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CONCENTRATING FLUORSPAR BY FROTH FLOTATION

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The invention described herein may be manufactured and used by or for the Government of the United States for governmental purposes without the payment to us of any royalty thereon in accordance with the provisions of the act of April 30, 1928 (Ch. 460, 45 Stat. L. 467).

This invention relates to an improved process for the concentration of fluorspar ores by froth flotation; more particularly it relates to the froth flotation of fluorspar of a high degree of purity from pulps containing calcite or barite.

An object of the invention is to provide a froth flotation process for the concentration of natural fluorspar ores and products for recovery of fluorspar. A further object is to provide an improved flotation process for separating fluorspar from calcareous gangue materials such as calcite or limestone. A still further object is to provide a flotation process for recovering fluorspar of a high degree of purity from ores containing barite. Still other objects include the development of an improved flotation process which will have greater selectivity in separating fluorspar from associated sulfide or non-sulfide gangue materials and thereby effect greater operating economies. Other objects, purposes, and advantages of the invention will hereinafter more fully appear or will be understood from the detailed description of its practice.

Fluorspar has wide and varied application in the chemical, ceramic, and metallurgical industries. Its uses range from a source of fluorine and hydrofluoric acid in chemical processes to that of a fluxing material in steel making. Commercial fluorspar, commonly referred to as "Spar," is furnished to meet a number of varying specifications as to size and analysis. The fluorspar content of the commercial products ranges from a minimum of 85 percent in the case of "gravel spar" for steel making to a minimum of 97 percent fluorspar in "acid grade" material for chemical processing. The specifications as to allowable impurities vary with the industry, but all demand a fluorspar product relatively free of silica, calcium carbonate, barite, and sulfides such as galena, sphalerite, or pyrite. Fluorspar ores as mined seldom meet market specifications, either as regard fluorspar content or freedom from impurities, and suitable methods of concentration, such as froth flotation, must therefore be employed to recover commercial products from the low grade or contaminated ores.

Geographically, fluorspar is widely distributed in minute quantities, but deposits of commercial value in the United States are not numerous.

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Fluorspar deposits occur in both igneous and sedimentary rocks as veins following faults, fissures, or shear zones; as horizontal or bedding replacement deposits in sedimentary rocks; or as incrustations in vugs and caves. Sizeable deposits of fluorspar are known in our Western States including California, Arizona, New Mexico, Nevada, Texas, and Colorado. The vein and bedded deposits of the Illinois-Kentucky district are reputed to be the largest in the world. It is to ores from these deposits that particular attention was given in developing the improved process of froth flotation hereinafter described, although ores from other localities can successfully be benefited by our invention.

The gangue minerals commonly found associated with fluorspar in commercial deposits are quartz, calcite, and barite. Other accessory minerals may include various sulfides such as galena, sphalerite, pyrite, or chalcopryrite, or oxidized lead and zinc minerals such as cerussite and smithsonite. Common gangue constituents of fluorspar ores are limestone and clay and many ores also contain shale and sandstone. Ores from different deposits, or from different portions of the same deposit, may show considerable variation both as regard mineral association and relative proportions of fluorspar and other minerals. In the Illinois-Kentucky fluorspar district, for example, the ore from a particular deposit may be devoid of barite whereas that from an adjacent deposit may contain 10 percent or more of barite. Similarly, the galena or sphalerite contents may also show considerable variation. Ore from a particular mine location may contain minute quantities of galena or sphalerite whereas ore from another part of the mine often contains sufficient galena or sphalerite to justify their recovery as valuable by-products in fluorspar milling. The lime and silica contents of fluorspar ores may likewise show considerable variation. Uniform deposits of fluorspar are an exception rather than the rule, and milling methods must be sufficiently flexible to permit treatment of a variety of ores of different grades and mineral association. An important object of this invention is to provide for the first time a flotation method applicable to a variety of ores of different grades and mineral association for recovery of the fluorspar from associated gangue materials.

As a result of extended research and experimentation, we have discovered that the lignin sulphonates used in conjunction with an addition agent, such as sodium fluoride, are effective for the retardation of barite and siliceous or cal-

careous gangue materials in the froth flotation of fluorspar by fatty acid or soap collecting agents. The combination of these reagents also enables retardation of sulfide minerals such as galena, sphalerite, or pyrite when floating fluorspar from pulps containing the minerals as gangue. Oxidized ore minerals and iron oxides, or other non-sulfide gangue minerals such as celestite, may also be retarded in fluorspar flotation by these depressants. Fluorspar concentrates of high purity have been recovered from a wide variety of fluorspar ores and products even when containing sulfide and non-sulfide gangue materials, by using lignin sulphonates and addition agents to selectively retard the gangue materials while floating the fluorspar with fatty acid collecting agents.

The lignin sulphonates which we prefer to utilize as gangue depressants in this invention are present in and may be derived from the by-product of the sulfite process of paper making commonly known as "sulfite liquor." These liquors separated as waste from the cellulose pulp contain soluble salts of the lignin sulphonic acids and other non-ligneous organic substances, such as hydrolyzed carbohydrates, resulting from decomposition of the wood by the acid solutions used in the pulping process. In the sulfite process, the lignin in the wood is dissolved by digesting the wood chips with an acid solution of calcium, magnesium, or sodium sulfite at an elevated temperature whereby the lignin forms soluble calcium, magnesium, or sodium lignin sulphonates depending on the base employed. The sulfite liquors containing the lignin sulphonates and non-ligneous materials may be used as the gangue depressants in our method of fluorspar flotation or the crude sulfite liquors may be purified by known methods to reject the non-ligneous substances and recover a substantially purified lignin sulphonate which may be employed to retard the gangue.

The crude or whole sulfite liquor recovered from the sulfite pulping process and containing the lignin sulphonates and non-ligneous organic substances, such as hemi-cellulose and various sugars, may be evaporated to yield a concentrated liquid or dehydrated residue for marketing. The liquid forms as marketed contain about 50 percent water whereas the powdered forms are substantially dehydrated. The liquid and powdered forms have been used interchangeably in our flotation and, based on their respective content of lignin sulphonate, are equally effective for retardation of gangue constituents. Comparative flotation tests using the calcium, magnesium, and sodium base sulfite liquors or dehydration residues gave substantially equivalent results. The non-ligneous materials present in the liquid or dehydrated residues appear to be an inactive diluent and exerts little or no deleterious effect in the froth flotation of fluorspar when using sodium fluoride as an addition agent. Pound per pound, the evaporated crude sulfite liquors or dehydration residues are slightly less effective than the corresponding purified lignin sulphonates relatively free of non-ligneous material, but are particularly attractive as gangue depressants in our method of flotation due to their lower cost.

The crude or evaporated sulfite liquors may be processed by numerous methods to reject the non-ligneous material and recover substantially purified lignin sulphonates. Fractional precipitation methods using sodium chloride, calcium chloride, mineral acids, lime water, basic lead acetate, or organic bases may be employed to recover the lignin sulphonate and reject the bulk of the non-

ligneous materials. The precipitated lignin sulphonate may be further purified by dissolution and re-precipitation, by dialysis, or other methods. The purified sulphonates are ordinarily marketed as the powdered forms but solutions containing from 15 to 50 percent of the lignin sulphonate are also available. Various of the commercially available purified lignin sulphonates including the calcium, magnesium, sodium, barium, aluminum, zinc and copper salts have been tested and found satisfactory as gangue depressants in our method of fluorspar flotation when used in conjunction with an addition agent such as sodium fluoride. The calcium, magnesium, and sodium sulphonate are less expensive than the heavy metal salts and are preferred. The purified sulphonates are somewhat more effective than the crude or unpurified compounds but all of the liquid or powdered forms of either the crude or purified sulfite liquor materials may be used in our method of fluorspar flotation and the ultimate choice of the particular material employed will largely depend upon economic factors.

The lignin sulphonates are recognized as being multi-basic in character and contain acidic groups of varying strength ranging from the strong sulphonic to the weak phenolic group, and some may also contain minor amounts of carboxyl groups. The sulphonic is the dominant acidic group and the amount depends on the degree of sulphonization employed in the pulping process to solubilize the lignin and allow its separation from the cellulose. Lignin sulphonates of either higher or lower degree of sulphonation may be made by re-treatment of the sulfite liquors to meet specific requirements. The lignin sulphonic acids readily react with metal salts to form the corresponding sulphonates. These salts may be made from the calcium salt by double decomposition reactions or from a solution of the free sulphonic acid. The type of salt formed depends on the conditions established for the reaction. In the normal or so-called acid salt at pH of about 5 in aqueous solution only the strong sulphonic groups are in their salt form; in the so-called neutral salts at about pH 7.0, the sulphonic and some of the phenolic groups are in salt form; and in the so-called basic salts at pH 11 and above all the acidic groups may be regarded as present in their salt form. The basic calcium salts are insoluble in aqueous solutions at high pH but disperse or dissolve under neutral or acid conditions. Otherwise all lignin sulphonates of normal degree of sulphonation are soluble in water under all pH conditions to give colloidal solutions or dispersions which we may use as gangue depressants in conjunction with addition agents such as sodium fluoride in our method of fluorspar flotation.

A variety of liquid and powdered forms of both crude and purified sulfite liquid products are commercially available and have been found satisfactory gangue depressants in the practice of this invention. Examples of the sulfite liquor materials which we have used successfully include those sold under the trade names "Bindarene liquid," "Binderene flour," "Goulac," "T. D. A.," "Marathon extracts M, T, NS, TanC, SL, DT-31, DT-32, DT-33, DT-34, and DT-35," and the "Daxads 11, 21, and 23." Other sulfite liquor products which have been found acceptable include the crude and purified magnesium lignin sulphonates, the acid, neutral, and basic calcium lignin sulphonates, and sodium, copper, zinc, aluminum, and barium lignin sulphonates.

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As far as we are aware the lignin sulphonates singly or together with addition agents such as sodium fluoride have not heretofore been employed for the retardation of gangue constituents in the flotation of fluorspar ores. In our method of froth flotation of fluorspar, retardation of the calcite and barite or other gangue constituents is sought and the quantities of lignin sulphonate employed must be sufficient to retard these constituents. The quantity of lignin sulphonate required varies with different ores and may be as little as 0.25 to as much as 5 pounds or more per ton of ore; the optimum must be determined by trial.

The mechanism of the retarding action of the lignin sulphonates on gangue minerals in our method of fluorspar flotation has not been definitely determined and this invention is not limited to any theory of action. It seems probable however, that an important effect of the sulphonates is to coat the surfaces of the gangue particles so that they present water-avid surfaces which prevents their attachment to the bubbles in froth flotation. The lignin sulphonate coating on the gangue may be induced as a result of either chemical reaction or adsorption to satiate the surfaces, and this coating prevents or greatly inhibits formation of collector coatings which normally would have formed to render the particles floatable. It may be further assumed that fluorspar particles in the pulp exhibit much less tendency than the gangue particles to become coated by the lignin sulphonates, and, as a consequence, the unsaturated fluorspar surfaces become collector-coated and are thus rendered floatable. Judicious use of the lignin sulphonates thus enables selective retardation of the gangue in fluorspar flotation.

The beneficial effect of addition agents such as sodium fluoride in the flotation of fluorspar when using the lignin sulphonates as gangue depressants was apparent in the testing of a variety of ores containing barite or calcareous gangue materials. Use of the fluorides enabled more rapid and complete flotation of the fluorspar and more effective retardation of the gangue constituents. The mechanism by which the fluorides accomplish these beneficial effects is not definitely known and no limitation to any particular theory of action is intended in this patent. It seems likely however that one of the important functions of the fluoride is to complex or precipitate soluble salts in the pulp which would otherwise impair selectivity of the separation. The fluorides are effective slime dispersants and may aid flotation by assisting in the proper dispersion of the pulp. The combined effect of complexing soluble salts and dispersion of the slime may possibly serve to clean the surfaces of the fluorspar particles to make them more readily floatable by the fatty acid collectors. Similar cleaning of the gangue particles renders them more susceptible to retardation by the lignin sulphonates. These factors may be effective in varying degree on different ores depending upon the soluble salts present and the relative proportions and surface purity of the fluorspar and gangue minerals. We have discovered that the fluorides are particularly advantageous and their beneficial effect is more marked when treating ores containing soluble salts or large amounts of calcite or barite. The need for the fluorides is less apparent and they may be omitted if desired, in the flotation of fluorspar from the highly siliceous ores rela-

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tively free of soluble salts or slime gangue constituents. We prefer to use addition agents such as sodium fluoride in conjunction with the lignin sulphonates for the flotation of fluorspar from all fluorspar ores. Less collector is required and flotation of the fluorspar is more rapid and complete.

Sodium fluoride was the preferred addition agent used in conjunction with the crude or purified lignin sulphonates. Ammonium and potassium fluoride were found equally effective but was less attractive due to their higher cost. Aluminum fluoride and sodium silico-fluoride were also satisfactory but had no particular advantage over sodium fluoride and were somewhat less soluble. Hydrofluoric and hydrofluosilico acids may also be used if desired. Our tests indicate that any inorganic fluorine-bearing compound which ionizes in aqueous solution to yield the fluoride ion may be used as addition agents in our method of flotation.

Addition agents, other than the fluorides, which we have used in conjunction with the lignin sulphonates to obtain more effective retardation of the gangue in fluorspar flotation include sodium sulfide, sodium sulfite and hydrosulfite, sodium cyanide, potassium dichromate, ammonium acetate, potassium ferro and ferri cyanides, sodium citrate, sodium meta and per borates, borax, soda ash, caustic soda, and sodium silicate. These reagents are less effective than the fluorides but may be advantageously employed on fluorspar ores to yield an improved separation. These reagents serve a multi-fold purpose and assist in flotation by complexing or precipitating soluble salts in the pulp, establish the optimum pH for flotation, or aid in proper dispersion of slime gangue constituents. Soda ash, caustic soda, sodium cyanide, and sodium silicate are particularly advantageous as auxiliary pH modifiers, pulp conditioners, and slime dispersants in conjunction with an inorganic fluoride in our method of flotation.

In our method of flotation we have found that the pulp should be dispersed. The lignin sulphonates and the fluoride addition agents which we employ in our method of flotation serve the two-fold purpose of dispersing the pulp and retarding the gangue materials. Supplementary dispersing agents are seldom required as sufficient lignin sulphonate and soluble fluoride to depress the gangue constituents in fluorspar flotation adequately disperses the ore pulp. Supplementary slime dispersing agents, such as sodium silicate, may be advantageously used on fluorspar ores containing large amounts of clay. Various organic dispersants including the tannin extracts, such as quebracho, chestnut, oak, or Borneo cutch, and the dextrans, starches, and gums may also be used to supplement the lignin sulphonates and enable reduced quantities to be employed. The tannin extracts are particularly helpful on those ores containing large quantities of calcite as they assist in the retardation of this contaminant. The quantity of tannin used in conjunction with the lignin sulphonate must be carefully controlled as an excess tends to retard the fluorspar.

We have achieved good flotation of fluorspar from both neutral and moderately alkaline pulps by the practice of this invention. Precise control of the pH of the pulp is not essential for an effective separation but we prefer that the pH be maintained in the range 8 to 10.0. The frothing proclivities of the fatty acid and soap

collecting agents increase progressively with increase in pH of the pulp and strongly alkaline pulps of pH 11 or more should be avoided as the voluminous froths are difficult to control. A pulp pH of 8 to 10 gave compact, heavily mineralized fluorspar froths on a variety of fluorspar ores containing barite and siliceous or calcareous gangue materials. We have found in many cases that the combination of sodium fluoride and a lignin sulphonate gave a pulp of suitable pH without the addition of any other pH modifying agent. A pulp of too high pH may be corrected by judicious addition of an inorganic acid to lower the pH within the optimum range and, conversely, a pulp of too low pH may be corrected by addition of a proper amount of an alkaline reagent such as soda ash, caustic soda, or sodium silicate. The pH modifying agent may be added to the pulp at any time before completion of the flotation, but we prefer to add it prior to or simultaneously with the lignin sulphonate and sodium fluoride.

The fatty acid and soap collecting agents have been found suitable for flotation of the fluorspar in the practice of this invention. The collectors which have been used in the flotation testing of a variety of fluorspar ores containing barite and calcareous or siliceous gangue constituents include crude and purified oleic acid, sodium oleate, fish oil soap, fish liver oil fatty acids, and tall oil. Saponified tall oil and sulfate soap or skimmings derived from sulfate paper mill black liquors may also be used provided the quantities are carefully controlled. The crude tall oil and sulfate soap products are violent frothers and an excess should be avoided.

In carrying out the flotation process according to this invention, the fluorspar ore or product to be treated is ground to proper size for flotation, if not already of such size, by conventional methods. The fineness of the grind may vary from 20 to 200 mesh or finer depending on the locking characteristics of the particular material; substantially complete liberation of the fluorspar from the gangue is essential for a satisfactory separation, and the fineness of grind should be selected accordingly. The ground material in the form of a pulp is then subjected to froth flotation to recover the fluorspar and reject the gangue materials in the following manner: The pulped material is conditioned with a sulfite liquor material containing lignin sulphonate; an addition agent such as sodium fluoride; and a fatty acid collector agent such as oleic acid. Also if desired a pH modifying agent and slime dispersant agent may be used. The conditioned pulp is then froth floated by customary mechanical or pneumatic methods to yield an enriched fluorspar froth and a tailings product essentially free of fluorspar and containing the gangue materials. The froth product may contain some quartz calcite, barite, or other gangue materials collected with the fluorspar in the initial frothing operation. The froth is repulped with additional water and refloatated to recover the fluorspar and reject the remaining gangue materials. One or more such cleaning steps suffices to yield final fluorspar concentrates of the desired commercial grade. Additional reagents, such as a small quantity of the lignin sulphonate, may be used in the cleaning operations to facilitate rejection of the gangue impurities. Also if desired, a froth agent such as pine oil or an alcohol may be used to promote complete and more rapid flotation of the fluorspar. The tailings material re-

sulting from the cleaning operations may be rejected as waste or returned to the preceding flotation step or other convenient points in the flotation or grinding circuit for retreatment.

The practice of this invention is not limited to any particular order of addition of the separate reagents. We prefer however to properly condition the ore pulp with the lignin sulphonate and sodium fluoride, or other addition agents, before adding the fluorspar collecting agent. The depressants and pH modifying agents, singly or together, may be added to the grinding step if desired. Our tests indicate that moderate conditioning of the pulp with the depressants ensures maximum retardation of the gangue constituents. Likewise, moderate conditioning with the collecting agent ensures maximum collection of the fluorspar.

The proportions of the several reagents used in this invention are subject to considerable variation, and the proper quantities are best determined by experimentation for any particular case. We have found the invention applicable to a wide variety of fluorspar ores containing barite and siliceous or calcareous gangue materials. Extensive flotation experiments on fluorspar ores from domestic and foreign deposits have demonstrated that the invention is particularly advantageous in that it enables recovery of high-grade fluorspar concentrates from ores which heretofore had been difficult or impossible to treat by known methods. A proper balance of the lignin sulphonate and sodium or other soluble fluoride effectively retards the gangue and enables rapid and complete flotation of the fluorspar with moderate quantities of fatty acid collecting agents. Excess of collecting agent or deficiency of the depressants results in an inferior separation and the proper quantities must be determined by trial. Moderate variation of the collector and depressant reagents is permissible on many ores however. The wider latitude in reagent control and more effective retardation of gangue constituents accomplished by this invention thereby effect greater operating economies and facilitate recovery of fluorspar from ores heretofore difficult to treat.

This invention is applicable to fluorspar ores and products containing associated sulfide minerals such as galena or sphalerite. Those ores containing sufficient sulfide minerals to warrant their economic recovery may best be treated by customary sulfide flotation methods to first recover the sulfides and the resulting tailings may then be retreated by this invention to recover the fluorspar and reject the gangue. We have found that the reagents customarily used for the flotation of sulfide minerals do not interfere with the subsequent flotation of fluorspar by our method. The lignin sulphonates adequately retard the remaining sulfides as well as barite, calcite, or other gangue materials and permits recovery of high-grade fluorspar concentrates essentially free of these impurities. Metal salts in the fluorspar feed carried through from the sulfide flotation step, wherein salts such as copper or zinc sulfate were employed as activators or depressants, may if desired, be overcome by conditioning the sulfide tailings with sodium cyanide prior to flotation of the fluorspar by this invention. The cyanide complexes or precipitates the metal salts and thus overcomes any deleterious effect these salts may exert in fluorspar flotation. Sodium or other soluble fluoride is also effective for overcoming the deleterious

effect of metal salts and complements the action of sodium cyanide.

Our method is also effective for recovering acid grade fluorspar directly from ore pulps containing substantial quantities of galena, sphalerite, or pyrite as gangue constituents. Recovery of acid grade fluorspar can thus be effected by our method not only when the pulp treated is substantially free of metallic sulfides but also when the sulfides are present in material amounts and it is also substantially immaterial whether a large or small amount of barite or calcite is present. Our method is therefore particularly advantageous for the concentration of ores of the type found in the Illinois-Kentucky fluorspar area containing galena and sphalerite associated with the fluorspar together with extremely variable amounts of barite calcite, or siliceous gangue constituents.

As a result of the practice of this invention, rapid and essentially complete flotation of fluorspar may be effected from ore pulps containing sulfide and non-sulfide gangue constituents without the necessity of desliming. Desliming of the flotation feed is not obligatory in our method of flotation but may be desirable when treating surface ores containing large amounts of clay or top-soil as contaminants. Less collector is required and the quantities of the lignin sulphonates and sodium fluoride may be materially reduced when floating fluorspar from deslimed pulps.

Anderson et al., in U. S. Patent 2,263,552 proposed the use of "soft" water, i. e. one having not to exceed 5 grains of hardness, to obviate necessity of desliming in the flotation of fluorspar from calcareous gangue materials. We have now discovered that neither desliming nor a soft water is obligatory in our method of fluorspar flotation. Although we prefer to use a soft or only moderately hard water in flotation, we have successfully used water containing as high as 20 grains of hardness without seriously impairing selectivity of the separation on many fluorspar ores. Collector requirements for flotation increase with increase in hardness of water employed and operating economy suggests that hard water be pre-treated by either lime soda or zeolite processes prior to use.

The invention will be further illustrated but is not intended to be limited by the following examples in which parts and percentage compositions are by weight unless otherwise designated:

Example I

A fluorspar ore consisting essentially of fluorspar associated with a siliceous gangue composed predominately of quartz and clay was obtained from a Colorado deposit. A head analysis gave 57.8 per cent CaF_2 , 0.7 percent CaCO_3 , 29.2 percent SiO_2 , and 6.2 percent R_2O_3 . A representative portion of the ore was wet-ground to 48 mesh in a laboratory ball mill and the pulp, including slime, was transferred to a laboratory mechanical flotation cell of standard design. Sufficient tap water was added to give a slurry containing about 20 percent solids for flotation. The pulp was conditioned for 5 minutes with the equivalent of 1.0 pound per ton of a magnesium base lignin sulphonate and 0.8 pound per ton of red oil (commercial oleic acid) was then added and the pulp conditioned for an additional 2.5 minutes. Air was then allowed to enter the cell and resulted in an immediate formation of a compact, heavily mineralized fluorspar froth es-

entially free of gangue material. The froth was collected for 2.5 minutes when flotation was completed. The rougher froth was triple cleaned by re-floating in the same cell using tap water and 0.08 pound per ton of lignin sulphonate in each step to further retard the gangue collected with the fluorspar in the roughing operation. The final fluorspar concentrates represented a weight recovery of 55.6 percent, assayed 98.2 percent CaF_2 , 0.1 percent CaCO_3 , 0.8 percent SiO_2 , and 0.7 percent R_2O_3 , and accounted for a recovery of 98.8 percent of the fluorspar in the ore.

The high recovery of acid-grade fluorspar in the test demonstrated the utility of the magnesium lignin sulphonates for retarding siliceous gangue materials in fluorspar flotation. Calcium or sodium lignin sulphonates gave substantially the same results. Combinations of sodium fluoride and crude or purified lignin sulphonate were even more effective and gave a higher recovery of fluorspar in concentrates of lower silica content. A duplicate of the recorded test using 1.0 pound of sodium fluoride per ton in addition to the magnesium lignin sulphonate yielded a final fluorspar concentrate which assayed 98.6 percent CaF_2 , 0.1 percent CaCO_3 , 0.6 percent SiO_2 , and 0.5 percent R_2O_3 , and represented a recovery of 97.6 percent of the fluorspar.

The results of the above mentioned tests were representative of those obtained on other siliceous fluorspar ores from deposits in Arizona, New Mexico, and Montana. Quartz, feldspar and other silicate minerals including clay, and associated iron oxides were readily retarded by the lignin sulphonates alone or preferably in combination with sodium fluoride and enabled a good recovery of the fluorspar in acid-grade concentrates by fatty acid or soap collectors.

Example II

A tailing pond material from a gravity concentration plant operating in the Southern Illinois fluorspar district was next examined. The material consisted of fluorspar associated with both siliceous and calcareous gangue constituents and assayed 43.1 percent CaF_2 , 35.4 percent CaCO_3 , and 18.2 percent SiO_2 . Grinding to 48 mesh was sufficient to liberate the fluorspar for recovery of acid grade fluorspar concentrates.

Numerous flotation tests were made on this sample using various of the commercially available liquid and dehydrated residues of crude and purified sulfite waste liquors containing lignin sulphonates, with and without sodium fluoride to retard the gangue while floating the fluorspar with fatty acid collectors. The lignin sulphonates while satisfactory, were less effective than the combination of depressants for retarding calcite and limestone and close control of the collector was essential for a satisfactory separation. A typical test using the equivalent of 1.0 pound per ton of substantially pure magnesium lignin sulphonate as the depressant and 0.64 pound of commercial oleic acid per ton as the collecting agent yielded a froth product in the roughing operation which assayed 76 percent CaF_2 , 20 percent CaCO_3 , and 2 percent SiO_2 , and contained about 75 percent of the fluorspar in the flotation feed. Triple-cleaning of the rougher froth gave a final fluorspar concentrate of acid grade assaying 98.0 per cent CaF_2 , 1.1 percent CaCO_3 , and 0.2 percent SiO_2 , and represented a recovery of 59.3 percent of the fluorspar. Substantially equivalent results were obtained with calcium and sodium salts of the lignin sulphonate

acids. The crude lignin products from partial or complete dehydration of the whole sulfite liquors while entirely operative, were less effective than the purified sulphonates for retarding calcareous gangue and closer control of the collector was essential for separation of fluorspar in concentrates of acid grade.

The combination of a lignin sulphonate and sodium fluoride was found particularly advantageous on the tailing pond material. Less collector was required and flotation of the fluorspar was more rapid and complete. Uniformly good results were obtained with either the crude or purified lignin sulphonates used in conjunction with chemically pure or insecticide-grade sodium fluoride. A proper balance of the collector and depressants had to be determined by trial, but moderate variation of the quantities of collector, sodium fluoride, or lignin sulphonate was permissible.

A typical test on the tailing pond material ground to 48 mesh in a laboratory ball mill and floated by the procedure described in Example I using 1.0 pound per ton of insecticide-grade sodium fluoride and sodium lignin sulphonate, respectively, in conjunction with 0.32 pound per ton of crude oleic acid as the fluorspar collector yielded a rougher froth containing 92 percent of the fluorspar in the feed and assayed about 75 percent CaF_2 , 20 percent CaCO_3 , and 3 percent SiO_2 . Triple cleaning of the rougher froth with 0.08 pounds per ton of additional lignin sulphonate in each step gave a final concentrate which assayed 98.5 percent CaF_2 , 1.1 percent CaCO_3 , and 0.3 percent SiO_2 , and represented a recovery of 83.4 percent of the total fluorspar.

A duplicate of the preceding test using a magnesium lignin sulphonate gave an 84.2 percent recovery of acid grade spar concentrates. Another test using calcium lignin sulphonate gave 77.1 percent recovery of fluorspar in concentrates of acid grade. Considerable latitude was apparent in the flotation testing of the tailing pond material both in the choice of the lignin sulphonate for retardation of the gangue, and in the relative proportions of collector, sodium fluoride, and lignin sulphonate employed.

Comparative flotation tests using sodium or ammonium fluoride as the addition agents in conjunction with the various lignin sulphonates gave substantially identical results. Aluminum fluoride and sodium silico-fluoride were also satisfactory but were less effective than the sodium or ammonium salts because of their lower solubility. Various other addition agents including sodium sulfide, sodium sulfite, sodium meta- and per-borate, ammonium and sodium acetate, potassium ferro and ferri cyanide, sodium ortho, pyro, and metaphosphate, soda ash, sodium silicate, and caustic soda were used in conjunction with the lignin sulphonates in other flotation tests on the tailing pond material. These reagents were somewhat less effective than the fluorides but enabled an improved separation of the fluorspar.

Sodium sulfide was particularly advantageous and a typical test using this reagent in conjunction with magnesium lignin sulphonate gave an 81.0 per cent recovery of fluorspar in concentrates which assayed 98.4 percent CaF_2 , 0.9 percent CaCO_3 , and 0.1 percent SiO_2 . The procedure employed in the test was as follows: The ground charge was conditioned 15 minutes with 2.0 pounds per ton of a crude sodium sulfide product commonly known as "60-percent Fused

Flakes." The pH of the pulp was 11.0 which exceeds the optimum desired for fluorspar flotation. Sulfuric acid equivalent to 0.6 pounds per ton of feed, was then added to reduce the pH of the pulp to 8.6, a more desirable value. Magnesium lignin sulphonate and oleic acid, equivalent to 1.0 and 0.32 pounds per ton, were added and the pulp conditioned an additional 5 minutes. Air was then admitted to the cell and resulted in the immediate formation of a heavily mineralized fluorspar froth. The froth was collected for 3 minutes when flotation was completed. The froth assayed 77.1 percent CaF_2 , and accounted for 91.5 percent of the fluorspar in the feed. Triple-cleaning of the rougher froth with an additional 0.08 pound per ton of magnesium lignin sulphonate in each cleaner yielded a final fluorspar concentrate of the grade and recovery indicated above.

Soda ash, caustic soda, and sodium silicate were used in conjunction with the combination of fluoride and lignin sulphonate in other tests on the tailing pond material to establish the optimum pH for flotation and to assist in dispersion of the ore pulp. These reagents were also helpful as a water conditioner and their use enabled hard water to be employed in flotation without impairing selectivity of the separation.

Tap water of moderate hardness was used in all of the flotation tests previously described. A number of tests were also made on the tailing pond material using a synthetic hard water containing the equivalent of 13 grains of lime and 7 grains of magnesia per gallon. A typical test using the hard water in the grinding, roughing, and cleaning operations gave a 79.4 percent recovery of the fluorspar in concentrates which assayed 98.3 percent CaF_2 , 0.5 percent CaCO_3 , and 0.07 percent SiO_2 . The ground pulp was conditioned 5 minutes with 2.0 pounds per ton of soda ash and 1.0 pound per ton, respectively, of sodium fluoride and magnesium lignin sulphonate. Oleic acid equivalent to 0.64 pound per ton was added as the fluorspar collector and the pulp conditioned for an additional 5 minutes. Flotation of the fluorspar in the roughing operation proceeded in a normal fashion and was complete in 3 minutes. The rougher froth was re-pulped with additional hard water and re-floated twice using 0.5 and 0.2 pounds per ton of the magnesium lignin sulphonate in the first and second cleaner. A third and final cleaning operation using hard water but without additional lignin sulphonate yielded acid grade fluorspar concentrates of the grade and recovery given above. Combinations of soda ash and caustic soda or soda ash and sodium silicate were used in other tests to pre-condition the hard water pulp before flotation of the fluorspar by the practice previously described. Good flotation of the fluorspar was achieved by the various modifications provided the pH of the pulp did not exceed 11, and preferably was less than 10.

Example III

The examples of practice described heretofore demonstrate the applicability of this invention to the recovery of fluorspar from ores containing siliceous or calcareous gangue constituents. We shall now describe the results obtained by its practice on an ore containing a substantial amount of barite together with calcite and quartz. The sample was from a Canadian deposit and assayed 53.5 percent CaF_2 , 7.0 percent

CaCO₃, 0.6 percent SiO₂, and 37.1 percent BaSO₄. Grinding to 65 mesh gave adequate liberation of the fluorspar for the production of acid grade concentrates by this invention.

A representative portion of the Canadian sample was ground to 65 mesh and froth floated by the procedure described in Example I using 2.0 pounds per ton of sodium fluoride, 5.0 pounds per ton of an evaporated crude sulfite waste liquor containing about 50 percent of magnesium base lignin sulphonate, and 0.32 pound per ton of crude oleic acid as the collecting agent. Roughing and triple-cleaning of the froth product yielded a final fluorspar concentrate which assayed 99.2 percent CaF₂, 0.4 percent CaCO₃, 0.13 percent SiO₂, and 0.05 percent BaSO₄, and represented a recovery of 87.1 percent of the fluorspar in the flotation feed. About 90 percent of the silica and 99 percent of the barite and calcite were rejected in the roughing and cleaning treatment.

Various of the commercially available liquid and dehydrated residues from crude and purified sulfite liquors were used in conjunction with sodium fluoride in other tests on the Canadian material for retardation of the gangue while floating the fluorspar with fatty acid or soap collectors. The relative proportion of the lignin sulphonates, sodium fluoride, and collector was subject to considerable variation and the proper quantities had to be determined by trial. Moderate variation in the quantities of the lignin sulphonate and sodium fluoride was permissible and did not seriously impair selectivity of the separation. The crude and purified lignin sulphonates were used interchangeably in flotation with uniformly good results. The crude products were slightly less effective than the purified sulphonates for retarding barite but were particularly attractive due to their lower cost.

Another test on the Canadian sample using 2.0 pounds per ton sodium fluoride and 1.0 pound per ton of substantially pure magnesium lignin sulphonate residue gave an 86.7 percent recovery of fluorspar in acid grade concentrates containing 0.15 percent BaSO₄. Similar tests using 2.0 and 5.0 pounds per ton of the magnesium sulphonate yielded recoveries of 89.4 and 95.3 percent of the fluorspar in concentrates containing less than 0.1 percent barite. Another series of tests using 0.5, 1.0, 2.0, and 5.0 pounds per ton of sodium fluoride, respectively, in conjunction with 2.0 pounds per ton of the lignin sulphonate and 0.32 pound per ton of oleic acid as the collector gave recoveries of 47.9, 89.2, 89.4, and 79.6 percent of the fluorspar in acid grade concentrates containing less than 0.1 percent barite. Calcium and sodium lignin sulphonates in conjunction with sodium fluoride gave results entirely similar to those obtained by the magnesium compound. These tests demonstrate that the combination of sodium fluoride and a lignin sulphonate is very effective for the retardation of barite in fluorspar flotation. The separation is highly specific and considerable latitude is apparent both in the choice of the lignin sulphonate and in the relative proportions of sulphonate and fluoride employed.

Although the combination of sodium fluoride and lignin sulphonate is particularly effective for retarding barite in fluorspar flotation, the lignin sulphonates may be used alone with good results. A typical test on the Canadian sample employing the procedure described in Example I using 2.0 pounds per ton of magnesium lignin sulphonate

and 0.64 pound of oleic acid as the collector gave a 67.9 percent recovery of the fluorspar in concentrates which assayed 98.4 percent CaF₂, 0.6 percent CaCO₃, 0.10 percent BaSO₄, and 0.14 percent SiO₂. These results are about average of those obtained with various lignin sulphonates without sodium fluoride or other addition agents.

Numerous flotation tests have been made on a variety of fluorspar ores containing from none to as much as 70 percent barite using the combination of sodium fluoride and lignin sulphonates to retard the barite. All of the ores responded readily to our method of flotation and yielded acid grade fluorspar concentrates essentially free of barite. Our method of flotation is applicable to fluorspar ores containing variable quantities of barite for the recovery of high grade fluorspar concentrates; conversely, the method may be used for the purification of barite ores containing fluorspar as a contaminant.

Example IV

A fluorspar ore from a Kentucky deposit containing barite, celestite, calcite, and quartz together with minor amounts of galena and sphalerite as the gangue materials was next examined. A head analysis gave 34.5 percent CaF₂, 5.9 percent CaCO₃, 46.7 percent BaSO₄, 7.5 percent SrSO₄, 3.6 percent SiO₂, 0.2 percent Pb, and 0.5 percent Zn. The fluorspar was intimately associated with the gangue and grinding to 150 mesh was required for liberation.

A representative portion of the ore was ground to 150 mesh and froth floated by the procedure described in Example I using 2.0 pounds per ton of sodium fluoride and magnesium lignin sulphonate as the depressants and 0.32 pound per ton of commercial oleic acid as the fluorspar collector. The rougher froth was triple-cleaned with 0.08 pound per ton of the lignin sulphonate in each step and yielded a final fluorspar concentrate which assayed 98.8 percent CaF₂, 0.8 percent CaCO₃, 0.07 percent BaSO₄, 0.10 percent SrSO₄, 0.2 percent SiO₂, and only a trace of lead or zinc. The fluorspar recovery in the test was 78.3 percent. An excellent rejection of barite, celestite, calcite, silica, and metallic sulfides was effected by the combination of sodium fluoride and the lignin sulphonate.

Example V

A fluorspar ore containing substantial amounts of galena (PbS) and sphalerite (ZnS) in addition to calcite and silica was obtained from the Cave in Rock area of the Southern Illinois fluorspar district. A head analysis gave 51.4 percent CaF₂, 10.9 percent CaCO₃, 15.5 percent SiO₂, 3.5 percent Pb, and 10.5 percent Zn.

A portion of the ore was ground to 100 mesh and froth floated by customary sulfide flotation methods to recover the galena and sphalerite. The sulfide tailing containing 0.2 percent Pb, 0.7 percent Zn, and 68.1 percent CaF₂ was re-treated by this invention to recover the fluorspar in acid grade concentrates. The tailing from sulfide flotation was conditioned 5 minutes with 2.0 pounds per ton of sodium fluoride and magnesium lignin sulphonate, respectively, and 0.32 pound per ton of oleic acid was then added and the pulp conditioned an additional 5 minutes. Air was admitted to the cell and the rougher froth collected for 3 minutes when flotation of the fluorspar was completed. The froth product assayed 86.1 percent CaF₂ and contained 97.0 percent of the fluorspar in the original sample.

The tailings assayed 5.8 percent CaF_2 and accounted for a loss of 1.9 percent of the total fluor spar. The fluor spar rougher froth was re-pulped with tap water and re-floated using 0.08 pound per ton of the lignin sulphonate to retard the gangue. Three such cleaning steps yielded a final fluor spar concentrate which assayed 98.2 percent CaF_2 , 0.6 percent CaCO_3 , 0.3 percent SiO_2 , 0.05 percent Pb, and 0.06 percent Zn, and represented a recovery of 95.0 percent of the total fluor spar in the original material.

The reagent used in the test for flotation of the galena and sphalerite included copper sulfate, potassium ethyl and amyl xanthates, phosphocresylic acid, and pine oil. These reagents exhibited no deleterious effect in the subsequent flotation of fluor spar by this invention. The combination of sodium fluoride and lignin sulphonate adequately retarded the metallic sulfides remaining in the fluor spar feed as well as the calcareous and siliceous gangue materials.

Sodium cyanide was used in other tests on the Cave in Rock sample to complex or precipitate the metal salts (i. e. copper and zinc sulfate) in sulfide tailings prior to flotation of the fluor spar by our method. The combination of sodium cyanide and fluoride was particularly advantageous for overcoming the deleterious effect of metal salts in fluor spar flotation. Cyanide and fluoride complement each other and the proper proportions for optimum retardation of the gangue by the lignin sulphonates may best be determined by experimentation.

Various of the commercially available liquid and dehydrated residues of sulfite liquors have been successfully used in conjunction with sodium fluoride and sodium cyanide, singly or together, for the retardation of metallic sulfides and calcareous and siliceous gangue materials in fluor spar flotation of sulfide tailings. No difficulty has been experienced in obtaining a satisfactory recovery of acid grade fluor spar concentrates essentially free of metallic sulfides.

Example VI

We have discovered that our method of flotation enables the recovery of coarser fluor spar than was formerly believed possible by older methods of flotation. Fluor spar as coarse as 20 mesh has been satisfactorily separated from calcareous and siliceous gangue constituents by the practice of this invention and it seems likely that even coarser material may be made to yield to our method of flotation. An illustrative example of the practice of this invention for the recovery of coarse fluor spar will not be given.

A jig tailing from an operating plant in the Southern Illinois fluor spar district was obtained for testing. The material as received was essentially finer than 6 mesh and assayed 44.6 percent CaF_2 , 42.1 percent CaCO_3 , and 12.1 percent SiO_2 . A representative portion of the sample was carefully ground to pass 20 mesh and froth floated to recover the fluor spar by the procedure described in Example I. Sodium fluoride, calcium lignin sulphonate, and oleic acid were used in the roughing operation in amount equivalent to 2.0, 2.0, and 0.64 pounds per ton respectively. The rougher froth, collected for 2.5 minutes, assayed 84.6 percent CaF_2 , 13.3 percent CaCO_3 , and 1.6 percent SiO_2 , and represented a recovery of 94.2 percent of the fluor spar. The flotation tailings assayed 5.1 percent CaF_2 , 70.5 percent CaCO_3 , and 22.4 percent SiO_2 , and contained 84.3 percent of the calcite and 93.4 percent of the silica in the original

sample. Triple-cleaning of the rougher froth using 0.08 pound per ton of additional calcium lignin sulphonate in each step yielded a final fluor spar concentrate which assayed 97.7 percent CaF_2 , 1.5 percent CaCO_3 , and 0.5 percent SiO_2 , and represented a recovery of 89.1 percent of the total fluor spar. A cumulative sizing analysis of the fluor spar concentrates showed that 22.8 percent of the fluor spar was coarser than 28 mesh, 45.0 percent was coarser than 35 mesh, and 60.1 percent was coarser than 48 mesh.

While we have disclosed the presently preferred embodiment of our invention, it will be readily apparent to those skilled in the art that many variations and modifications may be made therein without departing from the spirit and scope of the invention as defined in the appended claims.

What is claimed is:

1. The process of concentrating fluor spar by froth flotation of pulps containing fluor spar values, comprising adding to such a pulp sodium fluoride, a lignin sulphonate, and a fluor spar collecting agent selected from the class consisting of fatty acids and soaps, and subjecting said pulp to froth flotation to recover the fluor spar.

2. The process of concentrating fluor spar by froth flotation of pulps containing fluor spar values, comprising adding to such a pulp a soluble inorganic fluoride, a lignin sulphonate, and a fluor spar collecting agent selected from the class consisting of fatty acids and soaps, and subjecting said pulp to froth flotation to recover the fluor spar.

3. The process of concentrating fluor spar by froth flotation of pulps containing fluor spar values, comprising adding to such a pulp a pH modifying agent to establish a pH not to exceed 11, a soluble inorganic fluoride, a lignin sulphonate, and a fluor spar collecting agent selected from the class consisting of fatty acids and soaps, and subjecting said pulp to froth flotation to recover the fluor spar.

4. The process of concentrating fluor spar by froth flotation of pulps containing fluor spar values, comprising adding to the pulp sodium sulfide, a pH modifying agent to establish a pH not to exceed 11, a lignin sulphonate, and a fluor spar collecting agent selected from the class consisting of fatty acids and soaps, and subjecting said pulp to froth flotation to recover the fluor spar.

5. The process of concentrating fluor spar by froth flotation of pulps containing fluor spar values, comprising adding to the pulp a lignin sulphonate, sodium cyanide and an inorganic soluble fluoride, and a fluor spar collecting agent comprising oleic acid, and subjecting said pulp to froth flotation to recover the fluor spar.

6. The process of concentrating fluor spar by froth flotation of pulps containing fluor spar values, comprising adding to the pulp a metal salt of lignin sulphonic acid, an inorganic soluble fluoride, and a fluor spar collecting agent selected from the class consisting of fatty acids and soaps, and subjecting said pulp to froth flotation to recover the fluor spar.

7. The process of concentrating fluor spar by froth flotation of pulps containing fluor spar values, comprising adding to the pulp a substantially dehydrated residue of paper mill sulfite liquors, an inorganic soluble fluoride, and a fluor spar collecting agent selected from the class consisting of fatty acids and soaps, and subjecting said pulp to froth flotation to recover the fluor spar.

8. The process of concentrating fluor spar by froth flotation of pulps containing fluor spar val-

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ues, comprising adding to the pulp a paper mill sulfite liquor, an inorganic soluble fluoride, and a fluorspar collecting agent selected from the class consisting of fatty acids and soaps, and subjecting said pulp to froth flotation to recover the fluorspar.

9. The process of concentrating fluorspar by froth flotation of pulps containing fluorspar values, comprising adding to the pulp a lignin sulphonate, a tannin extract and a fluorspar collecting agent selected from the class consisting of fatty acids and soaps, and subjecting said pulp to froth flotation in the presence of a soluble substance yielding fluoride ions in solution, to recover the fluorspar.

10. The process of concentrating fluorspar by froth flotation of pulps containing fluorspar values, comprising adding to the pulp a tannin extract, a paper mill ligneous substance selected from the class consisting of sulfite liquor and dehydrated residues thereof, an inorganic soluble fluoride, and a fluorspar collecting agent selected from the class consisting of fatty acids and soaps, and subjecting said pulp to froth flotation to recover the fluorspar.

11. The process of concentrating fluorspar by froth flotation of deslimed pulps containing fluorspar values, comprising adding to the substantially deslimed pulp a paper mill ligneous substance selected from the class consisting of sulfite liquor and dehydrated residues thereof, a fluorspar collecting agent selected from the class consisting of fatty acids and soaps, and subjecting said pulp to froth flotation in the presence of a soluble substance yielding fluoride ions in solution, to recover the fluorspar.

12. The process of concentrating fluorspar by

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froth flotation of deslimed pulps containing fluorspar values, comprising adding to the substantially deslimed pulp a paper mill ligneous substance selected from the class consisting of sulfite liquor and dehydrated residues thereof, an inorganic soluble fluoride, and a fluorspar collector selected from the class consisting of fatty acids and soaps, and subjecting said pulp to froth flotation to recover the fluorspar.

13. In a process for the beneficiation of a fluorspar ore involving the froth flotation of an aqueous pulp of such an ore in the presence of a fatty acid collector and the recovery in the froth of a fluorspar concentrate, the step which comprises carrying out the flotation in the presence of a soluble substance yielding fluoride ions in solution, a substance adapted to depress barite in the presence of a soluble fluoride comprising a lignin sulphonate, and a substance adapted to depress calcite comprising a tannin extract, whereby the normal propensity of a tannin extract to float barite is inhibited by said fluoride.

14. The process of claim 13, wherein tall oil is employed as the collector.

15. The process of claim 13, wherein sodium fluoride is employed as the soluble fluoride.

16. The process of claim 13, wherein a lignin sulphonate derived from paper mill sulfite liquor is employed.

17. The process of claim 13, wherein quebracho is employed as the tannin extract.

18. The process of claim 13, accompanied by an additional treatment to diminish the pulp concentration of soluble polyvalent cations.

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