 8.4 to 8.8, for a minimum period of time, generally at least about 5 minutes, to obtain a fluorspar concentrate of the desired purity. Unless conditioning is effected at the pH ranges, temperature and time specified, substantial quantities of the sulfide minerals present in the pulp will be floated together with the desired fluorspar. Since different fluorspar ores will give varying pH values when slurried in water, it is usually necessary to adjust the pH of the pulp with conventional pH regulating reagents. The pH regulator may be added to the pulp at any time before completion of the conditioning stage of the process, but it is preferred to add the requisite quantities of pH regulator necessary to maintain the pH within the stated values simultaneously with the fatty acid collector and gangue depressant prior to conditioning of the pulp. A pulp of too low pH may be brought to the desirable pH by addition of an alkaline reagent such as an alkali metal hydroxide or carbonate exemplified by sodium hydroxide and sodium carbonate. In some instances, the addition of sufficient quantities of fatty acid collector and gangue depressant will give a pulp of suitable pH without the addition of any other pH modifying agent.

In effecting the preferential flotation of the fluorspar values contained in the crude ore in accordance with the present process, it is additionally required that an alkali metal silicate or alkali metal metasilicate such as sodium silicate or sodium metasilicate be employed in conjunction with the fatty acid collector during the conditioning step of the process. While this reagent may act together with the pH regulator as an alkalinity modifier, under the conditions of the present process it also serves as a depressant for gangue materials, and disperses slimes, thereby permitting selective flotation of the fluorspar values by the fatty acid collector. The quantity of silicate employed may also be varied widely and, in general, satisfactory results are obtained when the depressant is used in an amount of from about 2 to about 6, preferably from about 3 to about 5 pounds per ton of ore milled.

The novel process of this invention is described in detail below, reference being made to the appended drawing, which is a self-explanatory flow diagram of the novel process.

The composition of the ores treatable in accordance with the present invention generally comprises from about

40 to 90 percent calcium fluoride, 3 to 15 percent sulfide minerals including galena, sphalerite and pyrite, up to about 50 percent gangue minerals such as quartz and calcite, minor amounts, normally less than about 3 percent, of complex metallic salt contaminants such as iron sulfate, when present, and minor quantities of other impurities. In practicing the invention, the ore is first prepared for flotation by conventional methods. In accordance with these methods, the dry ore is crushed and ground sufficiently to pass a 48 mesh screen. The fineness of the grind may vary from 60 to 90 percent —200 mesh depending on the locking characteristics of the ore. However, substantially complete liberalization of the fluorspar from the gangue is required for a satisfactory separation and the fineness of grind should be selected accordingly. The ground ore is then mixed with sufficient quantities of water in a ball mill to form an aqueous pulp having a solids content of about 60 to 80 percent by weight based on the weight of the pulp. Although local water supplies may ordinarily be employed in forming the pulp, softened water having a total hardness of not greater than about 200 p.p.m. is preferred since the use of softened water reduces the fatty acid requirements in collection of the fluorspar rich froth. Thereafter, the solid particles contained in the aqueous pulp or slurry are classified to produce a pulp having a particle size suitable for flotation, generally ranging from about 48 mesh to 10 microns. The aqueous pulp is then fed to a concentrator or thickener to form a pulp having a solids content of about 35 to 45 percent by weight based on the weight of the pulp, and the water obtained as a result of thickening of the pulp is withdrawn as waste from the concentrator by any conventional manner as by decantation. If desired, any commercial flocculating or agglomerating agent may be employed in the concentrator to assist in settling of the pulp. In accordance with the present process, any complex metallic salt contaminants present in the pulped ore are solubilized in the waste water and removed therewith when the pulp is thickened in the concentrator. This contrasts with conventional procedures employing a preliminary sulfide flotation circuit wherein, under the conditions employed, the complex metallic salt contaminants are precipitated, carried over into the fluorspar froth flotation circuit and therein interfere with the selective flotation of the desired fluorspar values.

After the aqueous pulp has been classified and concentrated to produce a pulp having a particle size and solids content suitable for flotation, the pulp is fed into a conditioning tank where it is heated to its boiling point with agitation. The boiling temperature of the pulp may be higher or lower than 212° F. if the pressure at the point of location of the operation is higher or lower than atmospheric. Although the practice of the present invention is not limited to any particular order of addition of the separate reagents, it is preferred, however, to properly condition the pulp after the requisite quantities of fatty acid collector and gangue depressant have been added to the pulp together with suitable quantities of pH regulator to adjust the pH of the pulp to a value between 8.0 and 9.0, preferably between 8.4 and 8.8. If desired, a portion of the requisite quantity of the fatty acid collector and gangue depressant may be added to the pulp prior to heating and the remaining quantities may then be added to the pulp either intermittently or continuously during conditioning at the boiling temperature of the pulp. Although any conventional apparatus having external or internal heating means may be employed to condition the pulp, a preferred procedure involves introducing sufficient quantities of steam into the conditioning tank as through pipes discharging below the pulp level to bring the pulp to its boiling temperature. Sufficient conditioning of the pulp is normally achieved as the pulp is brought to its boiling temperature with agitation. However, it is generally necessary to condition the pulp at its boiling temperature for a period of 5 to 60 minutes, preferably 15 to 45 minutes, especially if high recoveries of the fluorspar content con-

tained in the pulped ore are to be realized. After conditioning of the pulp has been completed, the pulp, at or near its boiling temperature, or after being allowed to cool to ambient temperatures, is then froth floated by customary mechanical or pneumatic methods to produce an enriched fluorspar froth and a tailings product essentially free of fluorspar and containing the sulfide and gangue materials. One or more such cleaning operations after conditioning is reduced to about 20 to 30 percent by weight based on the weight of the pulp.

The froth product may contain some quartz, calcite, or other gangue materials collected with the fluorspar in the initial frothing operation. The froth is generally re-floated to recover the fluorspar and reject the remaining gangue materials. One or more such cleaning operations generally suffices to yield final fluorspar enriched concentrates having a fluorspar content of at least 97 percent and essentially free from sulfide impurities. Additional reagents, such as a small quantity of alkali metal silicate may be used in the cleaning operations to facilitate rejection of the gangue impurities. The tailings material, resulting from the cleaning operations, may be recycled to preceding flotation steps (as shown in the appended drawing) or other convenient points in the flotation or grinding circuit for retreatment, or may be rejected as waste.

It will be apparent to anyone skilled in the art that the process of this invention can be operated as a batch, intermittent batch or as a continuous process by means of recognizable variations in the apparatus and use thereof.

The following examples, while not intended to limit the scope of the invention, are illustrative of the benefits derived from the practice thereof.

Example 1

A crude broken fluorspar ore consisting essentially of fluorspar associated with appreciable quantities of a siliceous gangue composed predominantly of quartz, metallic sulfides including galena, sphalerite and pyrite, and minor amounts of sulfur (present as complex metallic salt contaminants) was obtained from a Colorado deposit. The ore had been stored underground in the mine for a period of about 52 weeks after being mined. The crude ore assayed 46.9 percent CaF_2 , 32.2 percent SiO_2 , 6.0 percent metallic sulfides, 2.5 percent CaCO_3 and 2.0 percent S.

The crude ore was subjected to staged crushing, screening, wet grinding and classifying operations to produce an aqueous pulp containing solids having a particle size such that 67 percent passed through a 200 mesh screen. The pulp discharging from the ball mill wherein the ore was wet ground had a solids content of 68 percent, based on the weight of the pulp, and the classifier overflow was maintained to produce a pulp having a solids content of 16 percent, based on the weight of the pulp. The water used for wet grinding of the ore contained the equivalent of 100 p.p.m. total hardness. Separan, a commercial flocculating agent, was added to the classifier in an amount equivalent to 0.04 pound per ton of ore milled to assist in settling the pulp. The aqueous pulp was then thickened by decantation to produce a pulp having a solids content of about 40 percent, based on the weight of the pulp. The thickened pulp was then transferred to a conditioning tank to which there was added the equivalent of 1.9 pounds per ton of Hyfac 400, a commercial hydrogenated fatty acid comprised of about 90 percent saturated fatty acids containing from 14 to 18 carbon atoms, the equivalent of 2.3 pounds per ton of Acintol FA2, a tall oil fatty acid comprised of about 50 percent oleic acid and 46 percent linoleic acid, the equivalent of 4.7 pounds per ton of sodium silicate and sufficient sodium carbonate (equivalent of 14.0 pounds per ton) to bring the pulp to a pH of about 8.8. The pulp was then conditioned at its boiling temperature (201° F.) by introducing steam at a temperature of 352° F. and 75 p.s.i. through pipes discharging below the pulp level for a period of 20 min-

utes. After conditioning, sufficient water was added to the pulp to produce a pulp having a solids content of about 25 percent by weight based on the weight of the pulp. The diluted pulp was then continuously fed into the first cell of a bank of flotation cells to which air was continuously introduced, thereby resulting in formation of a compact, heavily mineralized fluor spar forth. The underflow comprising the tailings was rich in gangue and sulfide materials. The rougher froth was then cleaned by refloating in a series of flotation cells. The final fluor spar concentrate assayed 97.07 percent CaF_2 , 0.94 percent SiO_2 , 0.85 percent CaCO_3 , 0.002 percent metallic sulfides and 0.0 percent complex metallic salt contaminants and accounted for a recovery of 90.8 percent of the fluor spar in the ore.

Example 2

A crude fluor spar ore assaying 51.1 percent CaF_2 , 31.0 percent SiO_2 , 3.0 percent CaCO_3 , 6.0 percent sulfide minerals and 2.0 percent S (present as complex metallic salt contaminants) was processed for recovery of fluor spar values contained therein in accordance with the procedure described in Example 1 except that essentially saturated fatty acids, Hyfac 400, present in an amount equivalent to 4.0 pounds per ton of ore milled, was used as the sole collector.

In this example, sodium silicate was added to the concentrated pulp together with the hydrogenated fatty acid collector in an amount equivalent to 3.2 pounds per ton of ore milled, and sufficient sodium carbonate (equivalent to 18.7 pounds per ton) was added to bring the pH of the pulp to a value of 8.4. The pulp was conditioned, floated and cleaned in the same manner as in the preceding example. The final fluor spar concentrate assayed 98.6 percent CaF_2 , 0.50 percent SiO_2 , 0.34 percent CaCO_3 , 0.003 percent metallic sulfides and 0.0 percent complex metallic salt contaminants and represented a recovery of 83.3 percent of the fluor spar in the ore.

Substantially similar results may be obtained with employment of sodium metasilicate as a conditioning agent and sodium hydroxide as a pH regulator.

The results of the above-described flotation procedures may also be reproduced on other fluor spar ores containing appreciable quantities of sulfide and gangue minerals. Metallic sulfides, quartz and other silicate minerals including feldspar, clay and associated iron oxide are readily retarded by the process of the present invention thereby enabling a good recovery of the fluor spar as "acid grade" concentrates without the use of a preliminary sulfide flotation circuit.

We claim:

1. A process for producing a fluor spar enriched concentrate having a fluor spar content of at least 97% from a crude fluor spar ore containing in addition to fluor spar appreciable amounts of gangue minerals and from 3 to 15% by weight metallic sulfide which consists essentially of a one-step fluor spar flotation circuit comprising

mixing the crude ore with water to form an aqueous pulp, adding to said pulp a collector for fluor spar, said collector selected from the group consisting of saturated fatty acids, mixtures of saturated and unsaturated fatty acids wherein the saturated fatty acid content of the mixture comprises at least about 40% of the total quantity of collector present, and soaps thereof, and a depressant for said gangue minerals selected from the group consisting of alkali metal silicates, and alkali metal metasilicates, conditioning this mixture by heating said pulp to its boiling point with agitation while maintaining said pulp at a pH between about 8.0 and 9.0, subjecting said pulp to froth flotation, thereby producing a froth rich in fluor spar and recovering in excess of 80%, based on the fluor spar content in the crude ore, of acid grade fluor spar from said froth.

2. The method of claim 1 wherein the saturated fatty acid content of the collector is present in an amount of at least 1.5 pounds per ton of ore milled.

3. The method of claim 2 wherein the pulp is maintained during heating at a pH within the range of about 8.4 to 8.8.

4. The method of claim 3 wherein the aqueous pulp is heated by the introduction of steam.

5. The method of claim 4 wherein the collector is a saturated fatty acid containing from 12 to 18 carbon atoms, and the depressant is an alkali metal silicate.

6. The method of claim 4 wherein the collector is a mixture of saturated and unsaturated fatty acids containing from 12 to 18 carbon atoms, and the depressant is an alkali metal silicate.

7. The process of claim 1 wherein the fluor spar ore additionally contains complex metallic salt contaminant.

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